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# Measurements of peroxyacyl nitrates (PANS) in Mexico City: implications for megacity air quality impacts on regional scales<sup>☆</sup>

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## Abstract

Peroxyacyl nitrates (PANs) were measured using gas chromatography with electron capture detection (GC/ECD) in north central Mexico City during February–March of 1997. Peroxyacetyl nitrate (PAN) was observed to exceed 30 ppb during five days of the study, with peroxypropionyl nitrate (PPN) and peroxybutyl nitrate (PBN) reaching 6 and 1 ppb maximum, respectively. Levels of total PANs typically exceeded 10 ppb during the period of measurement and showed a very strong diurnal variation with PANs maximum during the early afternoon and falling to less than 0.1 ppb during the evening hours. These levels of PANs are the highest reported values in North America (and the world) for an urban center, since levels of approximately 30 ppb were reported during the late 1970s in the Los Angeles area (South Coast Air Basin, Tuazon et al., 1978). Hydrocarbon measurements indicate that the levels of olefins, specifically butenes are significant in Mexico City. A time series taken of source indicator hydrocarbons taken before and during a Mexican National Holiday with reduced automobile traffic clearly show that mobile sources of butenes are as important as liquefied petroleum gas. Observations of 10–40 ppb C methyl-*t*-butyl ether (MTBE) are consistent with MTBE/gasoline fuel usage as a source of isobutene and formaldehyde. Both these reactive species can lead to increased oxidant and PAN formation. The strong diurnal profiles of PANs are consistent with regional clearing of the Mexico City air basin on a daily basis. Estimates are given using a simple box model calculation for a number of key primary and secondary pollutant emissions from this megacity on an annual basis. These calculations indicate that megacities can be important sources of both primary and secondary pollutants, and that PANs produced in megacity environments are likely to contribute strongly to regional scale ozone and aerosol productions during long range transport. © 1999 Elsevier Science Ltd. All rights reserved.

**Keywords:** Peroxyacyl nitrates; Peroxyacetyl nitrate; Mexico city air quality; Megacities; Butene sources; Nonmethane hydrocarbons

## 1. Introduction

Megacities are large urban and suburban complexes whose populations are in the millions of inhabitants

(Zarski, 1994). At the turn of the millenium, the largest metropolitan complexes are centered at Tokyo, Japan and Mexico City, Mexico. In both of these areas the projected populations in the year 2000 are at approximately 30 million people. With the rapid growth of the world's population and the continuing industrialization and migration of the populace towards major urban centers, megacities have become important sources of air pollutants from associated mobile and stationary sources.

Elevated levels of ozone in one of the largest megacities in the world, Mexico City, have been known for

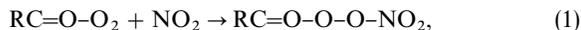
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sometime (Bravo et al., 1989; MARI: Mexico City Air Quality Initiative, 1994; Streit and Guzman, 1996; Fast and Zhong, 1998). Mexico City is located at an altitude of 7200 ft in an air basin surrounded by mountains (Fast and Zhong, 1998; Doran et al., 1998). Ozone levels exceeding 300 ppb are not uncommon, particularly during the late winter months of February and March. These very high levels of ozone require reactive hydrocarbons as well as elevated levels of nitrogen oxide emissions to produce the coupled OH and peroxyradical chemistry that is key to the formation of urban ozone (Finlayson-Pitts and Pitts, 1986). Hydrocarbon measurements taken in Mexico City (Blake and Rowland, 1995) have shown that the domestic and commercial use of liquefied petroleum gas (LPG) has led to very high levels of butane and propane in that megacities air, exceeding ppm C levels in many cases. Indeed, LPG associated propene and butenes, along with the butane were proposed as an important source of reactive volatile organic carbon (VOC) accounting for an appreciable portion of the observed urban ozone in Mexico City (Blake and Rowland, 1995).

Peroxyacyl nitrates (PANs) are a class of air oxidants that are important indicator compounds of peroxyradical activity in an urban air shed (Finlayson-Pitts and Pitts, 1986; Gaffney et al., 1989). They are formed by the reaction of peroxyacyl radicals with nitrogen dioxide and exist in equilibrium with the peroxy radical species as indicated in reaction 1:



where R is typically (in order of importance)  $\text{CH}_3$ - (peroxyacetyl nitrate, PAN),  $\text{CH}_3\text{CH}_2$ - (peroxypropionyl nitrate, PPN), and  $\text{CH}_3\text{CH}_2\text{CH}_2$ - (peroxybutyl nitrate, PBN) in an urban environment.

