Ventilation of liquefied petroleum gas components from the Valley of Mexico

Scott Elliott,[1] Donald R. Blake,[2] F. Sherwood Rowland,[2] Rong Lu,[3] Michael J. Brown,[4]
Michael D. Williams,[4] Armistead G. Russell,[5] James E. Bossert,[1] Gerald E. Streit,[4]
Marisa Ruiz Santoyo,[6] Francisco Guzman,[6] William M. Porch,[1]
Laurie A. McNair,[5] John Keyantash,[3] Chih-Yue Jim Kao,[1]
Richard P. Turco,[3] and William E. Eichinger[1]

Abstract. The saturated hydrocarbons propane and the butane isomers are both indirect greenhouse gases and key species in liquefied petroleum gas (LPG). Leakage of LPG and its component alkanes/alkenes is now thought to explain a significant fraction of the volatile organic burden and oxidative potential in the basin which confines Mexico City. Propane and the butanes, however, are stable enough to escape from the basin. The gas chromatographic measurements which have drawn attention to their sources within the urban area are used here to estimate rates of ventilation into the free troposphere. The calculations are centered on several well studied February/March pollution episodes. Carbon monoxide observations and emissions data are first exploited to provide a rough time constant for the removal of typical inert pollutant species from the valley. The timescale obtained is validated through an examination of meteorological simulations of three-dimensional flow. Heuristic arguments and transport modeling establish that propane and the butanes are distributed through the basin in a manner analogous to CO despite differing emissions functions. Ventilation rates and mass loadings yield outbound fluxes in a box model type computation. Estimated in this fashion, escape from the Valley of Mexico constitutes of the order of half of 1% of the northern hemispheric inputs for both propane and n-butane. Uncertainties in the calculations are detailed and include factors such as flow into the basin via surface winds and the size of the polluted regime. General quantification of the global propane and butane emissions from large cities will entail studies of this type in a variety of locales.

1. Introduction

Nonmethane hydrocarbons (NMHC) distributed through the terrestrial troposphere act as major indirect greenhouse gases [*Houghton et al.*, 1990; *Hauglustaine et al.*, 1994]. Decomposing in the presence of nitrogen oxides (NO and NO_2: NO_x), they produce the direct greenhouse species ozone; if NO_x is absent, NMHC decay can lead to ozone loss [e.g., *Crutzen*, 1973, 1988; *Chameides and Walker*, 1973; *Liu et al.*, 1987]. The effects are difficult to quantify on a global scale because the kinetics of the oxidation system are highly nonlinear and because sources/distributions for indirect greenhouse forcers are poorly understood and spatially variable [*Liu et al.*, 1987; *Penner et al.*, 1991; *Crutzen and Zimmerman*, 1991; *Houghton et al.*,

1990; *International Panel on Climate Control (IPCC)*, 1992; *Kanakidou and Crutzen*, 1993]. The C3 and C4 alkanes contribute significantly to overall NMHC oxidation. Integrated hydroxyl radical reaction rates indicate that the carbon-weighted global reactivity of propane and n-butane is 10% that of methane [*Singh and Zimmerman*, 1992].

C3 and C4 hydrocarbons leaking from liquefied petroleum gas reservoirs have recently been identified as prominent pollutants and ozone precursors in Mexico City [*Ruiz Santoyo et al.*, 1993; *Blake and Rowland*, 1995]. Oxidant production from liquefied petroleum gas (LPG) derived organics within the Valley of Mexico may rival that attributable to NMHC from automobiles. Propane and the butanes identified in Mexican LPG possess lifetimes with respect to hydroxyl radical attack of several days or more [*Singh and Zimmerman*, 1992; *Blake and Rowland*, 1995; L. A. McNair et al., Impact of diffusivity parameterization on pollutant modeling in Mexico City, submitted to *Atmospheric Environment*, 1995] (hereinafter referred to as McNair et al., submitted manuscript, 1995). They will not only oxidize locally to yield urban ozone pollution, but will also be exported from the basin that contains Mexico City. There are reasons to believe that the fluxes of C3 and C4 alkanes to regional scales will be larger than for most other urban areas. Absolute propane and butane concentrations in the Valley of Mexico are an order of magnitude greater than those typically observed in U.S. urban areas and several times larger than during peak pollution years in Los Angeles and Denver [*Mayrsohn et al.*, 1975; *Ferman et al.*, 1981; *Sexton and Westberg*,

[1] Earth and Environmental Science Division, Geoanalysis Group, Los Alamos National Laboratory, Los Alamos, New Mexico.

[2] Chemistry Department, University of California, Irvine.

[3] Atmospheric Sciences Department, University of California, Los Angeles.

[4] Technology and Safety Assessment Division, Energy and Environmental Analysis Group, Los Alamos National Laboratory, Los Alamos, New Mexico.

[5] Department of Mechanical Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania.

[6] Instituto Mexicano del Petroleo, Gerencia de Ciencias del Ambiente, Mexico D.F.

1984; *Seila et al.*, 1989; *Seinfeld*, 1989; *Singh and Zimmerman*, 1992]. As the world's most populous metropolis, Mexico City covers a large area in the horizontal. Furthermore, its boundary layer tends to be 2 to 3 km in depth during wintertime episodes of poor air quality [*Mexico City Air Quality Research Initiative (MARI)*, 1994; *Cooper and Eichinger*, 1994]. The mass of pollutants available for dispersion is thus extraordinarily large. On the other hand, stagnant meteorological conditions contribute to the high concentrations measured and suggest that escape from the basin is often a slow process.

In the present work we estimate rates of ventilation from the Valley of Mexico and couple with preliminary measurements of the LPG alkanes in order to evaluate the individual urban NMHC source in larger scale contexts. The exercise begins with the adoption of carbon monoxide as a relatively well understood inert tracer of pollutant flow. Emissions of CO are derived both from time dependent surface observations and from bottom-up inventorying [*Programa Integral Contra la Contaminacion Atmosferica (PICCA)*, 1990; *TUV*, 1992; *MARI*, 1994]. A time constant is computed for removal from a box model of the valley, and the value is then compared with available meteorological information as a means of validation [*Williams et al.*, 1995; McNair et al., submitted manuscript, 1995]. We next present heuristic arguments supporting the contention that propane and butane distributions will resemble those of carbon monoxide. Mass fluxes from the Mexico City urban area to the free troposphere follow from the ventilation and concentration estimates. Alkane budgeting is performed for the entire northern hemisphere to provide a point of reference. Wintertime LPG leakage within Mexico City can account for of the order of half a percent of the required hemispheric emissions for propane and n-butane.

In the discussion section the arguments connecting carbon monoxide and alkane fluxes from the valley are formalized through modeling. Simple one-dimensional simulations of the ventilation process are constructed, and limited application is made of some three-dimensional photochemistry/transport codes at our disposal. We deal qualitatively with the potential for surface winds to import the tracers of interest. Other major uncertainties in the analysis are then listed. Sources of error include our definition of the basin and urban periphery, the average height of the low nocturnal inversion, and alkane distributions. We conclude with some comments on the global ramifications of our findings. By our calculations, Mexico City in and of itself constitutes a significant source of the C3 and C4 alkanes to the terrestrial atmosphere. Recent sampling suggests that many other nondomestic (non-United States) urban areas contribute propane and the butanes through LPG leakage. We note that megacities with pollutant characteristics akin to those of Mexico are developing rapidly worldwide [*United Nations*, 1992; *Kretzschmar*, 1993, 1994; *Goldemberg*, 1995]. To better quantify their role in the global tropospheric ozone system, measurement of LPG component signatures will be required in many urban settings. We also outline relationships between regional dispersion of the C3 and C4 alkanes and transport of the nitrogen oxides in organic forms [*Crutzen*, 1979; *Singh and Hanst*, 1981].

2. Carbon Monoxide Ventilation Rates

We will draw now upon a variety of chemical and meteorological measurements to construct values for mass fluxes of some surface released gases from the basin which holds Mexico

City. The most complete collection of relevant data is currently to be found in volume 3 of the *Mexico City Air Quality Research Initiative (MARI)* [1994] report. Quantities not otherwise referenced were secured from this source. Our emphasis will fall upon periods of stagnation which cause pollution episodes. They have been studied not only from ground-based monitoring stations but also during intensive aircraft campaigns [e.g., *Nickerson et al.*, 1992]. Stagnant conditions dominate the meteorology of the city during the winter. A useful tracer for pollutant distributions and transport is carbon monoxide, which has been often measured and is nearly chemically inert within the valley.

