Exploring the Liquefied Petroleum Gas - Ozone Relation in Guadalajara, Mexico, by Smog Chamber Experiments

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Abstract. It has been hypothesized that liquefied petroleum gas (LPG) emissions can increase substantially the formation of ozone (O_3) in the ambient air. We tested experimentally such hypothesis in Guadalajara's downtown by captive-air irradiation (CAI) techniques. During November 1997-January, 1998, morning ambient air samples were confined in outdoor smog chambers and subjected to the following treatments: 35% addition of commercial LPG or one out of two mixtures of major LPG compounds (propane/butane: 70/30% or 60/40%), 50% dilution of total volatile hydrocarbons (VOCs), and 50% dilution of LPG associated VOCs (C2-C4). Captive and untreated morning ambient air served as experimental control. This experiment ran under ambient sunlight and temperature. Chamber O_3 was measured hourly from 08:00-18:00h, and the maximum O_3 concentration (O_{3max}) was used for treatment comparisons. Daily O_3 profiles within the control chambers and in open ambient air were fairly similar, though O_{3max} was consistently higher in the chambers. Only the 50% dilution of total volatile hydrocarbons (VOCs) had a significant effect on O_{3max}, which decreased by 16% on average. These results indicate that high O_3 levels in Guadalajara can not be explained by LPG emissions. A supplementary experiment with captive clean air added with commercial LPG or the same propane/butane mixtures showed that O_3 formation was less favoured by the 70/30% mixture.
Key words: Smog chamber experiments, ozone, air quality and liquefied petroleum gas.

Resumen. Se ha planteado como hipótesis que las emisiones del Gas Licuado del Petróleo (GLP) al aire ambiente, pueden incrementar sustancialmente la fomación de ozono (O_3). Se probó experimentalmente esta hipótesis en el centro de la ciudad de Guadalajara, Jal., utilizando la técnica de Irradiación en Aire Cautivo (CAI). Durante noviembre de 1997 y enero de 1998, muestras de aire ambiente matutino fueron alimentadas a cámaras de esmog exteriores y se sometieron a los siguientes tratamientos: una adición de 35% de GLP comercial, 35% de adición de mezcla sintética 70/30 de propano/butano y 35% de adición de mezcla también sintética 60/40 de propano/butano, 50% de dilución del total de los hidrocarburos volátiles (VOCs) y 50% de dilución de compuestos asociados al GLP. Aire ambiente matutino no tratado sirvió como control experimental. Este experimento se llevó a cabo bajo condiciones ambientales de luz solar (radiación) y temperatura. El ozono en las cámaras fue medido cada hora de la 08:00-18:00h y la concentración máxima de ozono (O_{3max}) se usó para el tratamiento de las comparaciones. Los perfiles diarios de ozono dentro de la cámara de control y en el aire ambiente fueron muy similares, aunque el O_{3max} fue consistentemente más alto en las cámaras. Solo la dilución de los hidrocarburos volátiles totales tuvo un efecto significativo en el O_{3max}, el cual disminuyó alrededor del 16% en promedio. Estos resultados indican que los altos niveles de ozono en la ciudad de Guadalajara, Jal. no están asociados a las emisiones de GLP. Un experimento adicional con aire limpio (aire cero), adicionado con LPG comercial o las mismas mezclas de propano/butano mostraron que la formación de ozono fue menos favorecida por la mezcla 70/30.
Palabras clave: Experimentos en cámaras de esmog, Ozono, Calidad del Aire y gas licuado del petróleo.

Introduction

Ozone is a major secondary air pollutant with important adverse effects on human and ecosystem health. Tropospheric O_3 is mostly produced by photochemical reactions between volatile organic compounds (VOCs) and nitrogen oxides (NO_x) exposed to ultraviolet solar radiation [1]. Understanding how VOCs and NO_x interact under local conditions to form O_3 has been instrumental in designing effective control strategies in a number of cities around the world.