Measurements of the temporal variability of PANs can be a very useful tool in determining the oxidative reactions involved in the formation of ozone as well as other secondary air pollutants such as nitric acid and ammonium nitrate. This is due to the fact that PANs serve as a measure of peroxy radical levels and simultaneously act as a reservoir for nitrogen dioxide. Since PANs have low aqueous solubilities, low reactivity with OH, and are slow to photolyze, they can lead to the long range transport of nitrogen dioxide which can have regional scale impacts on ozone, nitrate aerosols, and other pollutants (Gaffney et al., 1989).

In an attempt to better understand the Mexico City air chemistry with regard to oxidants and aerosols, a comprehensive collaborative study was carried out during February–March 1997 which included meteorological measurements (Edgerton et al., in press; Doran et al., 1998; Fast and Zhong, 1998). This field study program entitled *Investigación sobre Materia Particulada y Deterioro Atmosférico – Aerosol and Visibility Research (IMADA-AVER)* was jointly sponsored by the U.S.

Department of Energy's (DOE) Office of Biological and Environmental Research and the Instituto Mexicano de Petroleo (IMP). As part of IMADA-AVER, measurements of PANs and nonmethane hydrocarbons (NMHCs) were made at the Instituto Mexicano de Petroleo laboratories to determine the levels and temporal variability of these species. Presented here are the results of those measurements, and a discussion of the importance of these results with regard to the formation of PANs and ozone and their subsequent downwind transport from megacities.

## 2. Experimental

PANs and hydrocarbons were sampled at the IMP laboratories (Eje Central Lazaro Cardenas No. 152, Delegacion Gustavo A. Madero, Mexico, Distrito Federale). This site is located near the Northwest corner of the central part of Mexico City. Peroxyacyl nitrates (PANs) were determined using an automated gas chromatograph equipped with an electron capture detection system (GC/ECD). This analysis system has been described in detail previously (Gaffney et al., 1993, 1997, 1998), but will be briefly described here. A six-foot by 1/8-in Teflon™ column using carbowax 400 packing was used to separate the PANs. Ultrahigh purity nitrogen with an oxygen scrubber was used as the carrier gas at a flow rate of 30 cm<sup>3</sup>/min. An automated sampling valve (Valco Cheminert valve and electronics) was used to take a 2 cm<sup>3</sup> sample of air for analysis every 30 min. Data was collected using a recording integrator and processed manually for each of the 1380 samples analyzed during this experiment. Once analyzed the data was put into spreadsheets for data processing and comparison (Lotus 1-2-3, and Microsoft Excel). Calibration of the PANs were done by synthesizing standards using a strong acid nitration of the corresponding peracid, produced by hydrogen peroxide reaction with the anhydride (Gaffney et al., 1984).

Nonmethane hydrocarbon samples were collected by pressurizing ambient air to 273 kPa in Summa® passivated stainless-steel canisters (Scientific Instrumentation Specialists, Moscow, ID) with a Viton® diaphragm pump (Doskey and Gaffney, 1992). The samples were analyzed by a cryogenic preconcentration/high-resolution gas chromatographic technique with flame ionization detection (FID) that has been described in detail elsewhere (Fukui and Doskey, 1996, 1998). Briefly, the whole-air samples were preconcentrated at –100 C in a 15-cm section of a glass-lined stainless-steel tube (0.180-cm i.d.) packed with 60/80 mesh porous glass beads (Unibeads 1S; Alltech Associates, Inc., Deerfield, IL), were thermally desorbed at 100°C for 2 min, and were transferred to either (1) a 60-m × 0.32-mm-i.d. fused-silica capillary column coated with a 1 μm-thick film of

polydimethylsiloxane (DB-1; J and W Scientific, Folsom, CA), or (2) a 30-m  $\times$  0.53-mm-i.d. porous-layer open tubular column coated with alumina (GS-Alumina; J and W Scientific, Folsom, CA). Identifications were made by comparing retention times of standards prepared in static dilution bottles with samples injected under identical chromatographic conditions. The FID was calibrated daily with a mixture of C<sub>2</sub>–C<sub>6</sub> *n*-alkanes, benzene, and toluene at a level of 10 ppb each (Scott Specialty Gases, Inc., Plumsteadville, PA).

Data for hourly average ozone and nitrogen oxide species (NO<sub>x</sub>) were obtained from the Instituto Mexicano de Petroleo (IMP) for the northwestern sector of Mexico City taken by the monitoring network established by the Ministry of Environment for the Federal District of Mexico. Ozone was measured by long path ultraviolet spectroscopy, and NO<sub>x</sub> was determined by use of ozone chemiluminescence as total nitrogen oxide signal minus NO. Data were only available for the daylight hours for ozone and NO<sub>x</sub>, and are used for comparison to the continuous data set for PANs.