A first step in deriving the exchange rate of interest here is to define the volume and mass of polluted air in the basin. East-west aircraft traverses through the city center demonstrate that over much of the winter, CO concentrations are constant in the horizontal over at least the entire built-up area. Carbon monoxide readings at surface monitoring sites spread fairly evenly through the city confirm the result; few gradients are apparent. High quality topographical maps of the Valley of Mexico can be found in the works of *Bravo et al.* [1982], *MARI* [1994], McNair et al. (submitted manuscript, 1995), and in standard atlas materials. The basin is tightly bounded on the west and south by mountain ridges. To the north and east, peripheral measurement data are scarce. Total NMHC determinations made just north of the urban zone at Cuautitlan average a factor of 3 below their downtown counterparts, and 100 km farther on at La Reforma (state of Hidalgo), the organic loading appears to be lower by another factor of 2. *Blake and Rowland* [1995] report that C3 and C4 alkane concentrations have dropped by an order of magnitude at Teotihuacan, 50 km northeast of downtown. One CO traverse shows a concentration front inside the eastern edge of the city. We adopt the round value of 50 km by 50 km for the horizontal extent of the pollution regime. The area is somewhat larger than that of the city itself but fits physically within the basin. Lidar measurements of the boundary layer maximum height average close to 3 km in February. At a rough average air density of 1.8×10^{19} molecules cm^{-3} [*Jauregui*, 1971; *U.S. Standard Atmosphere*], the polluted basin contains 1.3×10^{38} molecules.

Diurnal variation of vehicular emissions in Mexico City and so also inputs of carbon monoxide approximate a square wave function, lasting from about 0700 to 2200 LT. This is to be contrasted with bimodal distributions in U.S. urban areas. Surface monitoring stations show an average rise in CO concentration of about 4 ppm h^{-1} over the first few morning hours during the month of February. A typical data set is reproduced in Figure 1. Extensive measurements of total suspended particulate mass and elemental composition document similar behavior for aerosols with vehicle related sources [*Aldape et al.*, 1991a, b, 1993; *Miranda et al.*, 1992, 1994; E. Vega et al., Application of a chemical mass balance receptor model to respirable particulate matter in Mexico City, submitted to *Journal of the Air and Waste Management Association*, 1995] (hereinafter referred to as Vega et al., submitted manuscript, 1995). The boundary layer top begins to lift at about 1000 LT. Prior to this, it maintains the low altitude established nocturnally. In lidar data the nighttime mixing height varies from 50 to 300 m above ground level (AGL). Analyses of 0600 LT soundings taken from morning airport rawinsonde releases give heights averaging closer to 300 m [*Porch et al.*, 1992] but are only resolved over 100 m increments. We will adopt a 150 m mixed layer for

our morning computations. The 4 ppm h^{-1} emissions figure for the volume defined by 150 m translates to 0.2 ppm h^{-1} over the atmospheric column up to the maximum height of the boundary layer, assuming for simplicity a constant average atmospheric pressure. Further, we derive 3 ppm d^{-1} for the column by integrating over the 15 hour square wave. Excluding the several hour morning traffic pulse, surface CO levels average about 5 ppm over the standard monitoring locations. During aircraft campaigns, concentrations were observed to drop by about a factor of 2 in the vertical within the lowest 2 km. An average vertical concentration is then about 3 ppm in the boundary layer. In its present configuration the built-up portion of Mexico City responsible for emissions covers something more than half of the pollutant volume we have outlined. A time constant of 2 days can thus be computed for the ventilation of CO from the basin.

A semi-independent assessment of the rate of carbon monoxide exchange can be constructed by appealing to inventories compiled from individual vehicle emissions and overall metropolitan traffic data. *MARI* [1994] and McNair et al. (submitted manuscript, 1995) take pollutant emissions from bottom-up inventories offered by *PICCA* [1990] and *TUV* [1992]. Under these databases, most CO emanates from vehicular sources, and inputs total roughly 3 × 10^6 metric tons (t) yr^{-1}, or 1.8 × 10^{32} molecules d^{-1}. For a total burden of 3 ppm or 4 × 10^{32} CO molecules the ventilation constant is again 2 days.

The tracer exchange computations can be rationalized mechanistically through several levels of physical argument. We outline them here based on our collective experience with the first few mesoscale meteorology programs to compute flow in the Valley of Mexico. The codes we have applied to the problem are HOTMAC [*Yamada*, 1985; *Yamada and Bunker*, 1988; *Williams et al.*, 1995], RAMS [*Pielke*, 1984; *Pielke et al.*, 1992; *Bossert and Cotton*, 1994a, b] and MMTD [*Lu and Turco*, 1993, 1994, 1995]. A useful qualitative understanding of flow from the basin can be obtained from study of the results of their prognostic simulations. Above the ridge tops which rise about a kilometer from the valley floor, upper level westerlies prevail. In the lower kilometer, daytime heating leads to upslope flow which is generally northeasterly in nature. Air parcels which begin upslope movement in the south of the city during the day can be entrained in upper level winds and removed within a few hours. Those which begin later or in other areas may roll back into the valley as late night brings downslope conditions.

The nighttime purging situation is particularly simple. Upper level winds flow across the city at several meters s^{-1} after the boundary layer has collapsed to tens of meters or a few hundred meters. There is the potential for daily purging of most of the daytime pollution zone, or for an exchange time constant of greater than or equal to 1 day. The possibility of recirculation is not precluded. Related concepts are in force during the daytime. Boundary layer mixing extends to almost 3 km AGL for 10 hours. A chimney effect over the mountain ridgetops effectively blocks upper level flow to a depth of 2 km AGL. Vertical mixing is rapid within the boundary layer, with a time constant of a few hours. Upper level velocities are about 3 m s^{-1} at the points where there is interaction with the boundary layer. An advective time constant for horizontal escape from the 50 km wide upper kilometer of the layer is about 2 × 10^4 s, and the fractional removal is up to one third of the polluted volume in that time. An exchange constant is again greater than or equal to 1 day. It may be noted that the daytime
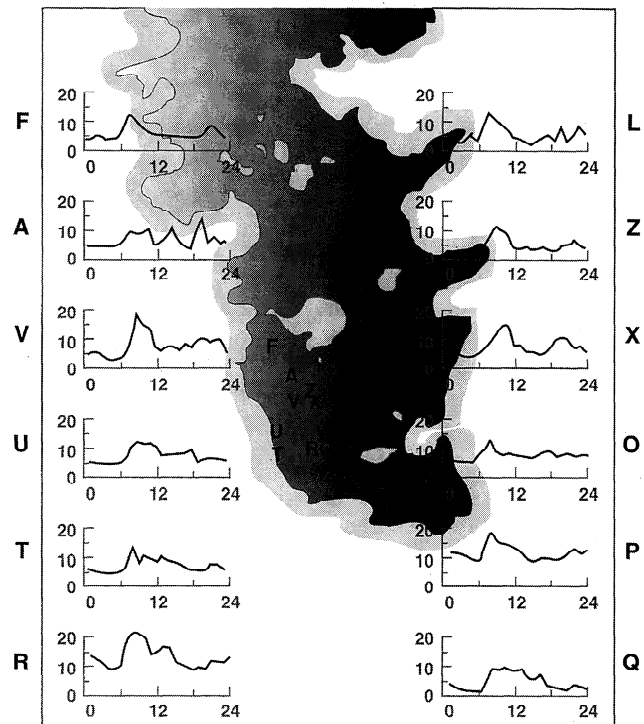

Figure 1. Variation in surface carbon monoxide readings with time at selected sites across Mexico City. Letters associated with the stations also provide their locations on the map at center. Measurements were made on February 22, 1991 [*MARI*, 1994]. Concentration units on the upward axes are parts per million. Shaded areas in the map are low elevation portions of the Valley of Mexico.

removal process can be conceived of either as an advective shearing of the top of the boundary layer or entrainment of upslope flow. The viewpoints are nearly equivalent since the ridgetop chimneys recirculate over much of the basin to form the overall boundary layer.