VOCs and NO_x emited into the ambient air largely derive from petroleum use. VOCs associated to liquefied petroleum gas (LPG) such as propane, isobutane, and n-butane were reported as an important factor behind the typical high levels of O_3 in Mexico City [2]. According to that report, uncontrolled leakages of unburned LPG from a variety of local sources and incomplete LPG combustion processes accounted for the high atmospheric concentrations of LPG associated compounds in Mexico City. Because some alkanes and other minor olefinic components of LPG may also produce substantial amounts of atmospheric hydroxyl radicals, another well-known participant in O_3 photochemistry, Blake and Rowland [2] recommended controlling LPG leakages and changing the chemical composition of this fuel to substantially reduce the O_3 levels in the Mexican capital.

Those findings prompted the Mexican oil company (PEMEX) to launch research projects addressing the LPG-O_3 relation in some large Mexican cities [3]. The present report is about the case of Guadalajara, where high O_3 episodes (>250 ppb) appear to develop when concentrations of total non-methane VOCs (TNMHC) and NO_x reach, respectively, about 6000 and 200 ppb in the ambient air [4]. However, similar O_3

episodes also occur with different ambient concentrations of those precursors, which suggest that other environmental factors may be involved.

It is not known how LPG emissions may relate to O_3 formation in Guadalajara. Its potential LPG emissions sources, as the second largest Mexican city, are variated. LPG leaks, for instance, may derive from about 763 thousand residences, which may also be a major source of many non-LPG VOCs. Guadalajara has also a quite large car fleet (663 thousand vehicles) and 369 industries [5], which are also important local sources of O_3 precursors.

To evaluate wheather LPG emissions or mixtures of its major chemical components (propane and butane) contribute significantly to O_3 formation in Guadalajara, outdoor smog chamber experiments (captive-air irradiation approach, CAI) were conducted under sunlight irradiation and ambient temperature. Although airshed models may be preferred by decision makers to set up O_3 control strategies, CAI experiments continue to provide direct quantitation of potential influences from particular O_3 precursors using ambient air or clean air as reaction matrix. CAI experiments have been used in different urban areas [6-12]. Today, they are mostly employed in determining empirical reactivity rates for O_3 forming compounds.

This is a report on experimental results to test the following hypothesis: 1) If LPG concentrations in ambient air were to increase in Guadalajara, O_3 would be expected to increase significantly over current levels; 2) The high O_3 levels in Guadalajara can be significantly abated by removing LPG compounds from the local airshed. These results also provide preliminary insights on the subject of how changing the composition of commercial LPG may help to improve the local air quality and the weight of VOCs, NO_x and ambient factors (UV light and temperature) on O_3 formation.

Experimental

Site

A temporary laboratory was placed close to the Guadalajara historical center on the roof of a public edifice. The experiment with confined ambient air was completed within 30 days (November-December, 1997); A supplementary experiment with clean air was completed within five days in January, 1998. Site VOCs and NO_x had high concentrations most of the experimental days. The average site VOCs/NOx ratio was 30/1, which was similar to the average ratio for the entire Guadalajara Metropolitan Area (GMA). Average site ambient conditions relevant to O_3 formation are summarized in Table 1.

Smog Chamber System

Ozone formation was studied in a nine-chamber CAI system. Chambers had 500 L in volume and were made of transparent FEP-Teflon (0.005 mm) heat-sealed with type A film (Figure 1). All fittings were also Teflon and were connected by Teflon

Table 1. Summary of average environmental conditions in downtown. Guadalajara

Variable	Values
Experimental days	30
Average T (ºC)	23.42 ±1.5
Tmax (ºC)	33.60 ± 2.0
UV_{max} radiation (%)	79.80 ± 4.14
Average UVmax radiation (%)	72.45 ± 4.56

UV_{max} radiation = average ultraviolet flux from 0800 to 1800h x 100/23.8, where 23.8 watt/m^2 is the largest measured ultraviolet average in the 0800-1800h interval

