

The impact of liquefied petroleum gas usage on air quality in Mexico City

J. Gasca*, E. Ortiz, H. Castillo, J.L. Jaimes, U. González

Instituto Mexicano del Petróleo, Eje Central Lázaro Cárdenas, # 152, Col. San Bartolo Atepehuacan, Delegación Gustavo A. Madero 07730, México, D.F., Mexico

Received 22 July 2003; accepted 27 December 2003

Abstract

Liquefied petroleum gas (LPG) is the main fuel used in the residential sector of the Metropolitan Zone in the Valley of Mexico (MZVM). LPG represents 16% of the total fuel consumption in the MZVM and its demand increased 14% from 1986 to 1999. Propane and butanes, the main compounds of LPG, constituted 29% of all non-methane hydrocarbons found in the air of Mexico City. Some researchers have reported that LPG losses are a significant cause of high ozone concentration in MZVM. Three analyses are carried out in this work to estimate LPG's share of responsibility for MZVM pollution problems. First, the correlation between LPG consumption and three ozone pollution indicators was calculated for the period of 1986–1999. The non-significant correlation of these indicators with LPG consumption in a monthly basis suggests that LPG associated emissions are not the foremost cause of ozone formation. Second, a simulation model is applied to three LPG related emission control strategies to estimate the reduction in the maximum ozone concentration. The most noticeable effect was obtained when both hydrocarbon (HC) and oxides of nitrogen (NO_x) emissions associated with LPG use were totally reduced. The other two strategies, that only reduce HC emissions, had a minimum effect on the ozone concentration. Third, organic compounds consumption in air samples captured and irradiated in outdoor smog chambers is used to determine the chemical loss rate of LPG associated species and aromatics in the MZVM. The smog chamber results showed that 70% of propane and *n*-butane remain at the end of a 1-day irradiation, therefore they remain in the MZVM atmosphere for several days being the reason for the high concentration of these compounds. LPG associated compounds only account for 18% of ozone formed but aromatics contribute 35% to ozone in smog chamber.

© 2004 Elsevier Ltd. All rights reserved.

Keywords: Mega cities; Propane; Butane; Ozone; Smog chambers

1. Introduction

Chemical analysis of air samples from the Metropolitan Zone in the Valley of Mexico (MZVM) showed that propane and butanes (*n*-butane and iso-butane) are hydrocarbon (HC) species with the highest concentrations in Mexico City (Arriaga et al., 1997). Blake and Rowland (1995) stated that liquefied petroleum gas (LPG) usage is a significant source of those HC contributing to the ozone pollution problem in the

MZVM, wherein 90% of the days ozone standard is exceeded (Gobierno del Distrito Federal (GDF), 2000). Since 1995, a few studies were carried to find the LPG contribution to the MZVM air contamination (Gamas et al., 2000; Hernández and Ortiz, 1999; Schifter et al., 2000).

Chromatographic analysis of air samples taken during seven experimental campaigns between 1992 and 1996 showed that non-methane hydrocarbons (NMHC) in the MZVM are composed of more than 200 chemical species, with a total average concentration of 3.52 ppmC early in the morning (Arriaga et al., 1997). The most abundant compounds were propane and butanes and

*Corresponding author. Fax.: +1-52-55-91-75-6935.

E-mail address: jgazca@imp.mx (J. Gasca).

they represented 29% of the NMHCs. In the Northern part of the city nitrogen oxides (NO_x) had a 0.26 ppm average concentration and the average NMHC/ NO_x ratio was 18; both values were obtained from 6 to 9 AM.

Gamas et al. (2000) estimated that $76,414 \text{ Mg yr}^{-1}$ of HC emissions were due to LPG usage in the MZVM. The main contributors were: domestic combustion (71%), low capacity domestic tanks (cylinders) distribution (10%) and leaks from domestic appliances (4%). Based on these results, several control measures to reduce LPG emissions were proposed. Modernization of domestic ranges with electronic lighters and more efficient burners, replacement of leaking cylinders, and repair of domestic appliances can reduce emissions up to $43,000 \text{ Mg yr}^{-1}$ (Gamas et al., 2000). Another proposed measure was the olefin reduction (from 3.1 to 1.1 mol%) in the LPG.

Hernández and Ortiz (1999) evaluated how much atmospheric concentration and emissions of propane and *n*-butane from all MZVM sources are contributing to ozone formation. A trajectory photochemical model, emissions and meteorological data from MZVM were used. Thus, it was observed that propane and *n*-butane were responsible for 23% of the maximum ozone concentration. This contribution can be split to 0.6% from propane emissions, 7.4% from *n*-butane emissions, 7.2% from propane accumulation and 7.9% from *n*-butane accumulation. Accumulation was represented as morning atmospheric concentrations in the model. Other significant emission sources of these ozone precursors in the MZVM are landfills, burning of garbage, and gasoline powered vehicle exhaust and evaporative emissions. The maximum concentration of propane decreased 69% from early morning to late afternoon. In addition to chemical reactions, the photochemical modeling considered the effects of dilution and deposition in the ambient propane concentration.

Schifter et al. (2000) evaluated the LPG vehicles program implemented in the MZVM. In Mexico City, from a total of 3 million vehicles, only about 28,000 LPG powered vehicles (LPGV) were in use. Most of these are light- and heavy-duty trucks originally fueled with gasoline and converted to LPG with certified devices. The exhaust emissions measurements of 134 LPGV showed that 95% of them exceeded the required environmental regulation values for certification, due to poor maintenance of vehicles, insufficient mandatory inspection and unreliable conversion kits used in MZVM. It was demonstrated that the conversion kits, calibrated for a mix of 70% propane works inefficiently due to the changes in fuel properties. Additionally, in order to improve the performance of vehicles, drivers often adjust the air/fuel ratio, decreasing the efficiency of emission control devices and their dynamic response.