3. Alkane Distributions and Mass Exchange

Several groups have now shown that concentrations of the C3 and C4 alkanes, along with a variety of other volatile organics, are extraordinarily large in the Valley of Mexico [*Ruiz Santoyo et al.*, 1993; *Blake and Rowland*, 1995]. The gas chromatogram in Figure 2 dramatizes the dominance of the propane peak which is typical of the relevant samples; the skewed C3-C4 signature is characteristic of LPG leakage. The same researchers have found that the distribution of LPG alkanes over the metropolitan area is quite even. For example, *Blake and Rowland* [1995] list measurement results for the central plaza or Zocalo which are comparable to those obtained by *Ruiz Santoyo et al.* [1993] at the Tlalnepantla site in the far northwestern corner of the city. Between the two groups, dozens of urban locations have been sampled, and indications are that leakage of the liquefied petroleum gas is ubiquitous. Surface propane and butane distributions seem to correspond with those of carbon monoxide. The overall contribution of LPG alkanes and alkenes to organic reactivity in the basin may be of the order of tens of percent [*Blake and Rowland*, 1995]. The atmosphere of Mexico City is sufficiently hydrocarbon rich, however, that it is not clear whether repairing liquefied gas
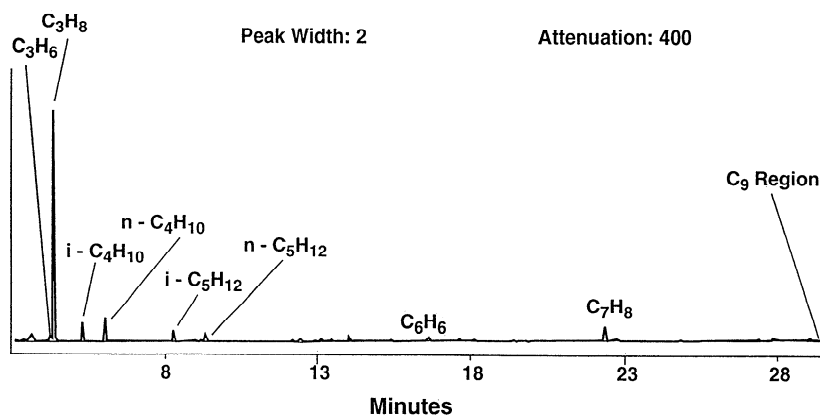
Figure 2. Gas chromatogram of a portion of the volatile organic loading in typical Mexico City surface air. Details of the analysis are given by *Blake and Rowland* [1995 and references therein]. Column materials employed in the hydrocarbon separation process included DB-1, DB-5MS, and Cyclodex-B. Detection was accomplished through flame ionization.

containers or altering the LPG mix will reduce ozone generation. A remediation strategy combining lower vehicular and C3-C4 pollutant emissions may be in order.

Photochemical removal of propane and the butanes from within the atmosphere of Mexico City will be controlled by reaction with the hydroxyl radical. The propane lifetime against this process will be much longer than our 2 day ventilation period, while the butane lifetimes may be comparable (C3 and C4 values of around 10 days and 2 days [*Singh and Zimmerman*, 1992; *Blake and Rowland*, 1995]). We will not attempt here to compute accurate photochemical losses. Hydroxyl concentrations for the construction of alkane reaction rates are available from the McNair et al. (submitted manuscript, 1995) model or empirical kinetic modeling approach (EKMA) runs described by *MARI* [1994]. Propane is clearly stable enough to be distributed through the basin as an inert tracer. The butanes may be partially depleted chemically during their residence over the city, but their removal constants exceed the timescales for vertical mixing in the lower boundary layer and for advection in the 2 to 3 km AGL regime. Their vertical distributions may thus mimic those of purely inert species. In the propane case, total ventilation is the equivalent of emissions. In other words, our techniques will give both input and removal. For the butanes, urban sourcing may exceed loss from the basin somewhat.

The report of *Blake and Rowland* [1995] and unpublished measurements from the same group offer some feeling for the time dependence exhibited by surface propane concentrations in and around Mexico City. The median for the 0500 to 0800 LT time period is 135 ppb. This drops to 30 to 50 ppb by midafternoon in response to the usual boundary layer rise. It can be concluded from mass conservation considerations that the several kilometers of depth into which the nocturally established boundary layer mixes must contain substantial amounts of propane all day. In fact, concentrations at ground level and aloft may be quite similar. Most surface data points taken near 0600 LT fall in the 100 to 200 ppb range, and one value of 35 ppb was obtained at midnight. The general rise in concentration from afternoon to morning can be explained by overnight releases. Source profile evidence indicates leaking LPG tanks are major contributors, and a conservative assumption is then that emissions take place around the clock. Since

nighttime emissions are confined to a restricted near-surface volume, it can again be argued that propane distributions will be akin to those of carbon monoxide. The butanes display similar diurnal/temporal dependence. Alkane values of *Ruiz Santoyo et al.* [1993] are not fully time resolved but appear to be somewhat higher than those of *Blake and Rowland* [1995]. The morning to afternoon falloff is a factor of 3.0 to 3.5 for propane. Both data sets cover essentially the entire urban area. We take afternoon propane, n-butane, and i-butane concentrations of 50, 30, and 15 ppb as representative of the bulk surface pollution regime in Mexico City. By analogy with the vertical CO profiles, total volume averages are about 30, 18, and 9 ppb. The corresponding mass ventilation rates from the Valley of Mexico are 5.2×10^4 t yr^{-1} (1.4×10^2 d^{-1}), 4.1×10^4 t yr^{-1} (1.1×10^2 d^{-1}), and 2.1×10^4 t yr^{-1} (5.7×10^1 d^{-1}).

It is possible based on the night sourcing to shallow boundary layers to perform a valuable cross check on our pollutant exchange time estimates. Propane concentrations rise about 100 ppb between early morning and the onset of traffic. This occurs over about a 5 hour period. Emissions to the low nighttime boundary layer are thus 20 ppb h^{-1}, and this translates to 480 ppb d^{-1}. Following our simple carbon monoxide example, additions to the total column over the built-up area for maximum boundary layer heights are then 24 ppb d^{-1}. Balance with concentrations of 30 ppb over an area of twice the city size suggests ventilation in 2 to 3 days.

4. Comparison With the Hemispheric Scale

Details of large scale budgets for the alkanes remain uncertain. We will perform crude global propane calculations here working from latitude spanning data reviewed by *Kanakidou et al.* [1991] and *Singh and Zimmerman* [1992] and supplemented for the central Pacific Ocean with unpublished values from D. R. Blake and coworkers. Propane concentrations north of the equator average about 0.2 ppb in the summer. They then increase to about 1 ppb in the winter at middle to high latitudes. Since propane is short-lived relative to the north-south interhemispheric exchange time of a year or two, intrahemispheric budgets can be decoupled. Our focus here is upon the northern half of the global troposphere. Concentrations are higher than in the south, indicating that terrestrial inputs play

a dominant role. We decompose the hemisphere conceptually into two vertical layers of equal mass and three horizontal columns with boundaries at latitudes 30° and 60° north. For local budget computations, two-dimensional longitudinally averaged hydroxyl radical fields are adopted from *Kanakidou et al.* [1991]. Equivalent data are available from *Logan et al.* [1981], *Crutzen and Zimmerman* [1991], *Law and Pyle* [1993], and many other global modeling studies. The propane rate constant for reaction with OH is given by standard tabulations such as *Atkinson and Lloyd* [1984] and *Demore et al.* [1990] or in more specialized texts [*Warneck*, 1988; *Singh and Zimmerman*, 1992]. Altitude profiles are constructed based on data reviewed by *Singh and Zimmerman* [1992]. Local temperatures could be obtained from many sources, but we have used values from *London* [1980].

Results of our propane removal rate computations are provided in Table 1. Low values in the upper and high latitude compartments reflect lack of reactant or oxidant or both. Overall rates in the top levels were of the order of 10% of those at low altitudes. In summer the hydroxyl concentrations are high enough to limit the propane lifetime to around 1 week. Latitudinally resolved surface concentrations may be thought of as existing in local equilibrium. Integrated hemispheric loss totals about 1.5×10^7 t yr^{-1}, or 4.2×10^4 t d^{-1}, and reflects instantaneous emissions. In the winter the 30° to 90° latitude region supports only very low hydroxyl levels, and the propane lifetime rises to many months or more. Emissions are best determined from the high latitude concentration buildup of about 1 ppb in 6 months, with an assumption of local steady state in the tropics. The calculations give similar values of 1.3×10^7 t yr^{-1} or 3.6×10^4 t d^{-1}. Our methods are not sensitive enough to detect seasonal source variations. However, a lack of seasonal emissions differences would in fact be indicative of anthropogenic production [*National Acid Precipitation Assessment Program (NAPAP)*, 1990]. *Kanakidou et al.* [1991] and *Singh and Zimmerman* [1992] have independently derived global (as opposed to hemispheric) propane inputs of 1.5 to 2.3×10^7 t yr^{-1}.