Average UVmax radiation = (maximum 1h ultraviolet flux) x 100/45.3, where 45.3 watt/m^2 was the largest 1 h. Flux

tubing to a Pyrex bulb (2 L) used to fill the chambers with air compressors. Filling rates were nearly identical between chambers. Four vacuum pumps also connected to the Pyrex bulb were used to remove air from the chambers in dilution experiments. This system allowed gas dilutions with a $\pm 1\%$ precision. Clean air was provided when needed from ultra pure (zero) air tanks. Eight chambers were used to apply the experimental treatments. Another chamber filled everyday with untreated ambient air served as a reference, and was used for temperature measurements along the day as well as for determining initial (morning) and final (afternoon) VOCs concentrations. Samples for VOCs analyzes were substracted from the reference chamber by canisters and analyzed by
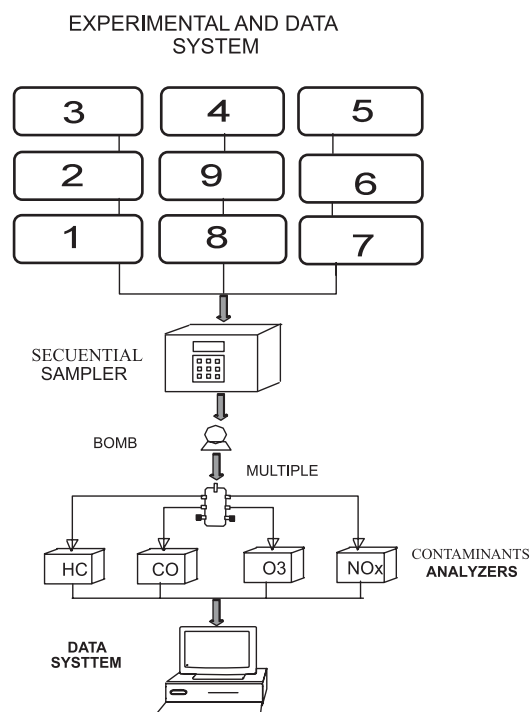
EXPERIMENTAL AND DATA SYSTEM

Fig. 1. Experimental CAI system.

cryogenic separation of condensable components, at liquid nitrogen temperature, by gas chromatography (EPA T0-14 procedure).

NO_x and O_3 analyzers (Thermo Environmental, models 42 and 49, respectively) collected automatically samples from each chamber. All gas, temperature and radiometer data were collected and displayed in real time by data logger. Gas analyzers were calibrated several times throughout the study with a dynamic calibrator coupled to a clean air generator and used a cylinder of NO of 99.5 ppm, EPA protocol grade [13]. An O_3 photometric calibrator (Thermo Environmental, model 49-PS) served to calibrate the O_3 analyzer. Measurements of ultraviolet radiation were done besides the CAI system with an Eppley TUVR radiometer calibrated by the Atmospheric Sciences Center at Universidad Nacional Autonoma de Mexico (UNAM). Temperature was monitored continuously within the reference bag with a calibrated type "J" thermocouple mounted through a 0.635 cm port. Thermocouple calibration was done at the IMP (Metrology Laboratory), credited with a T-14 certificate by the National Calibration System.

All experimental works started just before sunrise. Firstly, all chambers were cleaned out with clean air (50 L) by repeated refilling and evacuation. Then, they were filled with morning ambient air and treated according to the experimental design. Afterwards they were exposed to natural solar irradiation until sunset. After sunset, all chambers were again evacuated and refilled with clean air to minimize the so-called memory effect in the next day measurements.

Experimental design and data analysis

Prior to experimentation, a series of on-site O_3 measurements were conducted with the CAI smog chamber system to assess its performance under ambient conditions, especially for variability aspects, and to define experimental treatments.