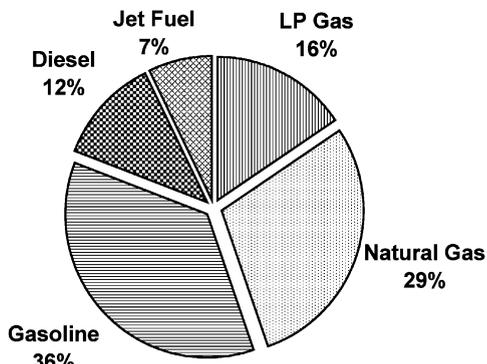


Fig. 1. MZVM fuel consumption distribution for 1999.

1.1. LPG consumption in the MZVM

LPG is the main household fuel in the MZVM. Cooking and water heating demanded 78.8 peta Joules (PJ) in 1986 and LPG demand increased to 89.7 PJ in 1999. This 14% LPG demand increment is lower than the 30% growth of the total fuel consumption during the same period ($446.5\text{--}577.7 \text{ PJ}$). LPG's share in MZVM fuel market decreased from 18% in 1986 to 16% in 1999. Fig. 1 shows the fuel consumption distribution in the MZVM.

LPG is used in 3.7 million ranges and 2 million water heaters, being distributed in portable cylinders to most of the houses (approximately 44 million cylinders are used/re-used annually). Another way of distribution is by gas delivery tank trucks (more than 300) supplying it to homes equipped with stationary tanks (Gamas et al., 2000).

We are estimating LPG's share in the MZVM pollution problem in this work. First, the correlations between LPG consumption and three ozone pollution indicators are being analyzed, from 1986 to 1999. Second, an air-quality simulation model is being applied to three LPG related emission control strategies, to estimate reduction in the maximum ozone concentration. Third, the kinetic reactivity of 28 compounds, quantified by using outdoor smog chambers, is being analyzed to determine the chemical saturated HC removal rate in the MZVM.

2. Methodology

2.1. Correlation of LPG consumption with MZVM ozone levels

Fig. 2 shows the LPG monthly consumption and three plots of ozone for the MZVM from 1986 to 1999. The plots are: the highest value of ozone (hourly average) in a month; the monthly average of daily ozone

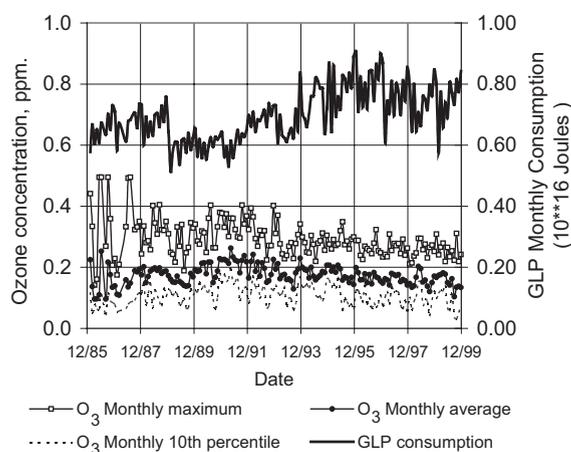


Fig. 2. LPG monthly consumption and ozone concentrations for MZVM.

maximums, and the monthly 10th percentile of daily ozone maximum. This last indicator is the upper threshold value and only 10% of the values are lower, so for 90% of the days in the MZVM, the ozone concentration is above the air quality standard (0.11 ppm 1 h average). The data correspond to the five main monitoring stations located in the different geographical areas of the MZVM (northwest, Tlalne-pantla; northeast, Xalostoc; Downtown, La Merced; southwest, Pedregal and southeast, Cerro de la Estrella). The data were recorded continuously from 1986 to 1999 reported as hourly averaged (Gobierno del Distrito Federal (GDF), 2000). The monthly ozone maximum value represents the highest one recorded at each and any of the five monitoring stations during the day, showing a decreasing trend from 1986 to 1999. The monthly average of daily ozone maximums and the 10th percentile of daily ozone maximums increased from 1986 to 1992, decreasing from 1992 to 1999. Correlation coefficients between LPG consumption and these indicators were obtained and are later discussed.

2.2. Air quality model

The effect of LPG emissions in MZVM air quality was simulated and evaluated by applying some of the tools, and results obtained by the Mexican Petroleum Institute; Los Alamos National Laboratory (1994) within the Mexico City Air Quality Research Initiative (MARI). The most relevant results and tools from MARI, related directly to the simulations, are as follows:

- Lagrangian (trajectory) air quality computer model (McRae and Russell, 1981), with atmospheric chemistry simulated using the Lurman et al. (1987)

photochemical mechanism. This vertically resolved model includes the effects of meteorology, emissions, surface removal processes and photochemistry.

- The effective mixing heights obtained from lidar measurements in 1992 and meteorological models.

Additional results used for air quality modeling were:

- 1995 measured concentrations and composition of NMHC polluting the air of the MZVM. More than 200 species were identified and grouped as required by the Lurman, Carter and Coyner (LCC) mechanism.
- 1995 emission inventory categorized by mobile and stationary sources, spatially and temporally distributed, with the NMHC grouped according to the inputs required by the lumped LCC mechanism.
- 25 February 1995, validated air quality and meteorology information from the MZVM Air Quality Monitoring Network (RAMA acronym in Spanish).

The ozone effects due to LPG emissions were obtained by changing the input emission data in the base case emissions and comparing the output results. The base case simulation represents the conditions of a typical winter day, associated with the highest ozone episodes in the MZVM. These meteorological conditions were chosen in order to focus on an air quality contingency plan.

