

Measurements of VOCs in Mexico City (1992–2001) and evaluation of VOCs and CO in the emissions inventory

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Received 15 August 2003; accepted 27 January 2004

Abstract

Measurements of ambient volatile organic compounds (VOCs) are reported from several field campaigns of simultaneous measurements in the Mexico City Metropolitan Area (MCMA). Conducted between 1992 and 2001, these measurements represent the longest and most complete record of VOC measurements available for Mexico City. Ambient air VOC samples were collected at surface air quality monitoring sites in electro-polished stainless-steel canisters, and analyzed by Gas Chromatography with Flame Ionization Detection for the C2 to C12 hydrocarbons and MTBE. This paper presents the total VOCs in morning measurements (06:00–09:00 AM) and its trend through time. Average concentrations of total VOCs in each campaign were between 3130 and 6711 ppbC at Xalostoc (northeast of the city center), 2994 and 4935 ppbC at La Merced (center), and 1136 and 2815 ppbC at Pedregal (southwest). A linear regression of the total VOCs reveals a slight decreasing trend from 1992 to 2001 which is statistically significant only at Xalostoc; the decreasing trends at the two other sites are not statistically significant and therefore inconclusive. This apparent stabilization and possible decrease in ambient concentrations, despite the growth in the vehicular fleet and other activities during this period, suggests that VOC emission control measures have been effective at reducing emissions. Co-located measurements of CO and NO_x from the Metropolitan Atmospheric Monitoring Automatic Network are used to calculate ratios of total VOCs/NO_x and CO/NO_x, in order to evaluate the official 1998 emissions inventory for the MCMA. The ambient ratios of VOCs/NO_x and CO/NO_x are found to be factors of 2–3 times higher than the corresponding inventory ratios. This discrepancy suggests that VOC and CO emissions may be significantly underestimated.

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Keywords: Volatile organic compounds; VOC/NO_x ratio; CO/NO_x ratio; Mexico City

1. Introduction

Air pollution from high surface ozone (O₃) arising from photochemical formation is present in many regions worldwide. Mexico City has been addressing its ozone air pollution problem for several years

(Comision Metropolitana para la Prevención y Control de la Contaminación, 1994). Daily activities lead to the emission of hundreds of reactive gases into the atmosphere. These include volatile organic compounds (VOCs), which in the presence of nitrogen oxides (NO+NO₂=NO_x) emitted mainly by combustion sources, form ozone through photochemical processes. Under favorable meteorological conditions, ozone can accumulate to hazardous levels. In Mexico City, this

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problem is accentuated by the high altitude (2240 m.a.s.l.), and high mountains that surround the metropolitan valley.

While measurements of ozone and NO_x are common in Mexico City, measurements of VOCs are much less common, but are important for understanding ozone formation (Molina et al., 2002). Historical measurements of ozone from the Metropolitan Atmospheric Monitoring Automatic Network (RAMA) show that during the past decade, incidences of very high ozone concentrations have become less common (SMA-DDF, 2002), despite the growth in the vehicular fleet and in other activities that cause emissions (SMA-DDF, 2001).

Prediction of the concentration of various species such as VOCs is possible if the meteorology, chemistry, and emissions are all reasonably well understood. An alternative that removes some of the meteorological uncertainties is to compare measured and predicted ratios of compounds (Finlayson-Pitts and Pitts, 2000). Discrepancies between emission inventories and measured VOCs and CO have been reported in the literature. Fujita et al. (1992) performed a “top-down” validation of the reactive organic gas and CO emission inventories for California’s South Coast Air Basin by comparing speciation profiles for nonmethane organic gases (NMOG) and ratios of CO/NO_x and NMOG/NO_x . They conclude that estimates of on-road motor vehicle carbon monoxide and NMOG emissions are seriously underestimated relative to NO_x in Los Angeles. Watson et al. (2001) likewise found that the relative motor vehicle source contributions of VOC determined by a chemical mass balance model are consistently two to three times their proportions in emissions inventories, in more than 20 urban areas, mostly in the United States.

In order to better understand the contribution of VOCs to the formation of ozone, to identify VOC sources, and to monitor the effectiveness of actions to control VOC emissions, systematic field studies of VOCs have been conducted in Mexico City since 1992, with campaigns occurring once or twice per year. The objective of this paper is to present the total VOC concentrations obtained during morning hours at selected urban sites in the Mexico City Metropolitan Area (MCMA) between 1992 and 2001. To identify trends in VOC concentrations in time, a linear regression analysis is applied to the data. In addition, the morning concentrations of total VOCs reported in this analysis are used together with measurements of NO_x and CO to evaluate the official 1998 emissions inventory for the MCMA, by comparing the ratios of different pollutants.

2. Field studies and sampling sites

Since 1992, field studies of VOCs have been conducted by the Instituto Mexicano del Petróleo (IMP) with

assistance from the US Environmental Protection Agency (EPA) and sponsored by Petroleos Mexicanos (PEMEX) and the Mexican Federal District (DDF). Measurements from early campaigns were reported by Seila et al. (1993), Arriaga-Colina et al. (1993, 1995, 1996, 1997), Ruiz et al. (1996), Riveros et al. (1998), Edgerton et al. (1999) and Elliot et al. (2000). These measurements are the longest and most complete record of VOC concentrations available for Mexico City. Other VOC measurements were reported by Blake and Rowland (1995), who conducted a field campaign in February 1993, collecting air grab samples at about 40 surface sites; nearly 75 samples were taken, and C1–C7 hydrocarbons and halocarbons compounds were reported.

The term VOCs is used to denote the entire set of vapor phase atmospheric organics species with vapor pressure above 10^{-2} kPa, excluding CO, CO_2 and methane. In this study, measurements of total VOCs include C-2–C-12 speciated hydrocarbons and the oxygenated MTBE. The present work focuses on the total VOCs concentrations, reported as parts per billion of Carbon (ppbC).

Samples were collected in canisters over 3-h periods beginning at 06:00 AM simultaneously at several sites, usually daily or every third day. The campaigns lasted between 3 and 30 days, occurring mainly in March and November, from 1992 to 2001. The field study dates, sampling periods, number of samples taken and number of sites are reported in Table 1.