The first formal experiment was done with captive morning ambient air. It was completed within 30 days and was designed to test effects from commercial LPG and its major compounds on O_{3max}. Five experimental treatments were compared: 35% addition of the LPG mixture commercialized in Guadalajara, 35% addition of one out of two propane/butane synthetic formulations (60/40% and 70/30%), a 50% dilution of total volatile hydrocarbons (VOCs), and a 50% dilution LPG associated VOCs. Two smog chambers containing untreated ambient air served as experimental control. To avoid a systematic bias, treatments were randomly assigned to the chambers every day. All treatments were replicated at least twice. Results from this experiment were subjected to variance homogeinity (Levene) and normality tests. Because they failed the variance homogeinity test, treatments effects were compared with the non-parametric Kruskal-Wallis test, which is the non-parametric equivalent to the one-way analysis of variance, using the Statistica (version 6) software.

For addition treatments, the added amounts (ppbC) were calculated daily from the initial (morning) NO_x concentration, as measured immediately after injecting ambient air into the chambers, and assuming a $VOCs/NO_x$ ratio equal to 30/1. The 50% dilution of total volatile hydrocarbons (VOCs) was achieved by substracting 250 L of the ambient air injected into the chambers and replacing this volume with clean air and NO_x. The 50% dilution of LPG associated VOCs was obtained by the same procedure, but injecting a synthetic mixture of non-LPG VOCs. In all cases the added NOx was calculated to restore its initial (morning) concentration.

A second five-day experiment was conducted with captive clean (zero) air as reaction matrix to compare the O_{3max} response induced by additions of commercial LPG and two propane/butane mixtures (60/40% and 70/30%) at three concentrations (2000, 4000 and 6000 ppbC). This experiment was done in early January, 1998, also under ambient sunlight and temperature.

Results and Discussion

All experimental data were included in a raw database (not shown) containing hourly O_3 and NO_x per smog chamber. Temperature and VOCs recorded in the reference chamber were assumed to represent the rest of chambers. Natural ultraviolet flux, which influences O_3 formation rates directly, was measured outside the chambers.

Preliminary Experiments

Preliminary hourly measurements of O_3 in untrated morning ambient air injected into the CAI system allowed us to test its performance under ambient sunlight and temperature. Potential chamber effects on O_3 formation were assessed by comparing the maximum and minimum O_{3max} values generated in the eight chambers. Because the greatest difference was only 3%, it can be assumed that effects associated to chamber structural differences were negligible.

As exemplified in Figure 2, daily O_3 profiles were quite similar between chambers. All of them reproduced the well-known daily pattern of O_3 formation in ambient air; i.e. morning concentrations were low and then increased steadily to a
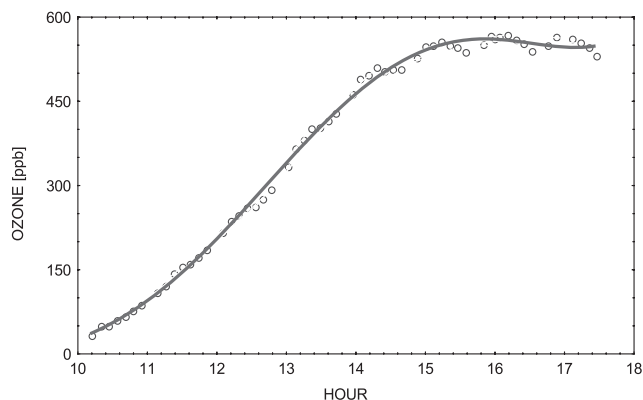

Fig. 2. Daily O_3 profile in confined ambient air (n = 8 chambers).

maximum in the afternoon, reflecting the strong role that sunlight in O_3 photochemistry. Nevertheless, O_{3max} in the captive ambient air was consistently higher than in the surrounding open air, 391% on average. As indicated by the large standard deviation for this average (321%), such difference was highly variable, which can be attributable to a number of environmental factors affecting O_3 in open ambient air, including dispersion and humidity changes, among others, all of which are excluded in the smog chambers. In fact, CAI systems somehow recreate a worst-case scenario for O_3 formation because: 1) Isolating parcels of ambient air within a smog chamber creates a condition ressembling atmospheric stability, which precludes pollutant dispersion by wind currents, as it occurs in open ambient air; 2) The captive air parcels usually, as in this case, are urban and collected in the morning, when human activity increases (e.g. vehicle transportation) causing the first daily air pollution peak that includes substantial amounts of O_3 precursors (VOCs and NO_x); and 3) Such air enriched with O_3 precursors is, in addition, subjected to the entire sunlight irradiation received across the day, whereas natural dispersion in ambient air dynamically dilutes both O_3 and its precursors. Thus, in interpreting results from CAI experiments, it should be kept in mind that they tend to overestimate O_3 formation.