A trajectory was established following a wind pattern which, early in the morning transports pollution from an industrial region in the northeast, through the downtown area, stressed by commercial activities, to a typical receptor site in the southwest, a residential area, where highest ozone concentrations are frequently observed. The trajectory is determined working backwards from the southwest. The procedure uses the data for wind speed and direction registered in that zone. From such data it is possible to infer the location where the air parcel was 1 h before. This procedure is repeated using the first output as input for the next iteration and so on, until the site corresponding to the air parcel location in the morning hours is determined. The trajectory selected coincides with the one predicted in MARI by the HOTMAC meteorological model for this time of the year (Williams et al., 1993). There are monitoring stations along the trajectory providing useful information to be used as input and to validate the model results. The trajectory starting point is the Xalostoc (XAL) station at 7:00 h; this station is located in a typical industrial area to the north of the city. La Merced (MER) station is located in downtown and represents mid-morning conditions, while Plateros and Pedregal (PED) stations provide the receptor characteristics in the afternoon and evening up to 21:00 h. Table 1 gives the meteorological conditions along the trajectory.

Table 1
25 February 1995 meteorological conditions along trajectory

Hour	Monitoring station	Temperature (K)	Relative humidity (%)	Wind velocity (m s ⁻¹)	Mixing height (m)
7	Xalostoc	282.3	70.5	3.8	53
8	Xalostoc	282.0	70.9	3.0	53
9	Xalostoc-Mer	284.6	64.3	3.2	109
10	Merced	286.6	57.9	2.9	723
11	Merced	288.4	54.1	3.4	1200
12	Merced-Plateros	291.2	48.7	3.7	1250
13	Pedregal	290.7	44.9	4.3	1300
14	Pedregal	290.7	40.2	4.1	1400
15	Pedregal	290.8	37.8	5.2	1500
16	Pedregal	292.5	37.9	2.8	2000
17	Pedregal	292.7	37.2	3.5	1900
18	Pedregal	292.0	36.8	5.3	1800
19	Pedregal	290.9	42.6	2.8	1741

The emissions, used as input for the model, correspond to those cells visited by the air parcel.

The Xalostoc station NMHC total concentration at 7 AM was set as 3.7 ppmC, the average of an experimental ambient air sampling campaign performed from 13 to 17 March 1995; the corresponding 6–9 AM mean NMHC total concentration for MER and PED stations was 3.8 and 1.8 ppmC, respectively. The initial NMHC/NO_x ratio used was 16.8. The values for NO_x concentration along the trajectory were derived from the RAMA monitoring stations.

The individual atmospheric HC species determined in the air sampling 1995 campaign are lumped according to the LCC mechanism (Lurman et al., 1987), yielding the species distribution shown in Table 2. This table includes formaldehyde, acetaldehyde and other carbonyl data obtained during March, 1993 in Xalostoc (Mexican Petroleum Institute; Los Alamos National Laboratory, 1994). The formaldehyde value (30 ppb) was consistent with those measured in the 1991 and 1992 campaigns (Mexican Petroleum Institute; Los Alamos National Laboratory, 1994); the median in all three campaigns was 17.6 ppb, the 90th percentile was 31.1 ppb and the 10th percentile was 12.9 ppb.

2.3. Emission inventory

There are six techniques used to estimate MZMV emission inventory (Ruiz and Gasca, 2002): Source sampling, emission models, emission factors, surveys, material balance and extrapolations. A total of 49 emission source categories are considered in MZMV emission inventory (Ruiz and Gasca, 2002). Industrial category includes 15 sources, all classified as point sources. Surveying is the main technique used to estimate emissions in this category, but the great emitters must measure their emissions. Service sector category includes 24 area sources. Emissions from this

Table 2
LCC species and corresponding carbon fraction

Lumped species	C fraction
Non-reactive	0.155
C4 + alkanes	0.575
Ethene	0.026
Higher alkenes	0.071
Mono-alkylbenzenes	0.053
Higher aromatics	0.063
Formaldehyde	0.008
Higher aldehydes	0.022
Methylethylketone	0.027

category are a consequence of activities in services, commerce and houses, and are estimated using emission factors, surveys and models. Transportation sector category includes 8 mobile sources and its emissions are estimated using models. Biogenic emissions are estimated using models and soil related emissions, mainly from erosion.

The most commonly used models for the integration of MZVM emission inventories are: Mobile5-MCMA.a3 (Gobierno del Distrito Federal-Radian, 1996) for mobile road sources, BEIS2 (USEPA, 1995a) for biogenic emissions, Tanks v 3.0 (USEPA, 1997) for fuel storage tanks evaporation, LANDFILL (USEPA, 1994) for landfills emissions, SIMS (USEPA, 1990) for water treatment plant emissions and FAAED 2.1 (Federal Aviation Administration, 1998) for airport emissions. Several assumptions, involved with the geographical location or local conditions of the MZVM, are considered in the application of those models.

Emission factors from USEPA AP-42 comprehensive set (USEPA, 1995b) are applied, taking into account differences in technology, quality of fuels and economic activity patterns between the United States and Mexico.