In all field campaigns, samples were collected simultaneously at the Xalostoc, La Merced and Pedregal sites. These three sites contain a full complement of pollutant monitors, operated by the RAMA, which routinely monitor other pollutants, including ozone, NO_x and CO. These three sites lie on a northeast to southwest line through the center of the city, shown in Fig. 1, which corresponds to the most frequent wind trajectory. In 1995 and before, measurements were taken at other stations and are presented by Arriaga-Colina et al. (1996, 1997). In November 2000, measurements were also taken at Tlanepantla and Iztapalapa. In addition to the morning measurements shown in Table 1, 6-h samples were taken at La Merced, from 06:00 to 12:00 and from 12:00 to 18:00 during the March 1997 campaign (Edgerton et al., 1999; Elliot et al., 2000). These 6-h results are not reported in this study.

Xalostoc lies northeast of the city center, with light to medium industries nearby. The area near Xalostoc has heavily traveled paved and unpaved roads, with old and new gasoline and diesel vehicles, and a dry lake (Lake Texcoco) lies approximately 5 km east of the site. La Merced is located in the city center near heavily traveled paved and unpaved curbed surface streets with

Table 1
Field studies of 3 h sampling (06:00–09:00 AM) at several sites within the Mexico City Metropolitan Area

Field study	Sampling periods	Number of days	Number of samples	Number of sites
2001 March–April	12–29 and 2	6	18	3
2000 March	13–17	5	25	5
1999 November	22–26	5	15	3
1998 November	16–20	5	14	3
1997 March	11–23	10	36	3
1996 November–December	25–30, 1–2	8	24	3
1996 March	11–18	8	21	3
1995 December	11–13	3	9	3
1995 November	9–15	7	18	3
1995 March	13–17	5	17	4
1994 November	8–10	3	9	3
1993 November	22–26	6	24	5
1993 March	25–27	3	12	4
1992 March	6–26	19	77	6
		Total 95	Total 304	

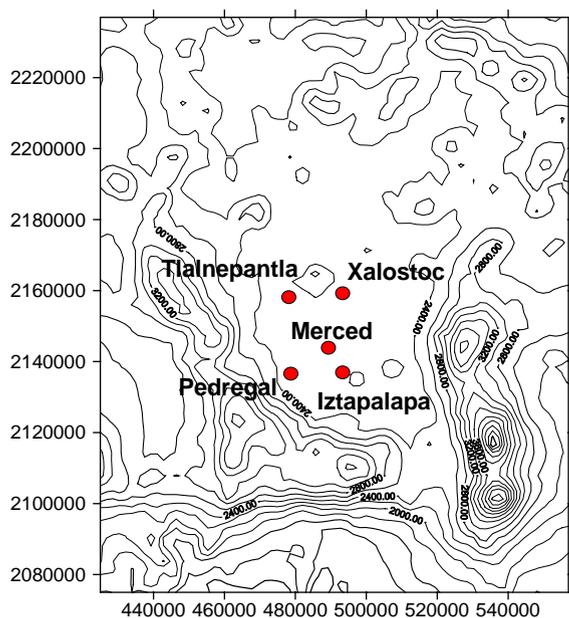


Fig. 1. Sampling sites within the Mexico City Metropolitan Area. Coordinate units are in UTM (m), and the topography is shown for reference.

light-duty vehicles and modern heavy-duty diesel buses. Pedregal (southwest) is a suburban neighborhood near clean, paved residential roads which are lightly traveled and have no nearby industries. Tlanepantla (northwest) has both industrial and residential characteristics. Iztapalapa (southeast) has paved and unpaved roads with heavy old and new vehicle traffic, and the sampling site was within the Metropolitan University campus.

3. Sampling and chemical analysis methods

Summa[®] electro-polished stainless-steel canisters heated at about 80°C were cleaned in four pressurization/evacuation cycles with humidified gas chromatograph (GC) grade helium, and stored under vacuum at no more than 33.3 Pa. Blanks contained less than 20 ppbC of total VOCs.

The samplers were located on the building rooftop, at a height of 4–5 m above the ground and away from the nearest building, so that air circulated freely. A controlled flow of ambient air was pumped into the 6, 1.8 or 0.81 canister, using an automated sampler (VOCCS-ANDERSEN and AVOCS-ANDERSEN models) with a Viton diaphragm pump. After sampling, the final pressure reached 48–103 kPa.

Samples were analyzed using a cryogenic pre-concentration/high-resolution GC technique, by the US EPA Atmospheric Research and Exposure Assessment Laboratory (EPA-AREAL) and by the Laboratorio de Química de la Atmósfera at the Instituto Mexicano del Petróleo (IMP), using methods similar to the TO-14A protocol (US EPA, 1999; McClenny et al., 1991). In brief, ambient air from the canisters was drawn through a stainless-steel loop, filled with glass beads of 60/80 mesh, and connected to a six-port gas-sampling valve situated inside the oven of a GC (see Fig. 2). A Hewlett-Packard 5890 Series II plus chromatograph, operated at constant flow of 2 ml min⁻¹ was used. To separate the air mixture a Quadrex fused silica capillary column of 60 m length, 0.32 mm internal diameter coated with a 1- μ m thick film of a non-polar cross-linked methyl silicone liquid phase was installed inside the GC oven. During sample loading, the oven was cooled to -50°C. Subsequently, the oven temperature was quickly raised