### 3. Results and discussion

One of the difficulties in evaluating the regional and global scale impacts of pollution arising from a megacity is the accurate estimation of primary emissions and secondary pollutant formation in the boundary layer. One of the major findings from the collaborative IMADA-AVER experiment was the observation of a consistent daily regional clearing of the Mexico City air basin (Fast and Zhong, 1998). This regional meteorology leads to very little carryover from day to day of the pollutants in Mexico City. Primary pollutants are emitted during the evening and early morning traffic rush before photochemical production occurs during the day and continue to be emitted throughout the daylight hours. Pollutant hydrocarbons and nitrogen oxides that are involved in the photochemical production of oxidants and secondary aerosols are diluted during the day due to local heating caused by solar radiation leading to increased boundary layer heights. Late in the afternoon the regional flow causes a strong advection of the boundary layer trapped pollutants leading to a clearing out of the primary and secondary pollutants released and formed during the day in the air basin. Thus, a very strong diurnal behavior was observed for ozone and peroxyacyl nitrates and other pollutants which was due to the strong coupling of the regional scale meteorology and the very large shallow air basin in which Mexico City lies at an elevation of 8000 ft.

Fig. 1 shows the time sequence observed for PAN, PPN, and PBN as an example of the strong diurnal pattern observed for these secondary pollutants. For almost every day during this period with the exception of March 6th (Julian Day 65), the PANs were observed to

build up to levels above 10 ppb and then due to the regional clearing drop to a few tenths of a ppb at approx. 5–6 p.m. in the late afternoon. On March 6th a synoptic situation occurred during which time high winds continued to sweep out emissions from the Valley of Mexico. Other secondary pollutants such as ozone showed similar patterns during the field study. Low reactivity primary pollutants such as butane and propane showed higher levels in the morning due to the lower height of the boundary layer followed by an approximately 50% reduction by midday due to the thermal heating and growth of the boundary layer. Primary pollutants (e.g. CO, SO<sub>2</sub>) were also seen to be lost late in the afternoon when the onset of regionally driven winds set in (Fast and Zhong, 1998). The Mexico City air flow patterns have been detailed previously (Doran et al., 1998) which indicate late afternoon flow patterns act to lift the pollutant laden air from Mexico City and advect it into the surrounding regional systems with minimal recycling of either primary or secondary pollutants. This is consistent with our observations of the diurnal behavior of PANs.

PAN levels greater than 30 ppb have not been reported in the literature since similar levels were observed in the Los Angeles airshed in the 1970s (Tuazon et al., 1981). The high levels of PPN (3–6 ppb max) and PBN (1 ppb max) are also significant, leading to total concentrations of PANs of approx. 40 ppb at the IMP site during 5 days out of the 30 sampled. Fig. 2 shows a plot of O<sub>3</sub> vs. PAN daily maximum concentrations. Note that the maximum ozone values for this period were less than 300 ppb. In past pollution episodes in the Los Angeles area, PAN/O<sub>3</sub> ratios were typically 0.1 or less. A least-squares fit to this data set leads to approximately 0.1 for this ratio with an approximate background concentration for ozone of 55 ppb (as indicated by the intercept). These are not unreasonable values from past experience for the relationship of PAN with ozone in polluted air masses (Tuazon et al., 1981; Finlayson-Pitts and Pitts, 1986; Gaffney et al., 1989). However for 11 days out of the period sampled, PAN/O<sub>3</sub> ratios exceeded 0.1 with a number of days at 0.2. An explanation for these high PAN days is that there are significant PAN precursors (higher aldehydes and olefins) in the Mexico City air and that the higher PAN levels act to hold NO<sub>2</sub> as a reservoir thus reducing the ozone production rate and subsequent O<sub>3</sub> levels. It should also be noted that the sampling site at the Instituto Mexicano de Petroleo laboratories is located just north of the central district of Mexico City. The sites south of the city are more likely to have even higher levels of PANs as ozone levels are typically higher at those sites due to the local winds (Fast and Zhong, 1998).

Statistical comparison of the data indicated that PAN and PPN were strongly correlated (See Fig. 3). However, PAN and ozone were not found to correlate linearly with NO<sub>x</sub> ( $R^2 = 0.17$  and  $0.03$ , respectively). PAN and PPN showed only a modest correlation with PBN ( $R^2 = 0.48$