LPG sales in Mexico City total around 2×10^6 t yr^{-1}, of which half or one million metric tons are propane [*Blake and Rowland*, 1995]. The figure represents a large fraction of estimated hemispheric/global propane emissions. It is immediately clear that significant leakage would create an important regional scale source. In fact, our basin ventilation rate estimates indicate that propane escape from the city constitutes of the order of half of 1% of northern hemispheric emissions for the species during the winter. We may also deduce relative to LPG

Table 1. Propane Removal in Various Compartments of the Northern Hemispheric Troposphere

	0°–30°	30°–60°	60°–90°
Summer			
Upper half	slow	slow	slow
Lower half	9.5×10^6	5.2×10^6	6.7×10^5
	2.6×10^4	1.4×10^4	1.8×10^3
Winter			
Upper half	slow	slow	slow
Lower half	9.8×10^6	3.5×10^6	slow
	2.7×10^4	9.6×10^3	

Units are metric tons year^{-1} (top) and metric tons day^{-1} (bottom). Concentrations used are as reviewed by *Singh and Zimmerman* [1992] and other sources (see text).

Table 2. Removal of n-Butane in Various Compartments of the Northern Hemispheric Troposphere

	0°–30°	30°–60°	60°–90°
Summer			
Upper half	slow	slow	slow
Lower half	7.7×10^6	4.3×10^6	5.7×10^5
	2.1×10^4	1.2×10^4	1.6×10^3
Winter			
Upper half	slow	slow	slow
Lower half	8.0×10^6	3.0×10^6	slow
	2.2×10^4	8.3×10^3	

Units are metric tons year^{-1} (top) and metric tons day^{-1} (bottom). Concentrations used were taken from *Singh et al.* [1988], *Rudolph* [1988], and other sources (see text).

sales that leakage falls between 1 and 10%, which seems intuitively reasonable.

Large scale n-butane measurements sets are also available [*Singh et al.*, 1988; *Rudolph*, 1988]. The data are more limited than for smaller alkanes, but overall latitudinal and temporal patterns are related. Again, we will rely on unpublished results from D. L. Blake and colleagues, which conform to less extensive literature reports. A set of removal rate calculations analogous to the above for propane is summarized in Table 2. The butane concentration is set at 50 ppt at all locations in the summer and year-round in the tropics. Growth in the burden from 30° to 90° north is 0.3 ppb over winter. Hydrogen abstraction by the hydroxyl is 3 times faster for n-butane than it is in the case of propane. At middle latitudes the photochemical time constant is around 1 month for much of the winter. We nonetheless make the simplifying assumption that the hydroxyl radical reaction is not occurring. The integrated wintertime sourcing is thus a lower limit, but it is small relative to tropical cycling so that our conclusions should be unaffected. Input of n-butane in the northern hemisphere is then 1.0×10^7 t yr^{-1} during winter (2.6×10^4 t d^{-1}), approximately half the propane value if expressed on a molar basis. The calculated oxidation rate is 1.3×10^7 t yr^{-1} (3.5×10^4 t d^{-1}) in the summer, and losses will again balance emissions. We have not located global C4 alkane budgets with the quality of the ones mentioned for propane. Since afternoon n-butane concentrations in the Valley of Mexico are close to those of propane [*Ruiz Santoyo et al.*, 1993; *Blake and Rowland*, 1995], the ventilation rates are also alike. Mexico City may also contribute half of 1% to the hemispheric scale n-butane source.

The urban to hemispheric scale emissions comparisons are summarized for propane and n-butane in Table 3. Few if any remote and latitudinally dependent isobutane measurements

Table 3. Estimates of Wintertime Emissions of Propane and n-Butane From the Basin Containing Mexico City to the Free Troposphere and for the Entire Northern Hemisphere

	Propane	n-Butane
Valley of Mexico	5.2×10^4	4.1×10^4
	1.4×10^2	1.1×10^2
Northern hemisphere	1.3×10^7	1.0×10^7
	3.6×10^4	2.6×10^4
Fraction from valley, %	0.4	0.4

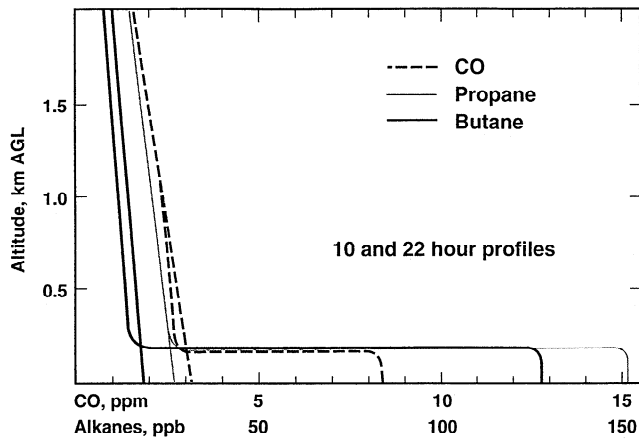The units are metric tons year^{-1} (top) and metric tons day^{-1} (bottom).

Figure 3. Steady state vertical tracer profiles from the one-dimensional model constructed here to help validate assumptions regarding similarity of alkane and carbon monoxide distributions. Results are given for hour 10 (1000 LT), at which point the low nocturnal inversion continues to confine night and morning emissions, and for hour 22 (2200 LT), after mixing to the boundary layer maximum has diluted the surface layer and before the onset of new inversions.

have been published thus far. However, because it is also present in the urban basin at concentrations in the 10 to 100 ppb range, the arguments we have made here for the other C3 and C4 alkanes may still apply.

5. Discussion

To arrive at estimates of mass fluxes of long-lived alkanes from the Valley of Mexico, we have assumed that the readily observed species carbon monoxide acts as a tracer for their behavior. A transport removal time constant was computed for CO based on its measured burden and emissions rate. The burden for propane was derived by transferring relative vertical CO profiles to surface alkane measurements. Division through by the transport removal time yielded a loss estimate. By virtue of lack of chemical activity, propane loss is also total emission. Our approach can be justified to first order by noting that both carbon monoxide and propane are inert on basin mixing timescales. However, there are certain complications which should also be considered. We have mentioned that emissions functions for LPG components probably differ dramatically from those of vehicular pollutants. Propane and butane leakage appear to take place around the clock. The interplay with areas of advective removal could be distinct for species with significant storage beneath low, nighttime inversions.

As a first step in exploring this subtlety, we constructed a time dependent one-dimensional model which simulates some features of transport for surface sourced species within the basin. The model divides the atmosphere within the polluted region into 60 layers of 50 m thickness with diffusive exchange between them. Advective removal is included above 2 km, and chemical losses can be turned on at all altitudes. Low nocturnal inversions are simulated through reductions in diffusion coefficients above the first three layers, or above 150 m.

Sample vertical profiles are shown from steady state model results in Figure 3. The carbon monoxide data are computed for the *PICCA* [1990] and *TUV* [1992] emissions, spread over the diurnal square wave and domain defined here. Major fea-

tures of surface and aircraft CO observations are reproduced [*MARI*, 1994], suggesting that results are reasonable. The computed CO lifetime is 1.8 days. To generate a propane profile, daily average emissions were reduced by a factor of 100 (the ratio of afternoon concentrations for the monoxide and alkane), and were also distributed evenly over 24 hours. The increased release period under the nighttime boundary layer is reflected in the larger morning surface concentration peak. The peak is confined to the lowest few hundred meters and only impacts the overall burden by of the order of tens of percent. Decay of the morning peak is not depicted but is complete by 1400 LT, so indeed it would seem that afternoon surface data can be taken as a basis for extrapolation to higher altitudes. Vertical gradients for CO and propane are very similar, and burdens differ by very nearly the ratio of emissions, or 100. It can be concluded that the time constants are alike for advection, the only removal process. A propane loss rate estimated assuming a CO-like vertical profile and CO-like advective removal is probably accurate. Absolute afternoon surface concentrations could be brought into agreement with measurements through slight adjustments in the advective removal rate, but this was thought to be an unnecessary refinement.