Figure 3 shows results from another preliminary experiment done to define the LPG treatments for addition experiments. Different amounts of commercial LPG were added into confined ambient air as proportions (0-60%) of the morning concentration of total VOCs. This experiment showed that O_{3max} increased with LPG concentration following a saturation pattern. Adding 30-40% of LPG increased O_{3max} by about 5% respect to control values (0% addition in Figure 3). Because such increase is greater than the previously measured difference of O_{3max} between chambers (3%), a 35% addition of LPG was selected for addition experiments.

Experiments with Ambient Air

Initial (morning) concentrations of O_3 precursors and the O_{3max} reached in the control chambers during the experimental
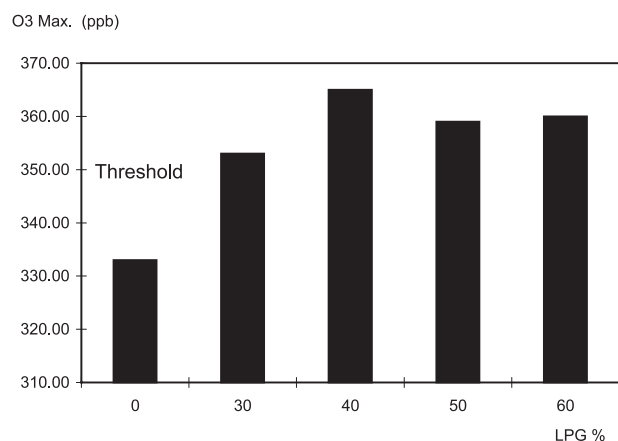
Table 2. Morning levels (ppbC) of O_3 precursors in ambient air of Guadalajara during the experimental period and maximum O_3 concentration in unperturbed confined ambient air.

Day	NO_x	VOCs	VOCs/NO_x	LPG VOCs	O_{3max}
11/10/97	56.8	1934	34.05	505	213.5
11/11/97	63.0	1497	23.76	320	184
11/12/97	190	5572	29.33	1418	456
11/13/97	87.2	2493	28.59	610	267
11/14/97	46.4	1725	37.18	567	209
11/15/97	88.2	5144	58.32	1142	324
11/17/97	41.7	1456	34.9	320	206.5
11/18/97	70.0	1749	24.99	578	269.5
11/19/97	75.0	1915	25.53	611	280
11/20/97	50.0	1493	29.86	511	240.5
11/21/97	121.0	4234	34.99	1412	383.5
11/22/97	187.0	6225	33.29	2025	461
11/23/97	165.0	5778	35.02	2135	480
11/24/97	82.0	2427	29.60	749	288
11/25/97	116.0	2579	22.23	661	334
11/26/97	116.0	2920	25.17	614	305.5
11/27/97	145.0	5026	34.66	1803	386
11/28/97	225.0	6096	27.09	2112	461
12/01/97	143.0	4959	34.68	1714	399
12/02/97	100.0	3174	31.74	1332	298
12/03/97	112.5	5684	50.52	2044	333
12/04/97	120.0	4480	37.33	1646	345.5
12/05/97	170.0	5973	35.13	1713	371.5
12/06/97	156.0	6432	41.23	2863	372.5
12/07/97	115.0	3491	30.35	1263	339.5
12/08/97	125.0	5560	44.48	2136	374
12/09/97	140.0	4614	32.96	1942	369.5
12/10/97	280.0	10138	36.2	3968	585
12/11/97	135.0	5503	40.76	1968	375.5
12/12/97	60.0	1360	22.26	313	199