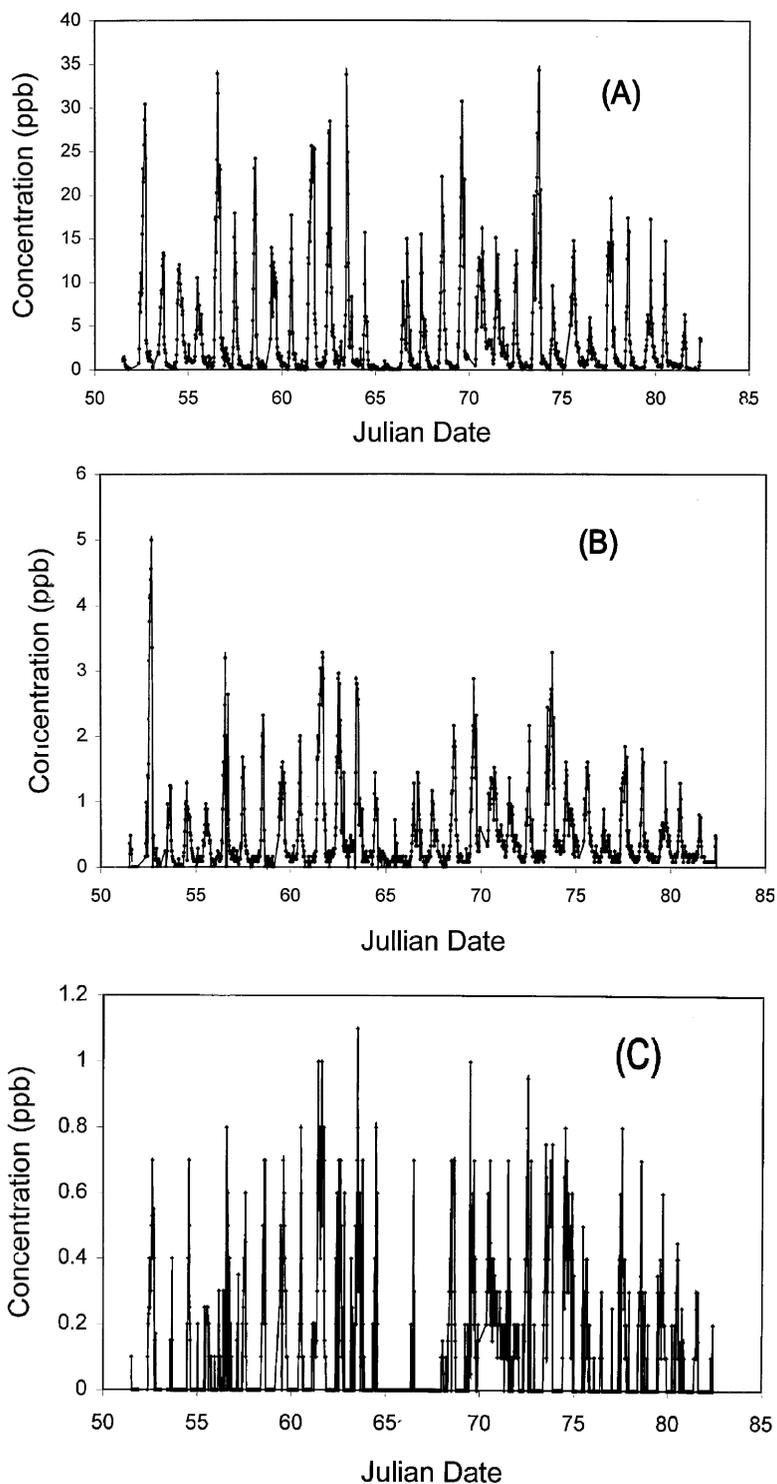


Fig. 1. Concentration profiles (ppb) for the peroxyacyl nitrates (PANs) measured in Mexico City at the Instituto Mexicano de Petroleo during IMADA-AVER. (A) Peroxyacetyl nitrate, PAN, (B) Peroxypropionyl nitrate, PPN, and (C) Peroxybutyryl nitrate, PBN.

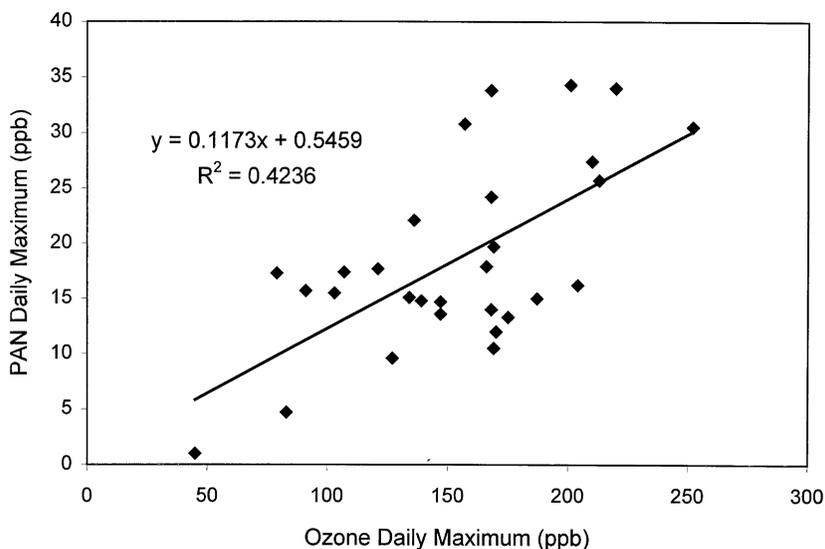


Fig. 2. Comparison of daily ozone and PAN maximum during IMADA-AVER and linear least-squares regression analysis.