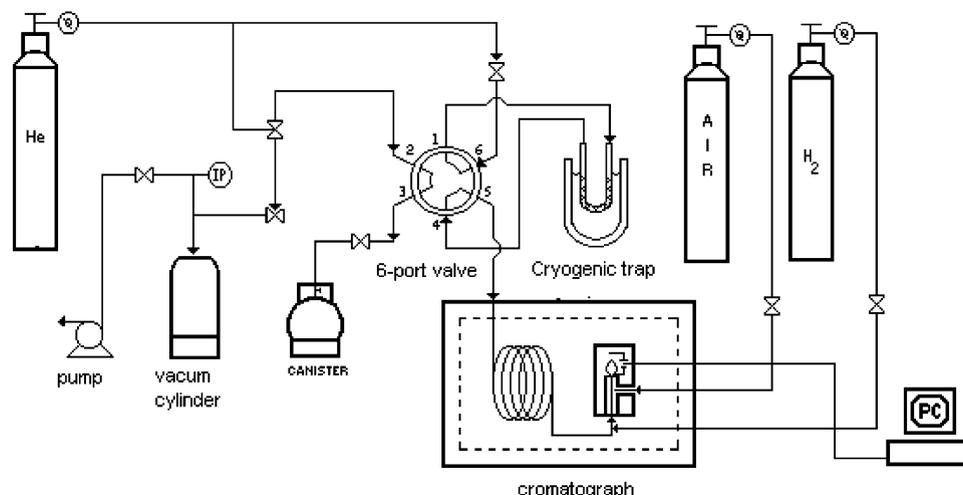


Fig. 2. Gas chromatograph–flame ionization detector (GC–FID) analytical system with the six-port chromatographic valve in the sample desorption mode.

at $8^{\circ}\text{C min}^{-1}$ to reach 200°C . The total analysis time was approximately 1 h.

Before running a sample, the flame ionization detector (FID) response was checked every day. A certified high-purity grade propane standard, a 3 ppm balanced ultra zero air (purchased from AGA, MG Industries and Praxair), was used to calibrate the FID. Standard deviations of replicate measurements were always lower than 1% ($\text{CV} = 1$). The detection limit is believed to be 1 ppbC. Individual species were identified by retention times, using a mixture of 55 hydrocarbon ozone precursors (purchased from Scotty Specialty Gases with an analytical accuracy of 10%), and a certified mixture of 33 halogen-containing compounds in nitrogen (purchased from Spectra Gases, with 10% of analytical accuracy).

4. Results

The total VOC concentrations measured in ambient air during morning hours at Xalostoc, La Merced, and Pedregal are summarized in Table 2, which shows the minimum, maximum, and mean concentrations measured in each field campaign. In general, the lowest total VOC concentrations were measured at Pedregal, followed by La Merced, and the highest concentrations were detected at Xalostoc. Because these measurements are taken in the morning, when winds are light, the highest concentrations near Xalostoc suggest that the density of VOC emissions is highest in the region near the Xalostoc site (northeast), while it is lowest in the residential area around Pedregal. There is no clear difference in concentrations between the March–April and November–December campaigns that could be

attributed to seasonal variations. The minimum, maximum, and mean total VOC concentrations obtained in the March 2000 campaign at Tlanepantla and Iztapalapa were 1428, 4119, 3519 and 2256, 3154, 2707 ppbC, respectively.

The measurements taken on individual days at the three sites are shown in Fig. 3. The large scatter in the data and relatively few days of sampling during each campaign make it difficult to identify a clear trend. This large scatter in the data is due mainly to daily variability in meteorology in the morning hours, and secondarily to daily variations in emissions. In order to identify temporal trends in the total VOC concentration at the three sites, a linear regression analysis was performed using all the data available at each site. Fig. 3 shows the linear regression at each site, when individual daily measurements are used (with day as the independent variable). The statistical results of this analysis are shown in Table 3, which shows that negative slopes are obtained at all sites, but that the negative slope is statistically significant only at the Xalostoc site, at the 95% confidence level. At La Merced and Pedregal the slopes are also negative, but are not statistically significant at the 95% level.

These linear regressions use all available measurements, regardless of whether those measurements came from the March–April or November–December campaigns. Combining these measurements is supported by the fact that both periods are in the dry season in Mexico City, with similar predominant meteorological conditions and similar observed concentrations (Table 2). Table 3 also shows results when regressing over the March–April and November–December measurements separately. These results are similar to the regressions over all measurements: the regression reveals a negative

Table 2
Minimum and maximum and mean concentrations of total VOCs present in the MCMA

Campaign Year month	Sampling site								
	Xalostoc			La Merced			Pedregal		
	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean
	Concentration (ppbC)								
2001 March	3607	5360	4296	2410	4194	3399	1209	2109	1508
2000 March	2049	5163	3618	1512	3960	3086	1466	1872	1659
1999 November	3720	6077	4836	2555	4831	3235	1211	2591	1815
1998 November	2292	5313	4138	1806	4630	2994	1303	1730	1569
1997 March	1216	5284	3130	2034	6677	4106	524	1573	1136
1996 November	1419	4852	3437	1594	7575	3776	1096	1739	1440
1996 March	1794	5273	3985	2511	4527	3874	1290	3275	2414
1995 December	3906	4717	4307	2255	4054	3298	1097	2343	1651
1995 November	1846	4144	3131	1273	4548	3044	760	2060	1475
1995 March	1712	5088	3708	3058	4839	3834	1002	2708	1575
1994 November	3525	5859	4398	2394	3972	3127	1674	1882	1798
1993 November	2602	7623	5800	3509	5104	3464	1959	4191	2815
1993 March	6135	7434	6711	3828	6555	4935	1224	1598	1374
1992 March	1928	6937	4642	2341	5944	3646	1624	2707	1919

slope at all sites, which is statistically significant (at the 95% confidence level) only at Xalostoc (for both time periods).

The negative slopes found at all three sites provide evidence that the high concentrations of VOCs in Mexico City did not continue to grow between 1992 and 2001, and suggests that concentrations may have decreased, with a statistically significant decrease observed at one out of three sites. This conclusion is the same using only the March–April and November–December campaigns, despite the fewer measurements available in these periods. This result using each period separately strengthens these conclusions and suggests that seasonal differences are not responsible for the negative slopes found when using all measurements.