days are shown in Table 2. Table 3 shows the relative amount of VOC species remaining by the afternoon, which indicate the relative extent of reaction undergone by those compounds in O_3 formation. Olefins disappeared almost completely by the afternoon, whereas those compounds associated to LPG (propane, n-butane and i-butane) remained unreacted by about two thirds of their morning concentration. Thus, olefins such as cis-2-butene and trans-2-butene could have potentially a greater impact than LPG's major constituents for O_3 formation in Guadalajara.

Table 3. Average remaining concentration of LPG VOCs as percent of initial (morning) concentrations as measured in unperturbed smog chambers

Compound	Remaining concentration (%)
Propane	72.4
n-Butane	69.2
i-Butane	65.8
1-Butene + 1,3 Butadiene	5.99
2-Methyl propene	4.75
Cis-2-Butene	0.12
Trans-2-Butene	0

O3 Max. (ppb)

Fig. 3. Test to define LPG additions. Each bar represents n = 2.

LPG and VOCs Effects on Ambient Air

Figure 4 compares effects on O_{3max} from five different treatments applied to captive morning ambient air. The percent change in O_{3max} was obtained by adjusting data for control effects; i.e. for O_{3max} developed in those chambers containing untreated ambient air from the same day. A Kruskal-Wallis test ($H = 65.688$; $p = .0000$) revealed a significant effect on O_{3max} from at least one treatment. Basically, those treatments including zero percent within their error bars, i.e. DNO_x, ALPG and A70/30 (Figure 4), had no effect on the O_3 peak. Thus, diluting the morning ambient air by 50% with zero air and restoring its O_3 precursors (NO_x and non-LPG VOCs) to initial morning values (DNO_x treatment), produced the same O_{3max} as the untreated ambient air. A 35% addition of commercial LPG (ALPG treatment) or LPG compounds (propane/butane 70/30%) did not cause any effect on O_{3max} either. Although a slight increase in O_{3max} (5% on average) was seen when adding the 60/40% propane/butane mixture, this effect did not differ significantly from that caused by DNO_x, ALPG and A70/30. The greatest effect observed was an average 16% decrease in O_{3max} caused by diluting ambient VOCs by 50% (DVOCs treatment). This confirms that, under ambient conditions in Guadalajara, and average VOCs/NOx $\cong$ 30, the LPG associated components did not have an important contribution to O_{3max} levels. Thus, O_3 events may be more likely associated to more reactive non-LPG VOCs present in the ambient air.

Altogether these results do not support a hypothetical increase in O_3 levels in Guadalajara by increasing the tropospheric levels of LPG compounds, as proposed by Blake and Rowland (1995) for Mexico City. This can be explained by the fact that LPG additions increased VOCs/NOx ratio over
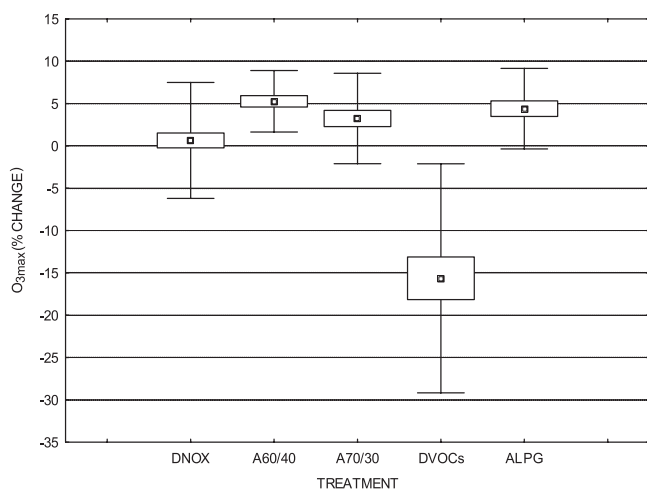

Fig. 5. Isoplete plot relating O_3 levels to NO_x and VOCs in Guadalajara. The empty dots represent the daily O_{3max} developed in the control chambers. The fitting line assumes a VOCs/NOx ratio = 32.9.