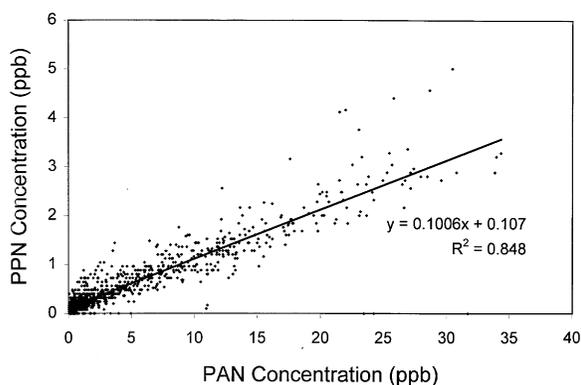


Fig. 3. Correlation of PAN with PPN showing least-squares best fit for a linear correlation.

and 0.58, respectively). PAN and ozone also showed modest correlation ( $R^2 = 0.49$ ).

Fig. 4. shows a comparison for Julian Day 56 of the  $O_3$ ,  $NO_y$ , and PAN at the IMP site. Note that there is a rapid conversion of  $NO$  to  $NO_y$  in the Mexico City air. By 10 am the  $NO_y$ , which is principally  $NO_2$  has reached approx. 140 ppb. At this time both ozone and PAN begins to be produced with the PAN maximum reached earlier than ozone. For this day, PAN was found to reach a max of 34 ppb with ozone reaching 220 ppb. This indicates a very rapid formation of PAN. Note also that by noon, the boundary layer mixing height has increased leading to a reduction of  $NO_y$ , with the concurrent formation of PAN, which will lead to less  $NO_2$  available

for photolysis and formation of ozone. In the late afternoon, PAN levels were observed to drop faster than the ozone. This is not likely due to PAN reaction with  $NO$ , as ozone would be lost faster than PAN by this titration reaction.

This behavior was observed on all of the high PAN days, and may be an indication of heterogeneous reactions of PAN on carbonaceous soot surfaces or other aerosols in the Mexico City Air. The 24-h average levels of particulate matter in the sub- $2.5 \mu m$  range (PM-2.5) were  $36 \mu g m^{-3}$  during this study, with  $10\text{--}20 \mu g m^{-3}$  carbonaceous aerosols present. Note that even more pronounced PAN loss relative to ozone in an urban environment has been reported for Santiago, Chile where PAN levels were found to approach 20 ppb (Rappengluck et al., 1998). This city has a very large diesel bus fleet and the levels of carbonaceous soot are likely to be even higher than those observed in Mexico City. In preliminary laboratory studies we have shown that PAN can be lost on soot surfaces at low ppb levels of PAN during relatively short contact times in support of heterogeneous PAN loss under high aerosol levels (Gaffney et al., 1998).

Liquefied petroleum gas (LPG), which is primarily used for domestic purposes (cooking, heating, etc.) in Mexico City, has been previously proposed as an important source of butenes and propene, which are reactants for ozone production (Blake and Rowland, 1995). However, these NMHCs are also found in vehicular emissions in Mexico City (Mugica et al., 1998). In order to examine the relative contributions of LPG and vehicles as sources of reactive hydrocarbons, hourly samples of ambient air were collected during the daytime at the IMP site on

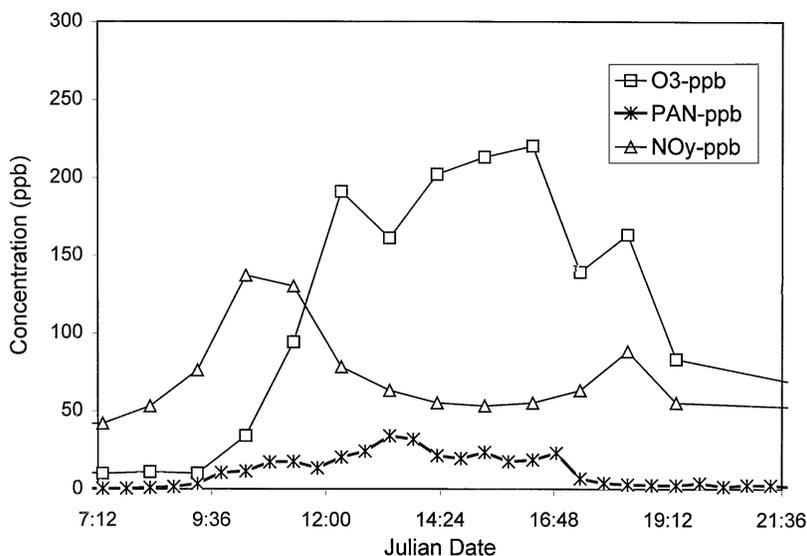


Fig. 4. Concentration profiles for ozone, PAN, and  $\text{NO}_y$  on Julian Date 56.