Using the linear regression parameters (Fig. 3 and Table 3), the morning VOC concentration is estimated to decrease between 1992 and 2001 by 26% at Xalostoc, 14% at La Merced, and 20% at Pedregal. During this same period, the vehicular fleet in Mexico City grew substantially, as did population and energy consumption. According to the government (CAM, 2001), the vehicular fleet increased approximately 20% from 1994 to 1998, accounting for approximately 3.3 million vehicles in 1998. Despite this growth in transportation and other activities that lead to emissions, ambient VOC concentrations have apparently stabilized and may be declining. Given that the number of vehicles and VOC emissions from other sources would have grown in the absence of controls, it is clear that emission control measures implemented during this period have been effective at stopping the growth of VOC emissions, and may have caused a decrease in emissions.

Over the same period from 1992 to 2001, daily 1-h peak ozone concentrations were observed to decrease by 32%, using the average of five sites that represent five regions of the MCMA (based on a linear regression of annual average daily 1-h peaks for 10 years). The average ozone concentration over all 24 h was observed to decrease by 47%. Meanwhile the average NO_x concentration at the five sites was observed to decrease by 24% and CO decreased by 56% (SMA-DDF, 2002). Because these measurements are taken hourly at many sites, these decreases are statistically significant. The large reduction in CO concentrations can be attributed to the introduction of catalytic converters on new vehicles, beginning in 1991, as well as to improvements in the inspection and maintenance program and to fuel quality. These reductions in vehicular emissions are also expected to have been important for VOCs and NO_x , as were government initiatives to address emissions from industries and other sectors. Despite these improvements, however, VOC concentrations in Mexico City continue to be very high compared to other urban areas, and ozone concentrations continue to exceed the Mexican air quality standard on about 80% of days of the year.

Finally, it is possible to use time trends of pollutants to consider whether the significant decrease in ozone peak concentrations is likely to have resulted from the decrease in NO_x emissions or the possible decrease in VOC emissions. In this way, one can perhaps learn whether the ozone formation in Mexico City is likely to have been NO_x -sensitive or VOC-sensitive. In this case, however, NO_x and VOCs are each estimated to decrease by similar percentages (using the linear regression

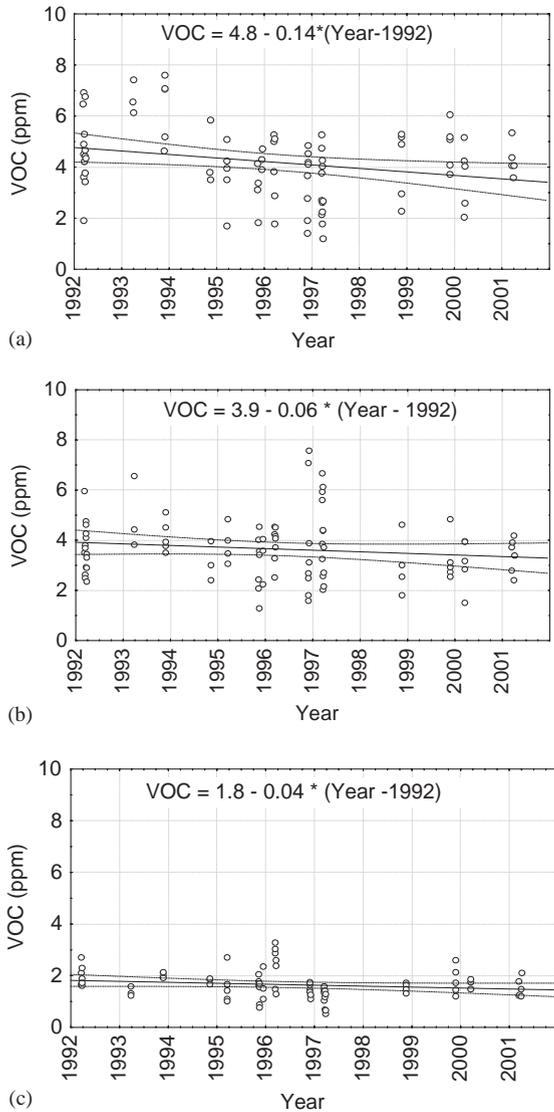


Fig. 3. Linear regression of the total VOC concentration at: (a) Xalostoc; (b) La Merced and (c) Pedregal. Points show measurements on each day (6–9) AM, the solid line is a linear regression of all points, and the dashed lines show the 95% confidence interval around the regression.

parameters for VOCs), and so this ozone reduction is not easily attributed to one precursor or the other.

5. Use of VOC/ NO_x ratios to evaluate the official emissions inventory

Measurements of total VOCs are used to evaluate the official emissions inventory for the MCMA, by comparing the ratio of total VOCs to NO_x in morning measurements, to the ratio in the emissions inventory

Table 3

Linear regression parameters for the total VOC concentration vs. time (1992–2001) for three sites in the MCMA, using all daily measurements, or only the March–April or November–December measurements, shown in Fig. 3

Parameters	Xalostoc	La Merced	Pedregal
<i>Using all daily measurements</i>			
Slope	-0.14 ± 0.05	-0.06 ± 0.05	-0.04 ± 0.02
Intercept	4.8 ± 0.3	3.9 ± 0.3	1.82 ± 0.1
<i>March–April</i>			
Slope	-0.14 ± 0.06	-0.05 ± 0.05	-0.04 ± 0.03
Intercept	4.67 ± 0.3	3.98 ± 0.3	1.8 ± 0.2
<i>November–December</i>			
Slope	-0.15 ± 0.1	-0.09 ± 0.1	-0.03 ± 0.03
Intercept	5.05 ± 0.7	3.88 ± 0.6	1.77 ± 0.2

The confidence interval is the standard error, the slope is in ppmC yr^{-1} and the intercept is ppmC .

(Fujita et al., 1992). Morning measurements are used, assuming that there is relatively little influence from pollution from the previous day, and that this morning period is before photochemical activity driven by sunlight changes pollutant concentrations significantly.

Here we use measurements of VOCs from 1995 to 2001 to evaluate the official emissions inventory for 1998 for the MCMA (CAM, 2001). We use measurements taken from 6 to 9 AM at Xalostoc, La Merced, Pedregal, and Iztapalapa. Measurements at Tlalnepantla are not used, since there are no concurrent measurements of NO_x at this site. Measurements of NO_x are collocated at the same measurement sites, using chemiluminescence monitors as part of the RAMA network, and are made following reference methods of the US EPA (INE, 2000). Although chemiluminescence monitors are known to measure more than the sum of NO and NO_2 , including also other nitrogen-containing species such as HNO_3 and PAN, morning measurements of NO_x are dominated by NO from fresh emissions, and the contribution of other species to the measured NO_x is small. Reported hourly measurements of NO_x are averaged over 3 h, for direct comparison with the VOC measurements.