Table 3
Emission inventory

Source	HC (Mg yr ⁻¹)	NO _x (Mg yr ⁻¹)
<i>Mobile sources</i>		
LPG low capacity domestic tanks distribution	7683.5	0
LPG mobile sources hot soak evaporative	186.7	0
LPG mobile sources running losses evaporative	218.2	0
LPG mobile tailpipe	1818.8	1936.3
Total LPG mobile sources	9907.2	1936.3
Total MZVM mobile sources	258,527.1	93,723.0
LPG mobile sources (%)	3.8	2.1
<i>Stationary (industrial and area) sources</i>		
LPG commercial combustion	2917.4	643.1
LPG industrial combustion	1045.1	315.4
LPG agricultural combustion	2289.2	690.3
LPG cargo tanks unloading	291.7	0
LPG distribution plant storage	228.5	0
LPG distribution auto tanks loading	486	0
LPG mobile sources loading	558.5	0
LPG low capacity domestic tanks loading	554.3	0
LPG residential tanks loading	488.8	0
LPG industrial losses	18.9	0
LPG commercial losses	135.2	0
LPG residential losses	3104.3	0
LPG residential combustion	53,921.6	3434.0
Total LPG stationary sources	66,039.6	5082.8
Total MZVM stationary sources	293,750.5	35,579.6
LPG stationary sources (%)	22.5	14.3
Total LPG emissions	75,946.7	7019.1
Total MZVM emissions	552,277.6	129,302.6
LPG emissions (%)	13.8	5.4

Source sampling at representative points of handling, distribution and consumption of LPG was the technique used to estimate HC emissions (PEMEX, 1997; Gamas et al., 2000) and AP-42 emission factors were used to estimate NO_x emissions. The base case emission inventory used in this paper is shown in Table 3. LPG emissions related sources are given in detail and the other sources are taken from 1994 MZMV emission inventory (Ruiz and Gasca, 2000). It can be observed that LPG use accounts for almost 14% of HC emissions and 5% of NO_x emissions.

Mobile sources temporary emission pattern was estimated by traffic census. The number of vehicles passing by several MZVM points were totaled and the hourly average was calculated. Point sources temporary emission patterns were obtained from survey. Each

industry facility reports its timetable and emissions, so a representative average can be obtained for each one of the 15 industrial sources. The same procedure was carried out for the commercial and services emissions. As the great quantity of LPG emissions are related to domestic activities, a survey was applied to estimate domestic emissions temporary pattern. The resulting pattern is illustrated in Fig. 3 for mobile sources and LPG domestic consumption.

In addition, each HC source in the emission inventory is speciated. The compositions of evaporative and tailpipe mobile source emissions were measured by gas chromatography for a reduced LPGV fleet and are shown in Table 4 (Schifter et al., 2000). The LPG mobile sources carbonyl speciation was taken from Chang and Rudy (1990). Gasoline-associated emissions speciation includes formaldehyde and acetaldehyde measurements from a reduced MZVM gasoline fleet also, LPG loss speciation is shown in Table 5. This composition was averaged from several LPG samples analyzed by gas

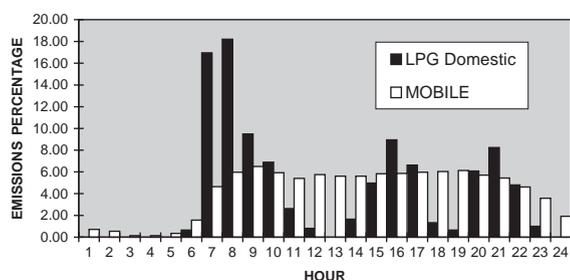


Fig. 3. Emissions temporal patterns.

Table 4
LPG mobile sources emissions composition

Compound	Weight fraction	
	Tailpipe	Evaporative
Methane	0.1014	0.0000
Ethylene	0.1036	0.0009
Acetylene	0.0298	0.0010
Ethane	0.0283	0.0123
Propylene	0.0364	0.0045
Propane	0.3466	0.4343
Isobutane	0.1647	0.2804
Isobutene	0.0064	0.0061
1-Butene	0.0015	0.0089
1,3-Butadiene	0.0011	0.0000
<i>n</i> -Butane	0.1676	0.2133
<i>trans</i> -Butene	0.0016	0.0165
<i>cis</i> -Butene	0.0012	0.0100
Iso-Pentane	0.0078	0.0087
<i>n</i> -Pentane	0.0019	0.0031
Total	1.0000	1.0000

Table 5
LPG loss composition

Compound	Weight fraction
Methane	0.0003
Ethylene	0.0071
Propane	0.4540
Isobutane	0.1491
<i>n</i> -Butane	0.2918
Isobutene	0.0014
1-Butene	0.0251
<i>trans</i> -Butene	0.0276
<i>cis</i> -Butene	0.0168
1,3-Butadiene	0.0005
Isopentane	0.0183
<i>n</i> -Pentane	0.0048
<i>n</i> -Hexane	0.0032
Total	1.0000

chromatography. Other emissions sources with MZVM composition are solvent use and vegetation. 72% of HC emissions have regional speciation. When this speciation is not available the air quality computer model (McRae and Russell, 1981) data base is used.

The emission inventory was spatially distributed in a 5600 km² simulation grid (16 × 14 cells, 5 km × 5 km each). Thus, the total emission in each grid cell is the sum from all of the source categories within the cell. The emissions along the trajectory are simply the particular emissions of the respective grid cells.

2.4. Scenarios

Different scenarios were simulated, through modifications of source categories in the emission inventory that properly reflect control options. In this study, only the source categories influenced by changes in LPG emissions were modified. Four scenarios were simulated. First, a base case scenario based on the conditions of 25 February 1995. A second scenario considered adapting electronic lighters to domestic ranges. Domestic stove pilots flame account for 27,338 ton yr⁻¹ of HC leaks (51% of the 53,921.6 LPG emissions in residential combustion) due to malfunctioning (Gamas et al., 2000). It is considered that adapting electronic lighters can reduce completely those emissions, i.e. a 100% efficiency control strategy.

The third scenario reflected the reduction of HC emissions from a variety of control measures:

- Reinforcement of the inspection program for LPG-fueled vehicles. Tail pipe emissions are estimated as 1818.6 ton yr⁻¹ and it is assumed that the inspection of LPG-fueled fleet can reduce these emissions an 80%, i.e. a reduction of 1454.9 ton yr⁻¹ (Gamas et al., 2000).