Three dimensional chemistry/transport models remain challenging to construct for topographically complex urban basins but are now available from several groups worldwide [e.g., *McRae et al.*, 1982a, b; *Russell et al.*, 1988; *Milford et al.*, 1989; *MARI*, 1994; *Williams et al.*, 1995; *Lu and Turco*, 1993, 1994, 1995; *McNair et al.*, submitted manuscript, 1995]. The first mesoscale meteorology program to simulate wind fields in the Valley of Mexico was HOTMAC [*Yamada*, 1985; *Yamada and Bunker*, 1988; *Williams et al.*, 1995]. The resulting data have been coupled to the California Institute of Technology (CIT) air chemistry code in order to elucidate ozone production patterns and consider pollution remediation strategies [*MARI*, 1994; *McNair et al.*, submitted manuscript, 1995]. We have recently altered the Mexico City CIT version slightly to address the basin internal distribution questions. Propane emissions were spread over the full 24 hour day and then raised at round increments until ground level gas chromatographic measurements could be reproduced roughly [*Ruiz Santoyo et al.*, 1993; *Blake and Rowland*, 1995]. Some of the vertical profiles simulated over the downtown area are shown in Figure 4 for a February time period. Layer divisions were set at 50, 200, 1000, 1600, 2400, 3100, and 3800 m in the chemistry code. The near-surface diurnal cycle is captured, and the relative structure aloft is consistent with carbon monoxide measurements and so also our assumptions. It must be noted, however, that boundary conditions for the LPG alkanes were set to zero concentration in the runs shown, and significant spillage off the urban grid ensued. Only upper limits to the basin ventilation rate can be derived, but they are consistent with the values obtained here. Grid losses also confound direct comparison with the overall valley burdens we estimate.

In extending ventilation estimates to the butanes we argued that their photochemical lifetime of a day or two [*Blake and Rowland*, 1995] was longer than timescales for mixing within the basin. The implication is that internal distributions again resemble those of carbon monoxide. The burden can then be divided by the usual ventilation constant to give loss from the valley, or by the chemistry constant to give internal removal. Butanes are simulated in the one-dimensional model by introducing a columnar 1 day removal process which operates during the photolytic period. Emissions remain at 1% of the car-

bon monoxide value. Although concentrations through the column drop in the morning, the nature of the vertical profiles remains essentially unchanged. The analogous drop in the afternoon is compensated somewhat by upward mixing from the ultrarich nighttime inversion. Contribution to the overall burden from below the night boundary layer is larger on a relative basis but is still only of the order of tens of percent. A quick expedient can be used to demonstrate that division by the CO escape constant still approximates basin ventilation. The integrated concentration of butane in Figure 3 is about half that of propane. The diurnally averaged chemical removal constant is 2 days, roughly equal to the ventilation time which balanced emissions for propane and carbon monoxide. Half of the 1% of CO emissions (half the butane input) can thus be accounted for by chemical removal. The remainder constitutes ventilation, or again burden turnover in 2 days.

Our box calculations of alkane escape do not account for potential sources which may lie external to the pollution regime. Carbon monoxide emissions from bottom-up and other inventories are generally thought to be around 3×10^6 t yr^{-1}, or 1.8×10^{32} molecules d^{-1}. Assuming a free tropospheric background level of 150 ppb [*Logan et al.*, 1981; *Seiler and Fishman*, 1981; *Novelli et al.*, 1994] and prevailing southwesterlies of 3 m s^{-1} between 2 and 3 km where the boundary layer interacts with upper level winds, an input of around 10% of the surface source can be deduced. The propane surface input is roughly 1% that of CO; we have noted that removal processes are similar, and the afternoon concentrations are related by a factor of 100. Wintertime background propane concentrations at the Mexico City latitude of 19° north are of the order of one half ppb, or 300 times less than the corresponding carbon monoxide level. Similar ratios apply for n-butane. It therefore seems unlikely that inclusion of finite remote tropospheric levels in box type computations would alter our results. Our one-dimensional numerical computations corroborate this logic because backgrounds were included as advective inflow.

The possibility of surface horizontal transport or recirculation pumping our tracers into the valley from the north is more difficult to dismiss. The input was not included in either the one- or three-dimensional simulations. No extensive carbon monoxide measurements have been published for the area at the opening of the Valley of Mexico. Total volatile organic carbon data taken at La Reforma, 100 km upwind, are down by only a factor of 5 from those in the urban area [*MARI*, 1994] but could contain species of biogenic (vegetative) origin. The propane and butane measurements made at Teotihuacan show concentrations only an order of magnitude below afternoon levels in the city but could themselves reflect local emissions. Surface northeasterlies tend to flow across the valley floor at 3 m s^{-1} for half a day everyday in the winter and influence much of the lowest kilometer of the air mass [*MARI*, 1994]. If CO concentrations in the inflow are down an order of magnitude relative to the city, at 500 ppb, the total flux could be several tens of percent of the standard surface emissions. The same sorts of relationships apply to the alkanes. Since models adopting the PICCA [1990] and TUV [1992] inventories give reasonable carbon monoxide balance (McNair et al., submitted manuscript, 1995), northeasterly sourcing would not seem to be a major problem. Furthermore, the estimates of surface influx are probably upper limiting in several ways: in that the concentrations chosen are high, and that the daytime surface flow is compensated in part by subsidence toward the basin center. However, the issue can only be adequately resolved
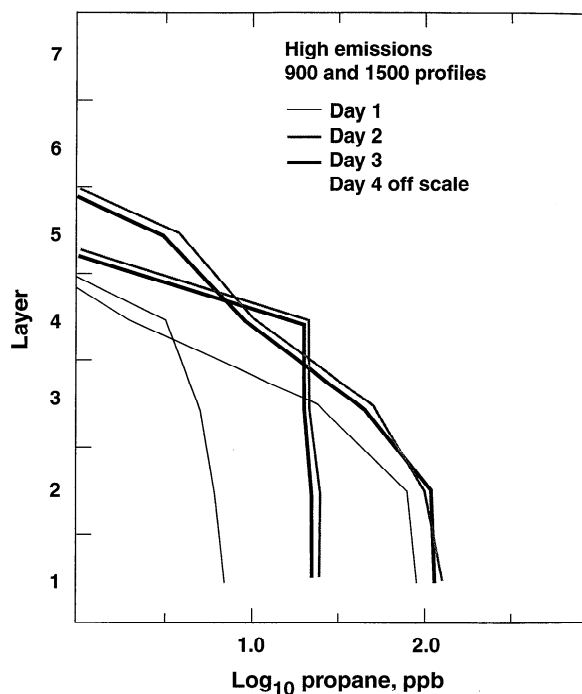

Figure 4. Evolution of the vertical propane profile over downtown Mexico City in a version of the CIT air chemistry model with propane emissions spread over 24 hours and adjusted to match gas chromatographic measurements. Since concentrations begin at zero, the approach to steady state is apparent.

through a combination of upwind measurements and three-dimensional transport modeling. An unexpected surface transport source would have the effect of reducing our calculated lifetime. Recirculations would form net cancellations relative to free tropospheric ventilation, but independent inputs could increase the net outbound mass flux.

Potential error sources in our manipulations extend well beyond transport considerations. The volume of the polluted region, nocturnal boundary layer heights, and carbon monoxide inputs all contain uncertainties which we would estimate informally to be a factor of 2 in either direction. Our assumptions regarding the ubiquity of small alkanes across the metropolitan area should be verified. *Blake and Rowland* [1995] point out that a constancy of C3 to C4 concentration ratios suggests widespread LPG leakage. It is of tangential interest that their atmospheric propane/n-butane ratios are everywhere close to the composition of typical Mexican LPG; this may mean that photochemical removal of the butane is slow. February propane measurements made by Blake and Rowland before the morning traffic pulse at locations scattered throughout the city average 136 ppb with an absolute low of 52 ppb. *Ruiz Santoyo et al.* [1993] sampled five sites during March at the center of and around the periphery of the built-up area. Their average propane concentration is around 150 ppb, and the lowest result obtained between 0600 and 0900 LT is 40 ppb. The two gas chromatography studies cited most heavily here are thus mutually quite consistent and strongly suggest that the surface concentrations we have adopted permeate the urban atmosphere and beyond. Some discrepancies are to be expected due to phase shifts in the measurements. By 0900 LT, several further hours of buildup can take place beneath low

morning inversions. For locales in the northwest and southwest of the city (Tlanepantla and Pedregal), *Ruiz Santoyo et al.* [1993] give afternoon values averaging 35 ppb, with a low of 15 ppb. Comparisons of butane values across the basin lead to similar conclusions. Our vertical alkane distributions are mainly deductions based on the carbon monoxide analogy. Aircraft measurements would definitely seem to be in order. To our basin C3-C4 alkane concentrations, we would again assign an informal uncertainty of a factor of 2.