Fig. 4 shows these measurements in scatterplots at the four sites. The relationship between total VOCs and NO_x is remarkably linear at La Merced, while significantly more scatter is seen in the measurements at Xalostoc. This suggests that La Merced is truly representative of emissions from this area of the city, as daily changes in wind direction have little effect on the observed relationship. It also suggests that there are little changes in relative source strengths on different days and in different years. The large scatter at Xalostoc suggests that there may be influences from local sources,

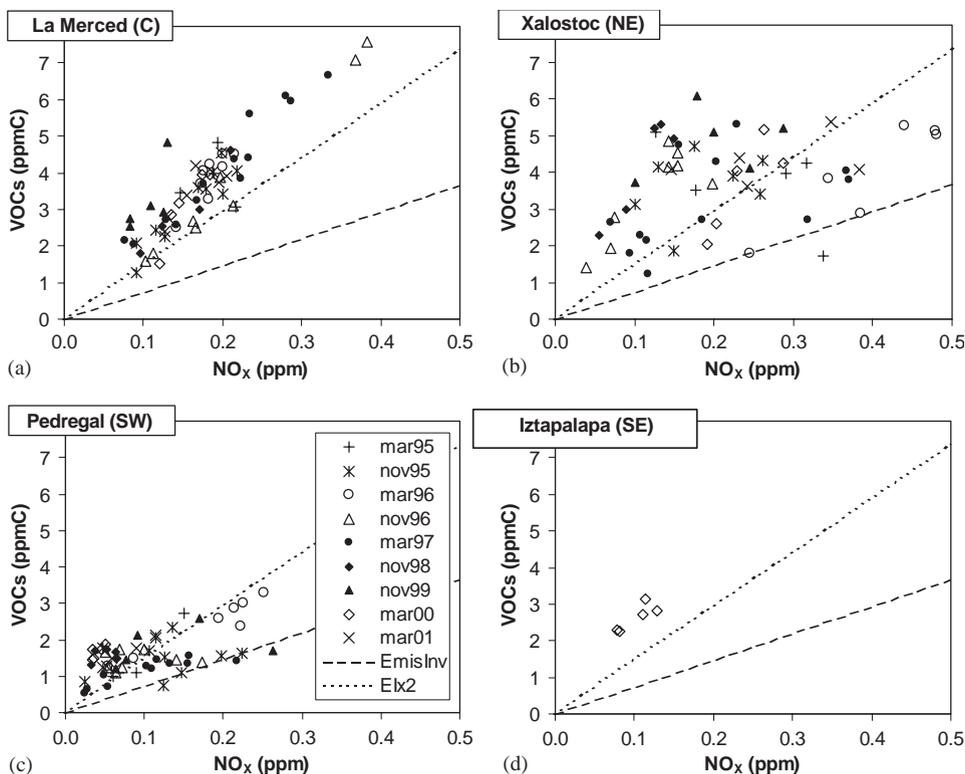


Fig. 4. Measurements of total VOCs and NO_x from 6 to 9 AM during nine measurement campaigns, at four sites: (a) La Merced; (b) Xalostoc; (c) Pedregal and (d) Iztapalapa. Each point represents measurements on 1 day. Also shown for comparison is the ratio of VOCs to NO_x from the official 1998 emissions inventory, corrected for 6–9 AM, and this ratio multiplied by two. Solid points indicate measurements from 1997 to 1999, which are closest to the year of the emissions inventory (1998). The November 1995 data include the three days of measurements in December 1995.

as changes in daily meteorology change the contributions of different sources to the measured concentrations. The measurements at Xalostoc may also reflect daily and yearly changes in emissions from local industries and other sources, as industrial operations change. Lower concentrations of both pollutants are observed in the morning at Pedregal, as this is a residential area that is less densely populated than the other sites.

From Fig. 4, averaging the ratios estimated on each day gives average ratios of 21.5 ± 10.3 (\pm one standard deviation), 20.9 ± 4.3 , and 20.2 ± 11.0 ppmC ppm⁻¹, respectively, at Xalostoc, La Merced, and Pedregal. The average ratio at Iztapalapa is estimated to be 26.3 ± 3.1 ppmC ppm⁻¹, but there are too few measurements at this site to draw conclusions.

These ratios can be compared to the ratio of VOC/NO_x in the emissions inventory, once the emissions ratios are changed from mass units (tonnes yr⁻¹) to concentration units (ppmC ppb⁻¹). This conversion is made using 64.52 g mol⁻¹ as the average molecular weight, and 4.855 as the average number of carbon

atoms per molecule, estimated for the mixture of VOC species in morning measurements at La Merced in 1997. For this conversion, the ratio of these numbers (13.29 g molC⁻¹) is used, and this ratio is very nearly the same for all non-oxygenated hydrocarbons, suggesting that the error in this conversion is likely to be small. The resulting VOC/NO_x ratio in the emissions inventory is 7.99 ppmC ppm⁻¹ as shown in Table 4.

Because the emissions inventory accounts for emissions over a whole daily cycle, these emissions should be corrected to represent the morning hours. Using information on the temporal and spatial distributions of total emissions in the MCMA, which is used for generating inputs to air quality modeling (West et al., submitted), the estimated VOC/NO_x ratio between 6 and 9 AM is 7.34 ppmC ppm⁻¹. Likewise, we can consider the VOC/NO_x ratio between 6 and 9 AM in an area of 13.5 km × 13.5 km around the measurement site (3 × 3 grid squares in the study of West et al. (submitted)). These local morning ratios are estimated to be 7.60, 6.61 and 8.13 ppmC ppm⁻¹, respectively, at Xalostoc, La Merced, and Pedregal. These differences in ratios

Table 4

Average ratios of VOC/NO_x in measurements at each site from 6 to 9 AM, and the factor of discrepancy by which the ratio in the emissions inventory is lower than the ambient ratio

Site	Measured ratio (ppmC ppm ⁻¹)	Factor of discrepancy		
		EI 1998 total (7.99 ppmC ppm ⁻¹)	EI 6–9 AM (7.34)	EI 6–9 AM at sites ^a
Xalostoc (NE)	21.5	2.7	2.8	2.8
La Merced (C)	20.9	2.6	2.9	3.2
Pedregal (SW)	20.2	2.5	2.8	2.5

Also shown are results where the emissions ratios are corrected for morning emissions and morning emissions near the measurement sites.