March 20–21, 1997. March 20th was a Thursday and March 21st, a Friday and a national holiday (Benito Juárez's birthday). Thus, we anticipated that automobile traffic would be reduced on Friday and expected LPG usage to be comparable on both days. Propane, *n*-butane, and isobutane were chosen as LPG source emission indicators. Blake and Rowland (1995) identified these compounds as the major NMHCs in the LPG that is used in Mexico City. Isopentane, benzene, and methyl-*t*-butyl ether (MTBE) were chosen as source indicators of motor vehicle emissions (Doskey et al., 1992, in press; Mugica et al., 1998). MTBE is used as an octane enhancer in Mexico City for non-leaded gasolines (Bravo et al., 1991). MTBE has been shown to be a source of isobutene and formaldehyde primary emissions from vehicles (Bravo et al., 1991; Zielinska et al., 1997).

The observed values for the LPG and vehicle indicator compounds are shown in Fig. 5. Ambient levels that were observed before 10 a.m. are representative of primary emissions into a nocturnal inversion which has not yet been eliminated by surface heating. As the day progresses the boundary layer grows and the NMHCs are diluted by mixing. Similar levels of the LPG components were observed in the morning hours on both days, indicating similar emissions of LPG. However, concentrations of vehicular indicators were a factor of 2 less on the national holiday, indicating reduced emissions from vehicles. The levels of the isobutene and 2-butenes were found to be approximately a factor of 4 lower on the national holiday (Fig. 6), indicating that vehicular emissions are an important source of butenes, if not the major source in Mexico City.

These results are consistent with the production of isobutene and formaldehyde from MTBE usage (Zielinska et al., 1997), and the reactive 2-butenes are also shown to be associated with vehicular emissions. Early morning levels of formaldehyde have been reported in Mexico City at levels exceeding 100 ppb (Andraca et al., 1997; Baez et al., 1995; Bravo et al., 1991). It had been suggested previously that the increase in formaldehyde after the introduction of MTBE in gasolines in Mexico City in 1989 could have modified the ozone production chemistry (Bravo et al., 1991). Indeed, the photolysis of formaldehyde at these levels will lead to the formation of  $\text{HO}_2$  which can react with  $\text{NO}$  emissions in the morning leading to the very rapid  $\text{NO}_y$  formation and levels observed at 7–9 a.m. in the morning. This chemistry will also produce  $\text{OH}$  in the absence of ozone as a source via photolysis to yield  $\text{O}(^1\text{D})$  and its subsequent reaction with water to yield  $\text{OH}$  radicals. Since the ozone levels are very low in the early morning, the photolysis of formaldehyde is an important radical initiator that will lead to the formation of aldehydes and PANs as well as converting  $\text{NO}$  to  $\text{NO}_2$  and forming ozone. Thus, the data indicates that the use of MTBE reformulated fuels in the absence of major catalytic reactor usage on motor vehicles is leading to increased reactive hydrocarbon emissions (i.e. isobutene and formaldehyde) as suggested previously (Bravo et al., 1991).

It is important to note that these observations indicate that emission control strategies that focus on hydrocarbons and ignore  $\text{NO}_x$  control may lead to elevated levels of ozone. This will occur as the hydrocarbon levels and reactivity are reduced which will lead to less formation of