We will not attempt to apply a rigorous error analysis to the urban ventilation computations in the present work and would hesitate even to ascribe relative values to the various origins of uncertainty. Clearly, the situation can be improved through more complete simulations and measurements. It should be noted that our comparison of basin emissions with the hemispheric introduces a new level of potential error. The large scale spatial and temporal averaging techniques employed for alkane and hydroxyl radical concentrations were extremely crude. The fact that other authors using established methods arrive at global budgets agreeing with our own [*Kanakidou et al.*, 1991; *Singh and Zimmerman*, 1992] provides some degree of confidence but also hints at yet another factor of 2 or so of uncertainty. Our feeling is that the hemispheric emissions figures derived here for propane and n-butane lie on the high side because we have superimposed average surface concentration measurements on the entire lower half of the tropospheric column (around 5 km of depth).

The contribution of Mexico City to the northern hemispheric propane and butane budgets is disproportionate from several perspectives. The human population of the metropolitan area is about one three hundredth of the total for the hemisphere [*United Nations*, 1992]. By our estimates, escape of C3-C4 alkanes from LPG containers and then from the Valley of Mexico reflects one two hundredth or so of all sources, anthropogenic or natural. The aseasonality of the large scale propane and n-butane emissions derived here is an expected feature of anthropogenic production [*NAPAP*, 1990], but the coarseness of our approach precludes authoritative statements. Natural inputs are known from the oceans and from vegetation [*Singh and Zimmerman*, 1992]. The disproportionality would be magnified in a regional analysis, which could readily be performed in mesoscale meteorology codes [*Pielke et al.*, 1992; *Williams et al.*, 1995]. Mexico City can be viewed as a prototype for megacities emerging in developing nations worldwide [*United Nations*, 1992; *Kretzschmar*, 1993, 1994]. Appearance of this new generation of megalopolis probably cannot be avoided [*United Nations*, 1992; *Goldemberg*, 1995; *Kauppi*, 1995] and provides a strong impetus for understanding connections between urban pollution and global chemistry. The work of *Blake and Rowland* [1995] and unpublished data from the same group suggest that further study of the liquefied petroleum gas signatures of city atmospheres would be beneficial. Short-lived olefinic components generated a large portion of the early interest in Mexican LPG because of their high reactivity and the concomitant ozone generation potential. However, the manufactured composition of the gas product is not constant internationally. The olefinic content varies markedly, while propane is usually a major constituent. Large scale influences of urban LPG on alkane budgets may thus be universal. The LPG hydrocarbon fingerprint has been detected not only in the Valley of Mexico but also in Israeli, Greek, and South American cities. A statistical knowledge of propane and butane signatures for urban atmospheres would permit bottom-up

quantification of global emissions from the LPG source. An alternative calculation would entail extrapolation of Mexico City leak rates to global LPG sales. Some of the required parameters are provided by this paper.

Stagnant wintertime conditions have been emphasized here because they amplify Mexican pollution episodes and so have been often examined [e.g., *Aldape et al.*, 1991a, b; *Miranda et al.*, 1992, 1994; *Ruiz Santoyo et al.*, 1993; *MARI*, 1994; *Blake and Rowland*, 1995]. Since propane is sufficiently stable to escape oxidation within the valley even under stagnation, it is probably always correct to equate urban emissions with total exchange to the free troposphere. The butanes come close to falling under this rubric as well. Tracer ventilation will be complicated during the summer by the very regular afternoon convective systems which develop along the surrounding ridges [*Mora and Jauregui*, 1968; *Jauregui*, 1971]. However, rates will again exceed those of internal oxidative loss. The concentration information needed to estimate summertime sourcing of LPG constituents to the free troposphere remains to be gathered. Limited preliminary data indicate concentrations in the hundreds of ppb for propane at night [*Blake and Rowland*, 1995], but it may not be safe to assume that summer and winter LPG leakage are alike. Usages are dominated by cooking and heating, activities which should be seasonally dependent.

The Valley of Mexico will constitute a large source to the free troposphere not only of hydrocarbons, but also of the nitrogen oxides [*MARI*, 1994]. The C3-C4 and overall organic richness of the photochemical milieu suggest that novel NO_x transport mechanisms may be at work. It is recognized that peroxyacetylnitrate (PAN) type substances and organic nitrates can carry NO_x over great distances [*Crutzen*, 1979; *Singh and Hanst*, 1981; *Atherton and Penner*, 1988, 1990; *Atherton*, 1989]. In some cases, thermal lability is an issue, and movement is most important in cold climates [*Singh and Hanst*, 1981]. At low latitudes, thermal equilibria may exist between species such as the peroxyacetyl radical and NO_2 [*Atkinson and Lloyd*, 1984]. The net nitrogen oxide partitioning within such relationships will be controlled by the concentration of oxidized organic fragments. Furthermore, it has been shown that organic peroxy radicals of carbon chain length greater than 3 (>C3) tend to react with NO to form organic nitrates at relatively high branching ratios [*Darnall et al.*, 1976; *Atkinson et al.*, 1982, 1984]. Liquefied petroleum gas contributes to an elevated propane loading in Mexico City. Vehicular pollution will do the same for larger alkanes [*MARI*, 1994; *Blake and Rowland*, 1995]. The abnormally high total volatile organic concentrations in the basin portend export of NO_x as nitrate compounds [*Atherton and Penner*, 1988, 1990].

The present work has focused on ventilation of small alkanes from the Valley of Mexico because LPG leakage is currently a timely topic [*Blake and Rowland*, 1995] and because a number of credible local measurements are available. It may be noted, however, that our preliminary geometrical approach to the characterization of basin mass loss could just as easily be applied to other pollutants. Carbon monoxide, the species we have relied upon as a primary tracer, is one logical candidate. The molecule is longer-lived than either propane or the butanes (about 1 month [*Logan et al.*, 1981]), while the ratio of Mexico City to remote concentrations is smaller (3 ppm/150 ppb versus 30 ppb/0.2 ppb for propane). A quick computation indicates that Mexico City accounts for of the order of tenths of 1% of the global budget, which can be found detailed by *Logan et al.* [1981] and many later references. The role of the

basin and its effluent in the regional aerosol system may also merit investigation. Concentrations of total suspended particulates, carbonaceous particles, and ammonium sulfate/nitrate aerosols are all higher in Mexico City than in Los Angeles, a domestic urban area with severe visibility degradation [*Aldape et al.*, 1991a, b; *Miranda et al.*, 1992, 1994; *Vega et al.*, 1995, also submitted manuscript, 1995]. The several day pollutant residence time typical of winter stagnation episodes begs investigation of the extent of internal/external mixing achieved among particles prior to their export from the basin (S. Schwartz, personal communication, 1995) [also see *Jacobson et al.*, 1994].

6. Summary

Leakage of liquefied petroleum gas (LPG) has been recognized as one of the factors lying behind enriched total volatile organic concentrations in the atmosphere of Mexico City. Constituents of LPG include propane, the butane isomers, and olefins. All these species will contribute significantly to ozone production as they oxidize locally [*Ruiz Santoyo et al.*, 1993; *MARI*, 1994; *Blake and Rowland*, 1995]. Propane and the butanes are also stable enough toward photochemical breakdown to be ventilated from the basin enclosing the urban area. Within the free troposphere the low molecular weight alkanes are responsible for tens of percent of total organic reactivity [*Singh and Zimmerman*, 1992]. Our goal in this text has been to perform a preliminary computation of ventilation rates from the Valley of Mexico for the saturated C3 and C4 hydrocarbons in LPG.