^aThe emissions inventory for 6–9 AM in the vicinity of the measurement stations give ratios of 6.61, 7.60, and 8.13 ppmC ppm⁻¹, respectively, at Xalostoc, La Merced, and Pedregal, using information from West et al. (submitted).

arise from differences in the spatial distributions of emissions from each source category, and the different temporal patterns associated with each source category, as described by West et al. (submitted). No corrections are made to emissions based on season, as we expect only minor differences in anthropogenic emissions in different seasons and biogenic emissions are small according to the emissions inventory (3% of total VOCs emissions). We likewise make no correction for day of the week—the majority of VOCs measurements are on weekdays, although some are on weekends, and none are taken on holidays.

In Fig. 4, the VOC/NO_x ratio in the emissions inventory for 6–9 AM (7.34 ppmC ppm⁻¹) is shown for comparison with the measured ratios, as well as this ratio multiplied by two. At all sites, very few points are observed below the ratio in the emissions inventory, and many points lie above the line indicating twice the ratio in the emissions inventory. Comparing the ratios in the measurements with the ratios in the emissions inventory (Table 4), the ratios in the measurements are estimated to be a factor of roughly 2.5–3 higher.

As an alternative, it is also possible to calculate the average ratio by first averaging the VOCs and NO_x measurements separately and then dividing them. The results using this method are very nearly the same at La Merced (20.5 ppmC ppm⁻¹) because of the strongly linear relationship in measurements. But using this method makes a significant difference at the other sites. Using the previous method, high ratios were estimated for data points with low NO_x concentrations; consequently, the average ratios are lower at Xalostoc (17.7 ppmC ppm⁻¹) and Pedregal (15.3 ppmC ppm⁻¹) than previously estimated. Dividing by the ratios in the emissions inventory as in Table 4, the discrepancy between the measured ratios and the emissions inventory using this method is estimated to be between a factor of 2 and 3.

6. Use of CO/NO_x ratios to evaluate the official emissions inventory

Previous work in other urban centers has found that in addition to the VOC emissions, CO emissions are also frequently underestimated in emissions inventories (Fujita et al., 1992). Here we use the same method of using ambient measurements of CO/NO_x to evaluate the official emissions inventory. Unlike VOCs, however, an abundance of CO and NO_x measurements exist from the RAMA network (INE, 2000). Collocated hourly measurements of CO and NO_x exist at 18 stations in the MCMA, although in any given hour, measurements may be missing (or considered invalid by RAMA's quality control system) at several stations. This spatial coverage includes the entire metropolitan region and a few outlying sites, and so should be fairly representative of the average of fresh emissions from the metropolitan region. CO measurements are made using EPA reference methods, and are thought to be of good quality with errors of < about 15% (NRC, 1991).

We analyze measurements from the years 1996–2000 separately to evaluate the official 1998 emissions inventory, averaging over the hours 6–9 AM, as was the case for the VOC/NO_x ratios. Only cases (station-days) where valid measurements of both CO and NO_x were available for each hour were used in the analysis. Some measurements of NO_x were reported as being very low, and therefore caused unusually high CO/NO_x ratios. These data were filtered by removing measurements where NO_x is < 0.015 ppm, or CO is < 0.1 ppm. The ratio of CO/NO_x in the official emissions inventory for 1998 is estimated (after converting units) to be 14.3 ppm ppm⁻¹ for the entire inventory, and for 6–9 AM is estimated to be 15.3 ppm ppm⁻¹ from the emissions analysis of West et al. (submitted).

Results of the analysis of CO/NO_x ratios are shown in Table 5, when averaging the ratios estimated individually at each station and on each day. Results vary

Table 5

Average ratios of CO/NO_x from ambient measurements from 6 to 9 AM, and the factor of discrepancy by which the emissions inventory is lower than the ambient ratio, comparing with the ratios in the emissions inventory, and the emissions ratios corrected for morning emissions

Year	Measured ratio (ppm ppm ⁻¹)	Factor of discrepancy	
		EI 1998 total (14.3 ppm ppm ⁻¹)	EI 6–9 AM (15.3 ppm ppm ⁻¹)
1996	35.6	2.5	2.3
1997	34.9	2.4	2.3
1998	42.9	3.0	2.8
1999	38.3	2.7	2.5
2000	37.7	2.6	2.5

somewhat from year to year, giving discrepancies in the range of factors of 2.3–3.0. As for the case of VOC/NO_x, we find different results if we average the measured concentrations of CO and NO_x first, and then divide to estimate the CO/NO_x. In this case, using the unfiltered data without removing station-days with low concentrations, we estimate discrepancies that are somewhat lower than in Table 5, ranging from 1.9 to 2.3. Overall, these results suggest that the CO/NO_x ratio in the emissions inventory is underestimated by a factor of roughly 2–3.

7. Assumptions and conclusions of emissions inventory evaluation

The analysis of VOC/NO_x ratios and CO/NO_x ratios in morning ambient measurements indicates that the official emissions inventory for the MCMA underestimates these ratios by factors of 2–3. Based on experience with emissions inventories in other urban areas (Fujita et al., 1992; CARB, 1997; Solomon et al., 1999), this discrepancy is more likely due to an underestimate of VOCs and CO emissions, than to an overestimate of NO_x emissions. If we assume that the NO_x emissions in the inventory are correct, this analysis suggests that VOC emissions and CO emissions are each underestimated by factors of 2–3, with greater confidence in the results for CO because of the greater availability of measurements.