- Maintenance of LPG-fueled vehicles. Hot soak evaporative emissions account for 186.7 ton yr⁻¹ and it is considered that proper maintenance can reduce these emissions 100% (Gamas et al., 2000).
- Installation of low-emission valves and magnetic level sensors in tanker trucks. An estimate leakage of 291.7 ton yr⁻¹ of HC occurs when tanker trucks discharge LPG to storage tanks at MZVM distribution plants. The installation of low-emission valves can reduce those emissions 1.9 ton yr⁻¹. A more effective measure is the installation of magnetic level sensors that can reduce 106 ton yr⁻¹ the HC emissions (PEMEX, 1997).
- Installation of low-emission valves in distribution plants. An estimate leakage of 554.3 ton yr⁻¹ of HC occurs when low capacity cylinders are filled with LPG at distribution plants. The installation of low-emission valves in the distribution plants can reduce those emissions 125.1 ton yr⁻¹ (PEMEX, 1997).
- Installation of low-emission valves and magnetic level sensors in distribution trucks. An estimate leakage of 486 ton yr⁻¹ of HC occurs when distribution trucks are refilled with LPG at distribution plants. The installation of low-emission valves and magnetic level sensors can reduce those emissions 483.7 ton yr⁻¹. Additionally, when residential LPG tanks are refilled by means of distribution trucks, an estimated leakage of 488.8 ton yr⁻¹ of HC occurs. The proposed control measure can reduce the HC losses 342.63 ton yr⁻¹ (PEMEX, 1997).
- Adapting electronic lighters and installation of new burners in domestic ranges. Besides the adaptation of electronic lighters that can reduce 27,338 ton yr⁻¹ of HC, this control measure considers the installation of new burners in domestic ranges. It is estimated that new burners can reduce LPG losses 7298.9 ton yr⁻¹. Therefore, both control measures applied to domestic ranges can reduce HC emissions 34,637.2 ton yr⁻¹ (Gamas et al., 2000).

The implementation of all previous listed measures can reduce a total of HC emissions 37,338.1 ton yr⁻¹. No control action to reduce NO_x emissions was identified.

Finally, the total reduction in NO_x and HC emissions associated with LPG use was established in the fourth scenario. Table 6 shows the HC and NO_x total emissions for each one of those scenarios.

2.5. Outdoor smog chamber experiments

Outdoor smog chamber experiments were carried out on captive MZVM air under natural irradiation (Sandoval et al., 2001). All experiments were performed in 500l chambers built with 0.05 mm FET-Teflon type A film. Chambers were heat sealed along the edges. Nine

Table 6
Simulated scenarios

Scenario	Description	HC (Mg yr ⁻¹)	NO _x (Mg yr ⁻¹)
Base case	25 February 1995	552,277.6	129,302.6
Control strategy 1	27,338.3 Mg yr ⁻¹ HC emissions reduction from residential ranges	524,939.3	129,302.6
Control strategy 2	37,338.1 Mg yr ⁻¹ HC emissions reduction from LPG plants, LPG distribution, LPG residential use and LPG mobile sources	514,939.5	129,302.6
None LPG associated emissions	Total reduction in the NO _x (7019 Mg yr ⁻¹) and HC (75,947.3 Mg yr ⁻¹) LPG associated emissions	476,330.3	122,283.6

chambers were filled with ambient air and were evaluated for leaks early in the morning.

In eight of the chambers, perturbed chambers, the initial NMHC and/or NO_x concentrations were varied by adding various combinations of a mixture of NMHC, clean air, or NO_x. These experiments were performed to determine the answer of maximum ozone levels, to changes in the initial concentrations of NMHC and NO_x, as reported by Sandoval et al. (2001). NO_x and ozone concentrations were measured every 58 min in all of the nine chambers until 17 h. A Thermo Environment Inc. 42 analyzer, equipped with a nylon filter to remove nitric acid was used to measure NO_x, and a Thermo Environment Inc. 49 analyzer was used to measure ozone. Ultraviolet (UV) flux was measured with an Eppley ultraviolet radiometer located besides the experimental system. Additional experiments showed that ozone and NO_x chambers-wall losses and line losses were negligible.

Temperature was taken inside the middle chamber with an aspirated thermocouple and with a single thermocouple outside this control bag, which was left with the MZVM ambient air. The differences between internal and external temperatures were negligible. In the morning, air samples from the control bag were caught in canisters and analyzed by gas chromatography to determine initial NMHC concentration, according to the EPA TO-14 procedure. The control bag was exposed to natural MZVM irradiation. In the afternoon, air samples were taken from it to analyze the remaining NMHC concentration. In addition to total NMHC concentration, the EPA-TO-14 method gives specific concentration for several HC. Consequently, it is possible to calculate for this control chamber the consumption of the more typical MZVM HC and to estimate their kinetic reactivity in the MVMZ conditions. The kinetic reactivity is the fraction of volatile organic compound (VOC) which undergoes chemical reaction in the atmosphere during the considered time period (Carter, 1998). It primarily depends on the rate constants for the VOC atmospheric reactions, but also on the overall levels of OH radicals, ozone and UV

radiation in the scenario the VOC react. Carter (1998) calculated kinetic reactivity for the majorities of HC encountered in USA cities. He considered three scenarios, but the more convenient is the maximum incremental reactivity (MIR) scenario, in which the effect of added HC is greatest on the ozone formed.

The mechanistic reactivity is the number of molecules of ozone formed for each molecule of VOC which reacts (Carter, 1998). It reflects both the nature of VOC reaction mechanism and also the efficiency of ozone formation from the reactions of VOC in the particular scenario. Carter (1998) calculated mechanistic reactivity for the MIR and other scenarios. The ozone formed can be calculated by multiplying the mechanistic reactivity and the amount of VOC that reacts.