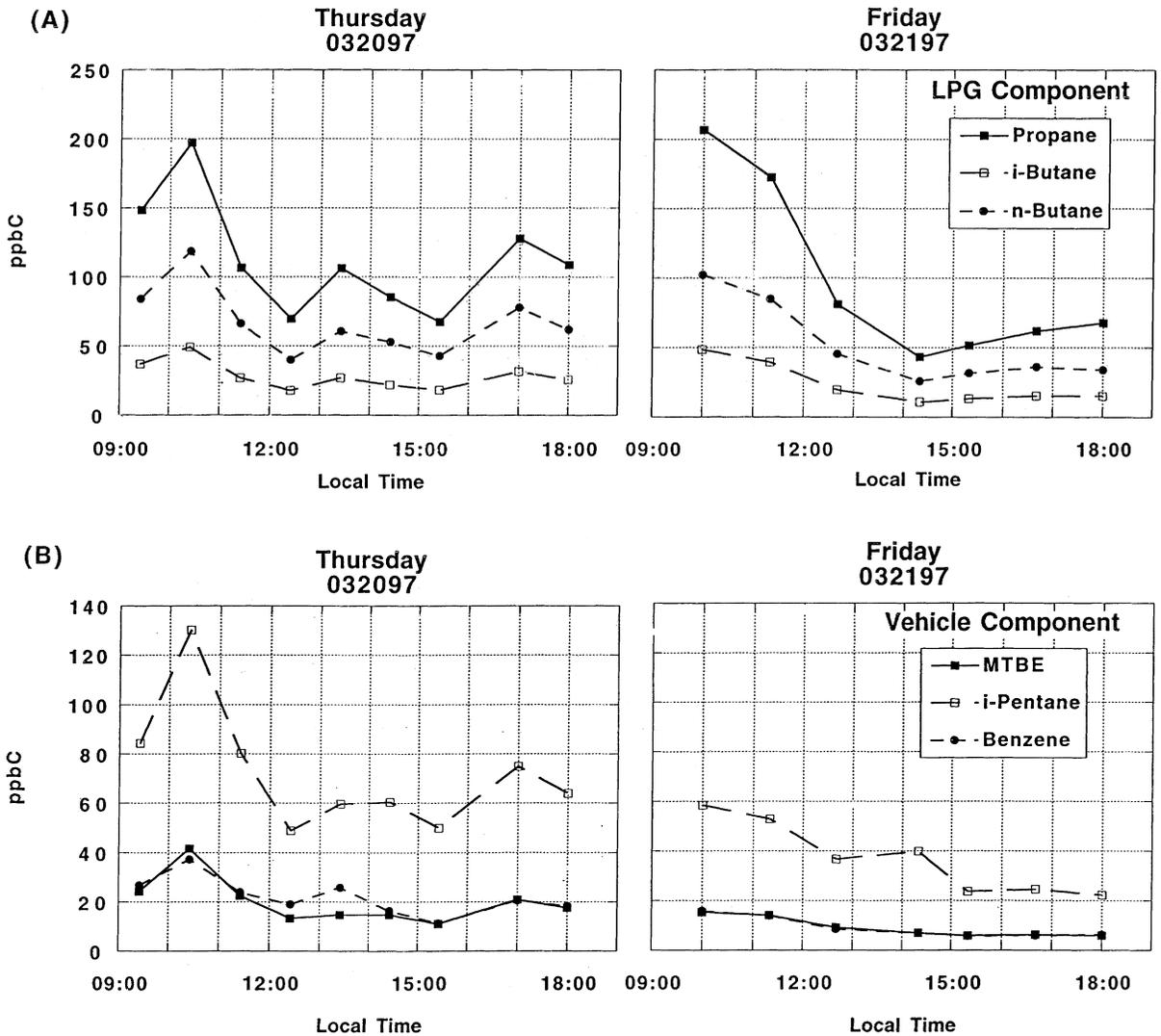


Fig. 5. Source indicator concentration profiles for (A) LPG component and (B) Vehicular component on March 20 and 21, 1997, a Thursday and Friday. Note Friday the 21st of March was a national holiday in Mexico City.

PANs and subsequently higher levels of NO<sub>2</sub> as that reservoir is diminished. Thus, it is important that both hydrocarbon and NO<sub>x</sub> controls are made to reduce ozone and other oxidants in the Valley of Mexico. Our measurements of nonmethane hydrocarbons showed that the total concentrations of these species were typically on the order of 1 ppm C. Thus, there is presently very high hydrocarbon levels in Mexico City as previously noted by Blake and Rowland (1995). Since, most of the chemistry is caused by one day events due to the regional clearing patterns, downwind chemical formation of oxidants and acids as well as secondary aerosols in the

Mexico City plume need to be addressed to determine the regional scale impacts of the existing plume. As well, control strategies should address both urban scale and regional scale impacts.

Substantial levels of PANs, which are stored peroxy radicals and NO<sub>2</sub>, and ozone along with other secondary pollutants are formed each day in Mexico City. As seen in Fig. 1, the diurnal pattern indicates that this material is transported out of the city almost completely during each diurnal period. The question arises, how much of this material from this megacity is being transported out of the basin each day. Recently this has been addressed for