30, carrying the system into the VOCs-saturation region. At this region, change in concentration of those compounds has a low impact on O_3 formation. According to these results, if LPG emissions were to increase in the Guadalajara´s ambient air by, for example, leakages, they *per se* may not raise O_{3max} above currently observed levels. Thus, if O_3 control strategies are to be effective, it should be taken into account that lowering LPG leaks by 50% in GCMA may be more important for energy use efficiency and safety issues than for reducing O_3 levels significantly. Removing total VOCs from the ambient air could have, according to our results, a greater impact for the purpose of lowering O_3.

The advantage of a control strategy based focused on total VOCs emission to lower O_3 levels in Guadalajara is illustrated in Figure 5. This isoplete plot is based on experimental data from the control chambers. It relates VOCs and NOx to O_3 levels, and shows the percent expected decrease in O_{3max} from four 50% reductions of preexistent concentrations on total VOCs concentrations. The percent change is indicated by the arrowheads to the left of the fitting line. Decrease values (20.8-23%), assuming a VOCs/NOxratio = 30, are roughly consistent with the observed experimental decrease (DVOCs treatment, Figure 4).

Experiments in Clean Air

Ozone formation in confined clean air added with either commercial LPG or two different olefin-free propane/butane mixtures (60/40% or 70/30%) was also studied by a five-day experiment. Three different concentrations of each material were added (2000, 4000 and 6000 ppbC). All treatments were brought to a VOCs/NOx ratio = 30 by adding NO_x because this is the average ratio in the ambient air of Guadalajara. Adding commercial LPG caused the greatest increase on O_{3max} followed by the 60/40% and 70/30% propane/butane mixtures (Table 4). According to these results a LPG formulation containing a 70/30% (propane/butane) could be potentially better than a 60/40% proportion to reduce O_3 levels in

Fig. 4. Average effects on O_{3max} in confined Guadalajara ambient air treated with 35% additions of commercial LPG (ALPG, n = 27), LPG associated compounds (A60/40, n = 29, and A70/30, n = 31), or 50% dilutions of total VOCs (DVOCs, n = 29) or non-LPG VOCs (DNOX, n = 61). Box-plot elements: centered at the mean value, standard error (major square) and standard deviation (error bar).
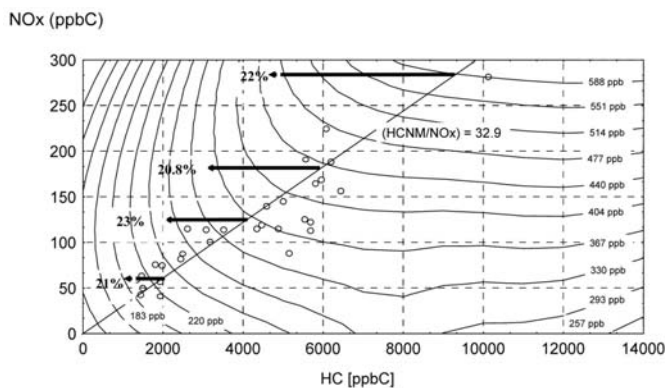
Table 4. Average O_{3max} formed in confined clean added with commercial LPG or either of two propane/butane synthetic mixtures. Experiment done under natural solar irradiance.