3. Results

3.1. Correlation coefficients of LPG consumption with MZVM ozone levels

Correlation coefficients (*r*) of monthly ozone maximum, monthly averages of daily ozone maximums, and monthly 10th percentile of daily ozone maximum with LPG monthly consumption were -0.18, -0.18 and -0.19, respectively, for the entire period 1986–1999. These values indicate a non-significant correlation. Therefore, LPG consumption is not the foremost cause for the ozone levels in the MZVM, between 1986 and 1999.

3.2. Simulated ozone concentrations

Table 7 lists the results for ozone concentrations, per hour from 8:00 to 21:00 h, for the base case and the simulated scenarios. This table also contains the monitored values, registered by the RAMA station, representative of the grid cell along the trajectory for 25 February 1995; the date chosen to calibrate the base case.

Table 7
Simulated ozone concentration

Hour	Measured in the RAMA station corresponding to the trajectory	Ozone (ppm)			
		Base case	First control strategy	Second control strategy	Without LPG associated emissions
7	0.019	0.040	0.040	0.040	0.040
8	0.022	0.002	0.002	0.002	0.002
9	—	0.012	0.011	0.012	0.011
10	0.021	0.033	0.033	0.033	0.033
11	0.036	0.058	0.058	0.057	0.056
12	0.080	0.105	0.106	0.105	0.103
13	0.184	0.175	0.176	0.175	0.172
14	0.253	0.212	0.213	0.212	0.209
15	0.260	0.224	0.224	0.224	0.221
16	0.238	0.224	0.224	0.224	0.221
17	0.235	0.207	0.207	0.207	0.204
18	0.223	0.196	0.195	0.196	0.193
19	0.186	0.170	0.170	0.170	0.168
20	0.148	0.108	0.118	0.108	0.118
21	0.058	0.038	0.061	0.038	0.037

The ozone reduction with respect to the base case is null for strategies that only reduce HC (scenarios two and three) and it is 1% for the scenario reducing totally the LPG HC and NO_x associated emissions.

3.3. Reactivity of HC in MZVM outdoor smog chamber

The initial NMHC concentration, NO_x concentration, temperature and irradiation showed a large day-to-day variability during the performance of the natural irradiance experiments. NMHC concentration varied from 1490 to 5962 ppbC; NO_x concentration varied from 37.4 to 271 ppb and NMHC/NO_x ratio ranged from 9 to 32 with an average of 20.6. Average temperature was 299 K and average UV irradiation was 21.4 W m⁻². As a result of these environmental conditions, control bags showed a strong variation in the capacity of the air in the morning in the MZVM to generate ozone, as the maximum of this pollutant ranged from 290 to 600 ppb.

Although the main objective of this experiment was to determine the effect of the initial NMHC and NO_x concentrations on maximum ozone levels in the MZVM (Sandoval et al., 2001), it was possible to estimate the kinetic reactivity for 28 compounds, including LPG associated compounds, using the control chamber data. The average compound consumption in 6 days and the experimental kinetic reactivity, calculated as the ratio of final to initial compound concentration, are shown in Table 8; the kinetic and mechanistic reactivity estimated

by Carter (1998) in the MIR scenario for those compounds are shown in the same table.

Contribution of each HC to ozone formed was estimated using the average compound consumption in 6 days and the MIR mechanistic reactivity (Carter, 1998). As this contribution depends on the chosen scenario, relative contributions are reported in the last column of Table 8 as this varies less between scenarios (Carter, 1998). Formaldehyde relative contribution was estimated using the MIR reactivities values because there are no formaldehyde smog chamber consumption data on MZVM conditions; the initial formaldehyde level was supposed to be 30 ppb.

4. Discussion

The non-significant correlation of monthly ozone maximum, monthly averages of daily ozone maximums, and monthly 10th percentile of daily ozone maximum with LPG monthly consumption in the 1986–1999 period, indicates that non-LPG-associated emission sources are more important to ozone formation than LPG-associated emissions. In fact, the control strategies implemented in the last 10 years in Mexico City were related mainly to gasoline-powered mobile sources (Comisión Ambiental Metropolitana (CAM), 2002). The slight reduction in the MZVM ozone levels obtained from 1992 to 1999 can be attributed to those strategies.

An analysis of the simulation results, particularly comparisons against the base case, showed that the most