The first step is the definition of a pollutant rich volume extending beyond the boundaries of the urban area but falling within the confines of the Mexico City basin. We restrict ourselves to a wintertime analysis because observational data are plentiful. The top of the polluted regime is set by the daytime mixed layer altitude [*Cooper and Eichinger*, 1994]. The periphery is chosen to reflect sharp horizontal gradients observed for carbon monoxide and for some of the hydrocarbons [*MARI*, 1994; *Blake and Rowland*, 1995]. Measurements of CO encompass lengthy horizontal aircraft traverses, several vertical profiles taken from aircraft, and reports from many surface air pollution monitoring stations. In a second phase of the work, emissions of CO in Mexico City are derived in order to permit the estimation of valley flushing rates. The inventory is first generated independently based on the morning concentration pulses resulting from buildup beneath low inversion ceilings [*MARI*, 1994]. The sources are then cross-checked against available bottom-up data [*PICCA*, 1990; *TUV*, 1992; McNair et al., submitted manuscript, 1995]. Inputs and the apparent burden indicate that carbon monoxide is purged from the Valley of Mexico in 2 days during winter pollution events. Flow simulations conducted within mesoscale models of meteorology in central Mexico corroborate the ventilation constant derived from the CO tracer analysis [*MARI*, 1994; McNair et al., submitted manuscript, 1995].

Propane and the butanes are long enough lived to be distributed through the basin in a manner analogous to that of carbon monoxide [*Singh and Zimmerman*, 1992; *Blake and Rowland*, 1995]. Surface determinations at sites dispersed evenly over the urban area give concentrations which are consistently many times higher than in domestic cities [*Ruiz Santoyo et al.*, 1993; *Blake and Rowland*, 1995]. Values seldom fall below 10 ppb for any of the specific compounds propane,

n-butane, or i-butane. Application of the carbon monoxide exchange time constant to integrated alkane burdens yields a set of estimates for mass fluxes from the valley. To provide a context for the estimates, comparisons have also been made with larger scale NMHC budgets. Overall emissions for the entire northern hemisphere are constructed for propane and n-butane using seasonally and latitudinally dependent measurements and hydroxyl radical concentrations from global models. The mass fluxes agree well with literature values [*Kanakidou et al.*, 1991; *Singh and Zimmerman*, 1992]. Absolute inputs from the Valley of Mexico, the hemisphere, and fractional emissions for the valley appear in Table 3. Escape from Mexico City constitutes about half a percent of the hemispheric winter budgets for propane and n-butane.

We explore the various uncertainties in our methods at some length in the discussion section. A one-dimensional numerical model of pollutant transport within and from the basin lends credence to our contention that stable hydrocarbon distributions resemble those of carbon monoxide. Since the model is time dependent, the effect of storage beneath low inversions could be investigated for several different release scenarios. The measurement evidence points to 24 hour LPG leakage as the dominant C3-C4 alkane source [*Blake and Rowland*, 1995]. By contrast, carbon monoxide is released in a daytime step function paralleling traffic patterns [*MARI*, 1994]. A three-dimensional photochemical model treated as a propane tracer transport code verifies our approximations of vertical profiles. Loss from the grid edges is too large to permit more than limiting estimates of the ventilation rate. Another transport-related issue is treated only heuristically; inputs of the key tracers in surface winds entering at the mouth of the valley are probably minimal. Other potential sources of error are detailed in the discussion as well. The boundaries for the polluted regime must of necessity be somewhat arbitrary. Nocturnal inversion altitudes, carbon monoxide emissions inventories, and extrapolation of alkane measurements over the basin all bring with them inherent and significant uncertainties. The hemispheric scale budgets with which ventilation rates are compared are uncertain in themselves because of the broad hydrocarbon/hydroxyl concentration averaging required [*Singh and Zimmerman*, 1992]. We note that confidence in our propane and butane budgeting can be improved through continued monitoring of the alkanes, both within and outside the basin, and at/above the surface.

The C3-C4 liquefied petroleum gas fingerprint has been identified first in Mexico City, but other urban areas may be subject to serious leakage as well [*United Nations*, 1992; *Blake and Rowland*, 1995]. The olefins which comprise a large portion of the organic reactivity from LPG will vary as a fraction of the manufactured mix from location to location, but propane is usually a major constituent. This means that export of the stable, saturated alkanes will be a recurring theme in studies of ventilation from cities where LPG use is common. We also reemphasize within the discussion section that our computations refer mainly to the winter season. Measurement campaigns have usually taken place during the pollution episodes which accompany stagnant meteorological conditions. Gas chromatographic hydrocarbon data, for example, are at present insufficient in the summer to support ventilation estimates. We conclude with some tentative extensions of key concepts to pollutants other than the liquefied petroleum gas species. Total NMHC measurements demonstrate that many organic molecules are present in the atmosphere of Mexico

City at unusually high concentrations [*MARI*, 1994]. It is likely that partially oxidized decay products react with the nitrogen oxides, storing them as nitrates for transport to the regional scale. Aerosol loadings in the Valley of Mexico are equally extraordinary [*Aldape et al.*, 1991a, b; *Miranda et al.*, 1992, 1994], and estimates of particle export rates would be valuable.

References

Aldape, F., M. J. Flores, R. V. Diaz, J. R. Morales, T. A. Cahill, and L. Saravia, Seasonal study of the composition of atmospheric aerosols in Mexico City, *Int. J. PIXE*, *1*, 355–371, 1991a.

Aldape, F., M. J. Flores, R. V. Diaz, J. Miranda, T. A. Cahill, and J. R. Morales, Two year study of elemental composition of atmospheric aerosols in Mexico City, *Int. J. PIXE*, *1*, 373–388, 1991b.

Aldape, F., M. J. Flores, R. V. Diaz, and D. Crumpton, Temporal variations in elemental concentrations of atmospheric aerosols in Mexico City, *Nucl. Instrum. Methods Phys. Res.*, *75*, *Sect. B*, 304–307, 1993.

Atherton, C. S., Organic nitrates in remote marine environments: Evidence for long range transport, *Geophys. Res. Lett.*, *16*, 1289–1292, 1989.

Atherton, C. S., and J. E. Penner, The transformation of nitrogen oxides in the polluted troposphere, *Tellus*, *40*, *Ser. B*, 380–392, 1988.

Atherton, C. S., and J. E. Penner, The effect of biogenic hydrocarbons on the transformation of nitrogen oxides in the troposphere, *J. Geophys. Res.*, *95*, 14,027–14,038, 1990.

Atkinson, R., and A. C. Lloyd, Evaluation of kinetic and mechanistic data for modeling photochemical smog, *J. Phys. Chem. Ref. Data*, *13*, 315–398, 1984.

Atkinson, R., S. M. Aschmann, W. P. L. Carter, A. M. Winer, and J. N. Pitts, Alkyl nitrate formation from the NOx-air photooxidations of C2-C8 n-alkanes, *J. Phys. Chem.*, *86*, 4563–4570, 1982.

Atkinson, R., S. M. Aschmann, W. P. L. Carter, A. M. Winer, and J. N. Pitts, Formation of alkyl nitrates from the reaction of branched and cyclic alkyl peroxy radicals with NO, *Int. J. Chem. Kinet.*, *16*, 1085–1089, 1984.

Blake, D. R., and F. S. Rowland, Urban leakage of liquefied petroleum gas and its impact on Mexico City air quality, *Science*, *269*, 953–956, 1995.

Bossert, J. E., and W. R. Cotton, Regional scale flows in mountainous terrain, I, A numerical and observational comparison, *Mon. Weather Rev.*, *122*, 1449–1471, 1994a.

Bossert, J. E., and W. R. Cotton, Regional scale flows in mountainous terrain, II, Simplified numerical experiments, *Mon. Weather Rev.*, *122*, 1472–1489, 1994b.

Bravo, H., R. Torres, M. I. Saavedra, and S. Aguilar, Correlation between T. S. P., F. S. P. and visibility in a high altitude city (Mexico City), *Sci. Total Environ.*, *24*, 177–182, 1982.

Chameides, W., and J. C. G. Walker, A photochemical theory of tropospheric ozone, *J. Geophys. Res.*, *78*, 8751–8760, 1973.

Cooper, D. I., and W. E. Eichinger, Structure of the atmosphere in an urban planetary boundary layer from lidar and radiosonde observations, *J. Geophys. Res.*, *99*, 22,937–22,948, 1994.

Crutzen, P. J., A discussion of the chemistry of some minor constituents in the stratosphere and troposphere, *Pure Appl. Geophys.*, *106*, 1385–1399, 1973.

Crutzen, P. J., The role of NO and NO_2 in the chemistry of the troposphere and stratosphere, *Annu. Rev. Earth Planet. Sci.*, *7*, 443–472, 1979.