The main assumption of this method is that morning measurements are representative of the ratios of emissions averaged over the metropolitan area. This requires that morning measurements carry little residual of pollution from the previous day, and that background concentrations are small or have the same ratios as the fresh emissions. This is supported by the modeling work of Fast and Zhong (1998) who show that overnight winds

clean the Mexico City basin fairly well of pollution from the previous day. It also requires that there is little chemical processing or deposition of species in the atmosphere, which should be a good assumption for morning hours, before photochemical activity becomes important. The good spatial and temporal coverage of the CO and NO_x measurements suggests that the measured CO/NO_x ratios should be representative of emissions during morning hours and throughout the entire year. How representative the measurements are is a more important issue for VOCs, since measurements are only available at few sites, and on a few days. The dispersion of points in the VOC/NO_x analysis at Xalostoc suggests the influence of local sources in this industrial region of the city, and therefore calls into question how representative this site is of emissions over a larger area. Clearly, more morning measurements of total VOCs at more sites and with greater frequency can help to improve this type of analysis in the future, as well as to improve more general understanding of VOCs concentrations.

Further, while the emissions inventory accounts for all species of VOCs, ambient measurements exclude some species. However, if including these species increases the ambient measurements of total VOCs substantially, then this would imply that a larger factor of correction is needed for the VOCs in the emissions inventory.

Finally, experience elsewhere has suggested that motor vehicles are often responsible for underestimates of VOC and CO emissions (Sawyer et al., 2000). To test whether motor vehicles are responsible for the underestimate, we compare the measured ratios of pollutant concentrations directly with ratios in fresh emissions from motor vehicles. CAM and IMP (2000) report measurements of in-use exhaust emissions from over 120,000 light-duty gasoline vehicles (mostly private autos) at 13 different sites in the MCMA, from March to October 2000, using infrared remote sensing techniques (Beaton et al., 1995). Because of the large number of vehicles and sampling locations, these measurements are thought to be representative of the Mexico City vehicle fleet. The average exhaust concentrations are reported to be 14000 ppm for CO (1.4%), 246 ppm VOCs, and 966 ppm NO_x. The VOC/NO_x ratio is therefore estimated to be 1.24 ppmC ppm⁻¹ (using 4.844 C per molecule), and the CO/NO_x ratio is 14.5 ppm ppm⁻¹. Both of these ratios are considerably smaller than the measured ambient ratios shown in Tables 4 and 5, suggesting that sources other than private motor vehicles may be important for VOCs and CO emissions, particularly sources which have higher VOC/NO_x and CO/NO_x ratios. For VOCs, this difference can be explained partially by emissions not associated with combustion, from a variety of evaporative sources and sources such as cleaning, painting, and industrial processes using solvents. For CO, heavy duty vehicle emissions and fires may be important sources.

8. Conclusions

To identify changes in the concentrations of total VOCs in the MCMA, systematic measurements of VOCs have been conducted every year since 1992. The resulting database is the longest coherent record of VOC concentrations in Mexico City. Morning measurements show very high concentrations of total VOCs relative to other urban areas, with some measured concentrations above 7000 ppbC, and the highest concentrations at Xalostoc in the northeast. Between 1992 and 2001, the total VOC concentrations measured at Xalostoc show a decreasing trend which is statistically significant. The measurements at the other two sites considered also show negative slopes in the linear regression, but these decreases are not statistically significant, and therefore inconclusive. The decrease in daily ozone peak concentrations of 32% from 1992 to 2001 cannot be attributed to decreases in NO_x or VOCs, since concentrations of both pollutants are estimated to decrease by roughly the same percentage. Given the growth in the vehicular fleet, population, and other activities related to emissions, these results showing that VOC concentrations have not increased and have possibly decreased suggest that government actions to control VOC emissions have been effective. However, the important challenges that remain to further control VOC emissions and to reduce ozone highlight the importance of continuing and supplementing this unique VOC dataset in the future.

The measurements of VOCs were further used to evaluate the 1998 official emissions inventory for the MCMA. The results indicate that the measured morning ratios of total VOC/ NO_x and CO/ NO_x were higher than the emissions inventory ratios, each by factors of two to three. Given experience elsewhere, this discrepancy is more likely due to underestimates of VOC and CO emissions than to an overestimate of NO_x emissions. Although there are important uncertainties in this simple ratio method, these results suggest that VOC and CO emissions may be substantially underestimated in the official emissions inventory, by as much as a factor of three.

Acknowledgements

The authors gratefully acknowledge the financial support of PEMEX, the DDF and the Instituto Mexicano del Petróleo, to obtain the data generated in several field studies conducted since 1992. In particular, Project D.00888 supported the 2000 and 2001 campaigns. The authors also thank the RAMA authorities for the database of NO_x and CO measurements. J. J. W. was supported by the US National Renewable Energy Laboratory under subcontract number ADC-2-

32409-01, and by an Environmental Fellowship from the American Association for the Advancement of Science.