Table 8
 NMHC outdoor smog chamber kinetic reactivity in the MZVM

	Name	NMHC reacted (ppbC)	Smog chamber kinetic reactivity (ppbC reacted/ppbC initial ⁻¹)	MIR kinetic reactivity Carter (1998) (ppbC reacted/ppbC initial ⁻¹)	MIR Mechanistic reactivity Carter (1998) (ppb-ozone/ppbC reacted ⁻¹)	Relative Contribution to Ozone formation (%)
1	Ethylene	66.90	0.52	0.69	3.20	15.44
2	<i>m/p</i> -Xylene	90.93	0.59	0.89	2.30	15.09
3	Formaldehyde	30.00	—	0.94	4.50	9.15
4	Toluene	83.67	0.39	0.57	1.32	7.97
5	Propane	100.94	0.31	0.16	0.93	6.77
6	3-Methyl-1-butene	42.43	0.40	0.96	1.90	5.81
7	<i>o</i> -Xylene	35.44	0.43	0.83	2.20	5.62
8	<i>n</i> -Butane	67.88	0.32	0.31	0.99	4.85
9	1,2,4-Trimethylbenzene	25.11	0.73	0.96	2.60	4.71
10	Propene	17.79	0.71	0.94	2.90	3.72
11	Isobutane	31.87	0.26	0.29	1.25	2.87
12	Iso-pentane	27.90	0.23	0.43	0.96	1.93
13	1-Butene	9.48	0.62	0.96	2.70	1.85
14	2-Methyl Pentane	23.78	0.38	0.55	0.83	1.42
15	Ethyl Benzene	16.13	0.39	0.63	1.18	1.37
16	<i>trans</i> -2-Butene	6.01	0.81	0.98	3.00	1.30
17	<i>n</i> -Pentane	24.20	0.31	0.45	0.70	1.22
18	Isobutene	20.13	0.81	0.98	0.83	1.21
19	<i>cis</i> -2-butene	5.21	0.91	0.98	3.00	1.13
20	3-Methylpentane	16.94	0.37	0.56	0.81	0.99
21	2-Methyl-1-butene	9.11	0.40	0.98	1.46	0.96
22	Ethyl-2-pentene	4.12	0.89	0.98	2.60	0.77
23	<i>n</i> -Hexane	19.32	0.23	0.55	0.53	0.74
24	3-Methyl hexane	13.61	0.36	0.64	0.65	0.64
25	2-Methyl-2-butene	4.39	0.96	0.99	1.90	0.60
26	1-Pentene	4.13	0.76	0.96	1.90	0.57
27	<i>trans</i> -3-octene	3.87	0.79	0.98	1.60	0.45
28	Isoprene	2.28	0.88	0.99	2.60	0.43
29	<i>cis</i> -2-pentene	2.25	1.00	0.98	2.60	0.42

noticeable effect is obtained when all emissions associated with the use of LPG are totally reduced (14% reduction for HC emissions and 5% reduction for NO_x emissions). In the case of the two first strategies, slightly reducing HC emissions (5% in the first control strategy and 7% in the second control strategy) the effect on the ozone concentration is minimal. It has been reported that the reduction of both NO_x and HC emissions is the best control strategy for Mexico City (Sandoval et al., 2001).

The correlation coefficient between experimental MZVM and MIR kinetic reactivity was 0.8. Butanes experimental and MIR kinetic reactivity are almost

identical, but propane experimental reactivity is almost twice his MIR kinetic reactivity, whereas isopentane experimental kinetic reactivity is half his MIR kinetic reactivity. On the other hand, experimental kinetic reactivity values of olefins are lower than the corresponding MIR kinetic reactivity (ranging from 35% lower for 1-butene to 7% lower for *cis*-butene) and aromatics experimental kinetic reactivity values are lower than the corresponding MIR kinetic reactivity (ranging from 48% lower for *o*-xylene to 31% lower for toluene).

The reaction rates of propane and butane are low enough to prevent their total consumption in single-day

irradiations in the smog chambers. As it is shown in Table 8 less than one-third of the initial quantity of LPG saturated compounds react (propane, nbutane and isobutene kinetic reactivities are 0.31, 0.32 and 0.26, respectively). Hernández and Ortiz (1999) found, by photochemical modeling, that the maximum concentration of propane decreased 69% from morning to evening. In their simulation, dilution and deposition were taken into consideration in addition to photochemical reactions. Smog chamber experiments and modeling results indicate that propane and butane remain in the MZVM atmosphere for more than a day. This fact explains the high concentration of these compounds in MZVM.

Conversely, 60% or more of the C4 olefins are consumed in the smog chambers, twice the consumption of propane and butanes. As MIR mechanistic reactivity for LPG-associated olefins is three times the mechanistic reactivity of propane and butanes, each olefin molecule can contribute six times to ozone formation as compared to a chemically saturated molecule. With this in mind, a suitable control strategy implemented in 1995 was the reduction in the content of LPG olefins, from 3.1 to 1.1 mol%.

However, propane and butanes concentrations in air are 30 times C4 olefins concentrations, so propane and butanes (LPG-associated saturated compounds) contribute 14.5% to the ozone formed, and the LPG-associated olefins (1-butene, *trans*-butene and *cis*-butene) contribute 4%.

The main contributor to ozone formed in smog chambers is ethylene (15%), mainly deriving from gasoline vehicles exhausts; although LPGV also emit ethylene. The contribution of aromatic chemicals (xylenes, 1,2,4 trimethylbenzene, ethylbenzene and toluene) to ozone formation was 35% in smog chambers. Aromatic chemicals in the MZVM come from gasoline and diesel exhausts, and the use of solvents (Mugica et al., 2003).

The formaldehyde contribution to ozone formed in MZVM conditions is important, but the 9% relative contribution reported in Table 8 is only a rough estimation.

5. Conclusions

- The non-significant correlation between LPG consumption and ozone concentration indicates that LPG emissions are not the foremost cause for ozone levels in the MZVM.
- According to the simulated scenarios, the most noticeable effect on ozone maximum is obtained (a 1.3% reduction) when all emissions associated with the use of LPG are totally reduced.

- From both, smog chamber experiments and modeling results, it can be inferred that propane and butanes remain for a longer time in the urban atmosphere than olefins. Almost 70% of C3 and C4 paraffin compounds do not react and can remain in the MZVM urban atmosphere until the following day.
- LPG associated chemical saturated compounds account for 14.5%, LPG associated olefins account for 4%, and aromatic compounds account for 35% of the ozone formed in smog chamber experiments in the MZVM.
- Each C4 olefin molecule contributes to form ozone six times the amount a saturate molecule does according to smog chamber experiments. A suitable control strategy in MZVM was the LPG olefin content reduction, from 3.1 to 1.1 mol%, implemented in 1995.

Acknowledgements

We are deeply grateful to Mr. Carlos Fernández from the Mexican Petroleum Institute for his most helpful advice in the preparation of the manuscript. Thanks to Nelson Kelly from General Motors Chemical and Environmental Science Lab for his comments.

Mexican Petroleum Institute supported this research as part of the project D888. PEMEX supported in 1995 smog chamber research and in 1997 LPG emissions data gathering.