Formulation	Concentration added (ppbC)	Average O_{3max}
Commercial	2000	171.0
Commercial	4000	185.0
Commercial	6000	120.0
60/40	2000	154.0
60/40	4000	156.5
60/40	6000	59.6
70/30	2000	134.3
70/30	4000	136.0
70/30	6000	42.0

Nomenclature

CAI	= Captive-air irradiation
VOCs	= Volatile organic compounds, except methane (ppbC)
NOx	= Nitrogen oxide concentration (ppb)
ppbC	= Parts per billion of carbon in air
ppb	= Part per billion in air
Commercial	= Commercial liquefied petroleum gas formulation
60% C3 / 40% C4	= Synthetic formulation 60% propane and 40% *n*-butane
70% C3 / 30% C4	= Synthetic formulation 70% propane and 3 % *n*-butane

Guadalajara, as the former produced 15.6% less O_3. It must be pointed out that, in real ambient air, that may depend on other factors such as the potential involvement of other VOC species and the actual VOCs/NOx ratio.

Conclusions

The potential role of LPG emissions on O_3 formation was studied by CAI experiments using captive Guadalajara ambient air. According to the results, O_3 formation was not significantly affected by substantial additions (35%) of either whole commercial LPG or isolated LPG compounds (propane/butane). When LPG associated VOCs where removed by 50% from the captive ambient air, O_3 was formed at the same level as in untreated ambient air. In contrast, a significant 16% decrease in O_3 formation was detected when total VOCs were removed from the captive ambient air. Thus, it can be concluded that non-LPG VOCs are more involved than LPG VOCs in O_3 formation. Furthermore, because O_3 formation is strongly enhanced in captive air these results suggest that LPG plays a negligible role in O_3 formation under real ambient conditions, where natural dispersion mechanisms help further to dilute O_3 precursors. In addition, these results suggest that O_3 control strategies in Guadalajara must better target total VOCs or non-LPG VOCs because they have a major influence on O_3 formation than LPG VOCs.

Acknowledgement

References

1. Carter, P. L. W. Status of Research on VOCs Reactivity in the United States, First US-Forman Workshop on the Photochemical Ozone Problems and its Control. Berlin, Germany, September 24-27, **1996**.
2. Blake, D. R.; Rowland, S. *Science* **1995**, *269*, 953-955.
3. Jaimes-López, J. L.; Sandoval-Fernández, J.; González-Macías, U.; González-Ortíz, E. *Atmos. Environ.* **2003**, *37,* 2327-2335.
4. RAMAG; Red Automática de Monitoreo Atmosférico de Guadalajara; *Reportes Diarios* **1997**.
5. INEGI, "Indicadores Sociodemográficos de México1930-2000", México, 2001.
6. Jaffe, R. J. *J. Air Pollut. Assoc Control* **1967**, *17*, 460.
7. Jeffries, H.; Fox, D.; Kamens, R. "Outdoor Smog Chambers Study: Effect of Hydrocarbon Reduction Nitrogen [on] Oxidizes", Report, EPA- 650/ 3- 75- 011, Jun. **1975**.
8. Ripperton, L. A.; Sickes, J. E.; Eaton, W. C. "Oxidant Forerunner Relationships During Pollutans Transport Conditions": An Outdoor Smog Chambers Study", Report, EPA- 600/ 3- 76- 107, Nov., **1976**.
9. Kelly, N. A. "Captive Air Irradiations in Houston Texas", Presentation, in "Air Pollution Control Association" (J. APCA Paper No. 80-50.6); On Montreal, Quebec, Canada, Jun, **1980**.
10. Kelly, N. A. "Photochemical Ozone Formation in Outdoor Smog Chambers and Sensitivity its Changes to Precursors in at Suburban Detroit Site", in "Air Pollution Control Association Specialty Conference", "The Scientific And Technical Issues Facing Post-1987 O3 Control Strategies", Hartford, Connecticut, Nov. 17-19, **1987**.
11. Kelly, N. A.; Gunst, R. F. *Atmos. Environ.* **1990**, *24*, 2991-3005.
12. Gunst, R. F.; Kelly, N. A. *Technometrics* **1993**, *35***,** 256- 267.
13. Environmental Protection Agency. Traceability Protocol for Establishing True Concentrations of Gases for Calibrations and Audits of Continuous Source Emissions Monitors: Protocol Number 1, Quality Assurance Division, Research Triangle Park, North Carolina, **1978**.