References

- Arriaga-Colina, J.L., García, C.I., Seila, R.L., 1993. Compuestos Orgánicos Volátiles en la Atmósfera de la Ciudad de México. Iberoamerican Congress on Atmospheric Environment (CIAMAA/93), Mexico City, 22–23 October.
- Arriaga-Colina, J.L., Martínez, V.G., Escalona, S.S., Figueroa, G.Y., Seila, L.R., 1995. Hydrocarbon and carbonyl ozone precursors in Mexico City ambient air. Presented at the International Symposium of Measurement of Toxic and related Air Pollutants. Air and Waste Management Association, 16–18 May, North Carolina.
- Arriaga-Colina, J.L., Martínez, V.G., Escalona, S.S., Martínez, C.H., Seila, L.R., 1996. Compuestos Orgánicos Volátiles en la Atmósfera de la ZMCM. Contaminación Atmosférica. El Colegio Nacional, pp. 23–38.
- Arriaga-Colina, J.L., Escalona, S.S., Cervantes, M.A.D., Ordúñez, M.R., López, V.T., 1997. Seguimiento de COV en aire urbano de la ZMCM 1992–1996. Contaminación Atmosférica, Vol. II. Universidad Autónoma Metropolitana, pp. 67–96.
- Beaton, S.P., Bishop, G.A., Zhang, Y., Ashbaugh, L.L., Lawson, D.R., Stedman, D.H., 1995. On-road vehicle emissions: regulations, costs, and benefits. *Science* 268, 991–993.
- Blake, D.R., Rowland, F.S., 1995. Urban leakage of liquefied petroleum gas and its impact on Mexico City air quality. *Science* 269, 953–956.
- CAM (Comisión Ambiental Metropolitana), 2001. Inventario de emisiones a la atmósfera, Zona Metropolitana del Valle México, 1998.
- CAM and IMP (Comisión Ambiental Metropolitana and Instituto Mexicano del Petróleo), 2000. Auditoría Integral al Programa de Verificación Vehicular, Mexico City, November 2000.
- CARB (California Air Resources Board), 1997. Public meeting to consider approval and verification of the California emissions inventory, November 1997.
- Comisión Metropolitana para la Prevención y Control de la Contaminación en el Valle de México, 1994. La Contaminación Atmosférica en el Valle de México: Acciones para su Control 1988–1994.
- Edgerton, S.A., Arriaga, J.L., Archuleta, J., Bian, X., Chow, J.C., Coulter, R.L., Neff, W., Petty, R., et al., 1999. Particulate air pollution in Mexico City. A Collaborative Research Project. *Journal of the Air and Waste Management Association* 49, 1221–1229.
- Elliot, S., Simpson, I.J., Blake, D.R., Bossert, J.E., Chow, J., Arriaga-Colina, J.L., 2000. Mexico City and biogeochemistry of global urbanization. *Environmental Science Policy* 3, 145–156.
- Fast, J.D., Zhong, S., 1998. Meteorological factors associated with inhomogeneous ozone concentrations within the Mexico City basin. *Journal of Geophysical Research* 103 (D15), 18927–18946.

- Finlayson-Pitts, B.J., Pitts Jr., J.N., 2000. Chemistry of the Upper and Lower Atmosphere. Academic Press, New York (Chapter 16).
- Fujita, E.M., Croes, B.E., Bennett, C.L., Lawson, D.R., Lurmann, F.W., Main, H.H., 1992. Comparison of emission inventory and ambient concentration ratios of CO, NMOG, and NO_x in California's South Coast Air Basin. *Journal of the Air and Waste Management Association* 42 (3), 264–276.
- INE (Instituto Nacional de Ecología), 2000. Almanaque de datos y tendencias de la calidad del aire en Ciudades Mexicanas. JICA, INE, CENICA, Mexico.
- McClenny, W.A., Plei, J.D., Evans, G.F., 1991. Canister based method for monitoring toxic VOCs in ambient air. *Journal of Air and Waste Management Association* 41, 1308–1318.
- Molina, M.J., Molina, L.T., West, J.J., Sosa, G., Sheinbaum, C., San Martini, F., Zavala, M.A., McRae, G., 2002. Air pollution science in the MCMA: understanding source–receptor relationships through emissions inventories, measurements and modeling. In: Molina, L.T., Molina, M.J. (Eds.), *Air Quality in the Mexico Megacity*. Kluwer, Boston, pp. 137–202.
- NRC (US National Research Council), 1991. *Rethinking the Ozone Problem in Urban and Regional Air Pollution*. National Academy Press, Washington, DC.
- Riveros, G.H., Arriaga-Colina, J.L., Tejeda, J., Julian-Sánchez, A., Riveros-Rosas, H., 1998. Ozone and its precursors in the atmosphere of Mexico City. *Journal of the Air and Waste Management Association* 48, 866–871.
- Ruiz, M.E., Arriaga, J.L., García, I., 1996. Determinación de Compuestos Orgánicos Volátiles en la Atmósfera de la Ciudad de México Mediante el Uso de Sistemas Ópticos y Métodos Convencionales. *Atmosfera* 9, 119–135.
- Sawyer, R.F., Harley, R.A., Cadle, S.H., Norbeck, J.M., Slott, R., Bravo, H.A., 2000. Mobile sources critical review: 1998 NARSTO assessment. *Atmospheric Environment* 34, 2161–2181.
- Seila, L.R., Lonneman, A.W., Ruiz, S.M.E., 1993. Proceeding of International Symposium on Measurement of Toxic and Related Air Pollutants. Air and Waste Management Association, 4–7 May, Durham, NC.
- SMA-DDF (Secretaría del Medio Ambiente - Gobierno del Distrito Federal), 2001. Acervo. Evaluación del Programa “Hoy No Circula”. www.sma.df.gob.mx/acervo/10anos/evaluacion.htm.
- SMA-DDF (Secretaría del Medio Ambiente - Gobierno del Distrito Federal), 2002. Compendio Estadístico del Sistema de Monitoreo Atmosférico de la ZMCM 1986–2001. <http://www.sma.df.gob.mx/simat>.
- Solomon, P.A., Cowling, E.B., Hidy, G.M., Furiness, C.S., 1999. Comprehensive overview of scientific findings from major ozone field studies in North America and Europe, NARSTO critical review, TR-114238, available at <http://narsto.owt.com/Narsto>.
- US Environmental Protection Agency, 1999. Compendium method TO-14a. Determination of volatile organic compounds (VOCs) in ambient air using specially prepared canisters with subsequent analysis by gas chromatography (EPA/625/R-96/010b). Compendium of methods for the determination of toxic organic compounds in ambient air, 2nd Edition. US EPA, Cincinnati, OH.
- Watson, J.G., Chow, J.C., Fujita, E.M., 2001. Review of volatile organic compounds source apportionment by chemical mass balance. *Atmospheric Environment* 35, 1567–1584.
- West, J.J., Zavala, M.A., Molina, L.T., Molina, M.J., San Martini, F., McRae, J., Sosa, G., Arriaga-Colina, J.L. Modeling ozone photochemistry and evaluation of hydrocarbon emissions in Mexico City. *Journal of Geophysical Research*, submitted for publication.