References

- Arriaga, J.L., Escalona, S., Cervantes, A., Orduñez, R., Limón, T., 1997. Seguimiento de COV en el aire urbano de la ZMCM. 1992–1996. In: Colín, L.G., Varela, J. (Eds.), Contaminación Atmosférica, Vol. 2, 1ª edición. El Colegio Nacional, México, D.F., pp. 67–96.
- Blake, R.B., Rowland, F.S., 1995. Urban leakage of liquefied petroleum gas and its impact on Mexico City air quality. *Science* 269, 953–955.
- Comisión Ambiental Metropolitana (CAM), 2002. Programa para Mejorar la Calidad del Aire de la Zona Metropolitana del Valle de México 2002–2010, 1ª edición. Gobierno del Estado de México, Gobierno del Distrito Federal, Secretaría de Medio Ambiente y Recursos Naturales, Secretaría de Salud, pp. 1–7.
- Carter, W.P.L., 1998. Development and application of an up-to-date photochemical mechanism for airshed modeling and reactivity assessment. Final Report Contract No. A932-094, California Air Resource Board, Sacramento CA, USA, April 1998.
- Chang, T.Y., Rudy, S.J., 1990. Ozone-forming potential of organic emissions from alternative-fueled vehicles. *Atmospheric Environment* 24A, 2421–2430.

- Federal Aviation Administration, 1998. Aircraft engine emission user guide and database. FAEED v3.1. Office of Environment and Energy, Federal Aviation Administration, Washington, DC, USA.
- Gamas, E., Magdaleno, M., Díaz, L., Schifter, I., Ontiveros, L., Alvarez-Cansino, G., 2000. Contribution of liquefied petroleum gas to air pollution in the metropolitan area of Mexico City. *Journal of the Air and Waste Management Association* 50, 188–198.
- Gobierno del Distrito Federal-RADIAN, 1996. Manual de factores de emisión para fuentes móviles M5MCMA.a3. Secretaría del Medio Ambiente, Gobierno del Distrito Federal México D.F.
- Gobierno del Distrito Federal (GDF), 2000. Compendio Estadístico de la Calidad del Aire 1986–1999, 1ª edición. Secretaría del Medio Ambiente, México, D.F.
- Hernández, F., Ortiz, E., 1999. Application of photochemical trajectory model to evaluate ozone formation by atmospheric concentrations and emissions of propane and butane in Mexico City Metropolitan Zone. *Molecular Engineering* (Dated 2000) 8, 447–458.
- Lurman, F.W., Carter, W.P.L., Coyner, L.A., 1987. A Surrogate Species Chemical Reaction Mechanism for Urban-Scale Air Quality Simulation Models, Vol. I. Adaptation of the Mechanism, Vol. II. Guidelines for Using the Mechanism. Environmental Protection Agency, Research, Triangle Park, NC, USA (Contract 68-02-4104).
- McRae, G.J., Russell, A.G., 1981. Vertically resolved Lagrangian trajectory model, Report 206-40, Environmental Quality Laboratory, Pasadena, CA, USA.
- Mexican Petroleum Institute; Los Alamos National Laboratory, 1994. Mexico City Air Quality Research Initiative, Report IMP/LA-12699, Mexico, DF, Mexico and Los Alamos, NM, USA.
- Mugica, V., Ruiz, M.E., Watson, J., Chow, J., 2003. Volatile aromatic compounds in Mexico City atmosphere: levels and source apportionment. *Atmósfera* 3, 15–27.
- PEMEX, 1997. Efecto de los componentes del gas licuado de petróleo en la acumulación de ozono de la atmósfera de la Zona Metropolitana de la Ciudad de México, 1a edición. México, ISBN 968-6699-36-8.
- Ruiz, M.E., Gasca, J., 2002. Emissions trends and pollution control strategies in the Mexico city metropolitan area. In: Fenn, M.E., Bauer, L.I., Hernandez-Tejeda, T. (Eds.), *Urban Air Pollution and Forests. Resources at Risk in the Mexico City Air Basin*, Springer Verlag Ecological Series, 1st Edition. USA, ISBN 0-387-95337X.
- Sandoval, J., Marroquín, O., Jaimes, J.L., Zúñiga, V.A., González, E., Guzmán, F., 2001. Effect of hydrocarbon and nitrogen oxides on ozone formation in smog chambers exposed to solar irradiance of Mexico City. *Atmósfera* 1, 17–27.
- Schifter, I., Díaz, L., López-Salinas, E., Rodríguez, R., Ávalos, S., Guerrero, V., 2000. An evaluation of the LPG vehicles program in the metropolitan area of Mexico City. *Journal of the Air and Waste Management Association* 50, 301–309.
- USEPA, 1990. Background documents for the surface impoundment modeling systems, SIMS. Version 2.0 PA-450/4-90019b. Environmental Protection Agency, Washington, DC, USA.
- USEPA, 1994. LANDFILL Model. Environmental Protection Agency, Washington, DC, USA.
- USEPA, 1995a. Compilation of Air Pollutants Emissions Factors, AP-42 Vols. I and II. Environmental Protection Agency, Washington, DC, USA.
- USEPA, 1995b. User's guide to the personal computer version of biogenic emission inventory system (PC-BEIS2) EPA-600/R-95-091. Environmental Protection Agency, Washington, DC, USA.
- USEPA, 1997. TANKS 3.1 Installation Instructions. Environmental Protection Agency, Washington, DC, USA.
- Williams, M.D., Brown, M.J., Cruz, X., Sosa, G., Streit, G., 1993. Development and testing of meteorology and air dispersion models for Mexico City. Proceedings of the International Conference on Regional Photochemical Measurement and Modeling Studies, San Diego, CA, USA, November 1993.