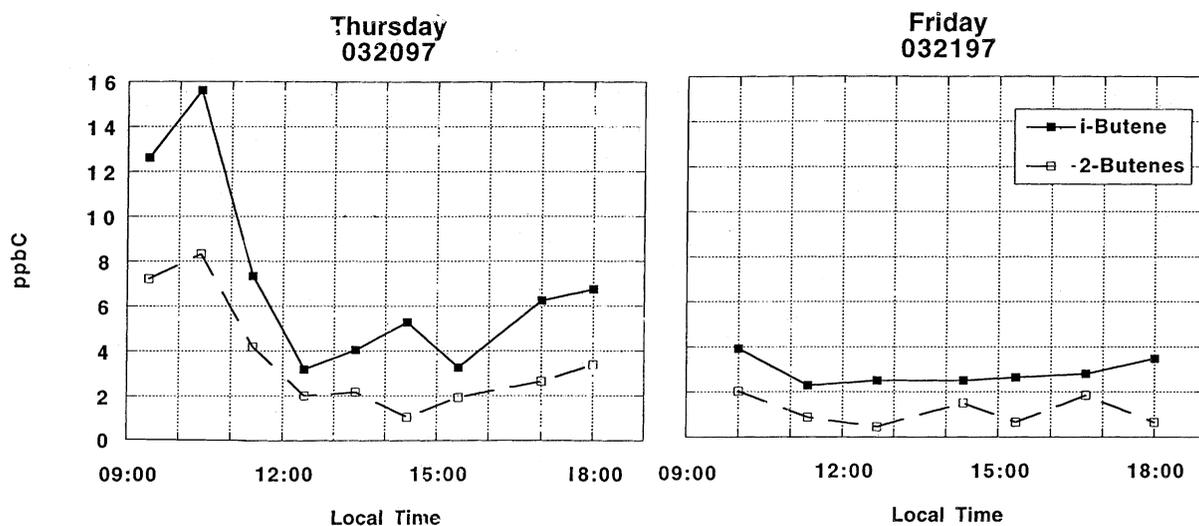


Fig. 6. Concentration profiles measured for 2-butenes and isobutene on March 20 and 21, 1997 showing reduction on the national holiday consistent with vehicular emission reductions.

the case of the longer lived alkanes emitted from LPG (i.e. propane, butane, and isobutane) (Elliott et al., 1997).

Boundary layer heights were observed to increase during the day to approximately 2–4 km in height due to surface radiative heating of the ground (Doran et al., 1998). This relatively unique situation in Mexico City can allow us to directly estimate the mass of emissions from this megacity air basin on a daily and yearly basis by making the following simple assumptions. Assuming that the air pollutants are relatively well mixed into the boundary layer height of approx. 2 km and horizontally into the 5000 km<sup>2</sup> area of Mexico City, a simple box model calculation (780 mbar and 300 K) can be performed using some typical late afternoon concentrations measured for a number of gas phase and aerosol species (Edgerton et al., in press, this work). In Table 1, the results of such an estimate are given for a number of important air pollutants. Comparison with this simple calculation for the more detailed analysis for propane, butane, and isobutane done previously (Elliott et al., 1997) show reasonably good agreement for the NMHC estimate. Thus, 1 ppm carbon would lead to an annual emission rate of 1.7 megatons compared to our estimate of 1.6. Note that the PM-2.5 concentrations are for total mass. Measurements of the composition of this aerosol fraction indicates that this is typically 50% organic and elemental carbon, 20% nitrate, 20% sulfate, and 10% wind blown dust and other. Thus, primary carbonaceous soot emissions are estimated to be approx. half of the PM-2.5 values given in Table 1. This result for carbonaceous soot emissions indicates that for at least Mexico City (and likely many other megacities) that the soot

comprises a very important fraction of the fine aerosol. Increased diesel engine usage for trucks, buses, etc. is a likely factor in this observation, along with most cities using lower sulfur content fuels in both stationary and mobile sources.

These data indicate that megacities can indeed act as very large sources of regional air pollution. Indeed, the propane emissions alone can account for close to 0.4% of the sources necessary to maintain the propane levels observed in the remote atmosphere (Elliott et al., 1997). It is clear that both short lived and long-lived air pollutants can be transported into regional air masses from these megacities. Reactive emissions such as nitrogen oxides and hydrocarbons may also lead to substantial formation of ozone and other important oxidants on regional scales, besides the direct transport of ozone produced in the valley. Certainly the control of regional oxidant and PM-2.5 levels will require a better understanding of their long range transport and lifetimes, however, it is evident that much of the sources of these materials are likely due to megacity complexes world wide. Thus, controlling global and regional air pollutants will require global cooperation from all of the large populated metropoli world wide if we are to lower levels of regional ozone, PM-2.5, air toxics, radiatively important trace gases, and other air pollutants in order to maintain air quality and reduce global change impacts. Megacities as sources of regional and global pollutants cannot be ignored if we are to adequately assess and control air pollutants leading to global change impacts, such as global warming, terrestrial and aquatic ecosystem damage, and human health effects.

Table 1

Estimated mass of emissions in Mexico City plume based upon the following assumptions: 770 mbar, 27 C, 2 km mixing layer, 5000 km<sup>2</sup> metropolitan area, no dry deposition, air mass is completely mixed and flushed out once a day

Pollutant	Concentration	Metric tons per day	Mega-tons per year
NMHC	1 ppm C	4500	1.6
CO	5 ppm	43,000	16
NO <sub>y</sub>	50 ppb	710	0.26
Ozone	200 ppb	3000	1.1
PAN	20 ppb	750	0.27
PM-2.5	50 mg/m <sup>3</sup>	40,000	15

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