Crutzen, P. J., Tropospheric ozone: An overview, in *Tropospheric Ozone*, edited by I. S. A. Isaksen, pp. 3–32, D. Reidel, Norwell, Mass., 1988.

Crutzen, P. J., and P. H. Zimmerman, The changing photochemistry of the troposphere, *Tellus*, *43*, *Ser. AB*, 136–151, 1991.

Darnall, K. R., W. P. L. Carter, A. M. Winer, A. C. Lloyd, and J. N.

Pitts, Importance of RO2 + NO in alkyl nitrate formation from C4-C6 alkane photooxidations under simulated atmospheric conditions, *J. Phys. Chem.*, *80*, 1948–1955, 1976.

Demore, W. B., S. P. Sander, D. M. Golden, M. J. Molina, R. F. Hampson, M. J. Kurylo, C. J. Howard, and A. R. Ravishankara, Chemical kinetics and photochemical data for use in stratosphere modeling, *JPL Publ.*, *90-1*, 1990.

Ferman, M. A., G. T. Wolff, and N. A. Kelly, An assessment of the gaseous pollutants and meterological conditions associated with Denver's brown cloud, *J. Environ. Sci. Health*, *16*, *Part A*, 315, 1981.

Goldemberg, J., Energy needs in developing countries and sustainability, *Science*, *269*, 1058–1059, 1995.

Hauglustaine, D. A., C. Granier, G. P. Brasseur, and G. Megie, The importance of atmospheric chemistry in the calculation of radiative forcing on the climate system, *J. Geophys. Res.*, *99*, 1173–1186, 1994.

Houghton, J. T., G. J. Jenkins, and J. J. Ephraums, *Climate Change: The IPCC Scientific Assessment*, Cambridge Univ. Press, New York, 1990.

International Panel on Climate Control (IPCC), *Greenhouse Gases*, Cambridge Univ. Press, New York, 1992.

Jacobson, M. Z., R. P. Turco, E. J. Jensen, and O. B. Toon, Modeling coagulation among particles of different composition and size, *Atmos. Environ.*, *28*, *Part A*, 1327–1338, 1994.

Jauregui, E., *Mesomicrodima de la Ciudad de Mexico*, Univ. Nac. Auton. de Mexico, Ciudad Univerisitaria, Mexico D. F., 1971.

Kanakidou, M., and P. J. Crutzen, Scale problems in global tropospheric chemistry modeling: Comparison of results obtained with a three dimensional model adopting longitudinally uniform and varying emissions of NOx and NMHC, *Chemosphere*, *26*, 787–801, 1993.

Kanakidou, M., H. B. Singh, K. M. Valentin, and P. J. Crutzen, A two-dimensional study of ethane and propane oxidation in the troposphere, *J. Geophys. Res.*, *96*, 15,395–15,413, 1991.

Kauppi, P. E., The United Nations climate convention: Unattainable or irrelevant, *Science*, *270*, 1454, 1995.

Kretzschmar, J. G., Air pollution levels and trends in Latin American megacities, in *Air Pollution*, edited by P. Zannetti et al., pp. 131–137, Comput. Mech., Billerica, Mass., 1993.

Kretzschmar, J. G., Particulate matter levels and trends in Mexico City, Sao Paulo, Buenos Aires and Rio de Janeiro, *Atmos. Environ.*, *28*, 3181–3191, 1994.

Law, K. S., and J. A. Pyle, Modeling trace gas budgets in the troposphere, 2, CH_4 and CO, *J. Geophys. Res.*, *98*, 18,401–18,412, 1993.

Liu, S. C., M. Trainer, F. C. Fehsenfeld, D. D. Parrish, E. J. Williams, D. W. Fahey, G. Hübler, and P. C. Murphy, Ozone production in the rural troposphere and the implications for regional and global ozone distributions, *J. Geophys. Res.*, *92*, 4191–4207, 1987.

Logan, J. A., M. J. Prather, S. C. Wofsy, and M. B. McElroy, Tropospheric chemistry: A global perspective, *J. Geophys. Res.*, *86*, 7210–7254, 1981.

London, J. L., Radiative energy sources and sinks in the stratosphere and mesosphere, in *Proceedings of the NATO Advanced Study Institute on Atmospheric Ozone*, *Rep. FAA-EE-80-20*, pp. 703–721, Natl. Tech. Inf. Serv., Springfield, Va., 1980.

Lu, R., and R. P. Turco, Numerical investigation of the formation of elevated pollution layers over the Los Angeles air basin, in *Air Pollution*, edited by P. Zanetti et al., pp. 43–56, Comput. Mech., Billerica, Mass., 1993.

Lu, R., and R. P. Turco, Air pollutant transport in a coastal environment, I, Two dimensional simulations of sea breeze and mountain effects, *J. Atmos. Sci.*, *51*, 2285–2308, 1994.

Lu, R., and R. P. Turco, Air pollutant transport in a coastal environment, II, Three dimensional simulations over the Los Angeles basin, *Atmos. Environ.*, *29*, 1499–1518, 1995.

MARI, The Mexico City Air Quality Research Initiative, *Los Alamos Natl. Lab. Rep.*, *LA-12699*, 1994.

Mayrsohn, H., M. Kuramoto, J. H. Crabtree, R. D. Sothern, and S. H. Mano, Atmospheric hydrocarbon concentrations, June–September 1974, report, State of Calif. Air Resour. Board, Sacramento, April 1975.

McRae, G. J., W. R. Goodin, and J. H. Seinfeld, Development of a second generation mathematical model for urban pollution: Model formulation, *Atmos. Environ.*, *16*, 679–696, 1982a.

McRae, G. J., W. R. Goodin, and J. H. Seinfeld, Numerical solution of the atmospheric diffusion equation for chemically reacting flows, *J. Comput. Phys.*, *45*, 1–42, 1982b.

Milford, J. B., A. G. Russell, and G. J. McRae, A new approach to

photochemical pollution control: Implications of spatial patterns in pollutant responses to reductions in nitrogen oxides and reactive organic gas emissions, *Environ. Sci. Technol.*, 23, 1290–1301, 1989.

Miranda, J., J. R. Morales, T. A. Cahill, F. Aldape, and J. Flores, A study of elemental contents in atmospheric aerosols in Mexico City, *Atmosfera*, 5, 95–108, 1992.

Miranda, J., T. A. Cahill, J. R. Morales, F. Aldape, M. J. Flores, and R. V. Diaz, Determination of elemental concentrations in atmospheric aerosols in Mexico City using proton induced X-ray emission, proton elastic scattering, and laser absorption, *Atmos. Environ.*, 28, 2299–2306, 1994.

Mora, C. S., and E. Jauregui, *Cartografia de Elementos Bioclimaticos en la Republica Mexicana*, Univ. Nac. Auton. de Mexico, Ciudad Universitaria, Mexico D. F., 1968.

National Acid Precipitation Assessment Program (NAPAP), *NAPAP State of Science and Technology*, vol. 1, U.S. Govt. Print. Off., Washington, D. C., 1990.

Nickerson, E. C., G. Sosa, H. Hochstein, P. McCaslin, W. Luke, and A. Schanot, Project Aguila: In situ measurements of Mexico City air pollution by a research aircraft, *Atmos. Environ.*, 26, Part B, 445–451, 1992.

Novelli, P. C., K. A. Masarie, P. P. Tans, and P. M. Lang, Recent changes in atmospheric carbon monoxide, *Science*, 263, 1587–1590, 1994.

Penner, J. E., C. S. Atherton, J. Dignon, S. J. Ghan, and J. J. Walton, Tropospheric nitrogen: A three-dimensional study of sources, distributions, and deposition, *J. Geophys. Res.*, 96, 959–990, 1991.

PICCA, *Programa Integral Contra la Contaminacion Atmosferica de la Zona Metropolitana de la Ciudad de Mexico*, Secr. Tec. Interguber-namental, Mexico City, 1990.

Pielke, R. A., *Mesoscale Meteorological Modeling*, Academic, San Diego, Calif., 1984.

Pielke, R. A., et al., A comprehensive meteorological modeling system—RAMS, *Meteorol. Atmos. Phys.*, 49, 69–91, 1992.

Porch, W. M., L. Auer, W. Clements, and J. P. Mutschlecner, Air pollution mixing height studies in Mexico City, *Los Alamos Natl. Lab. Rep.*, LA-UR-92-1296, 1992.

Rudolph, J., Two-dimensional distribution of light hydrocarbons: Results from the STRATOZ III experiment, *J. Geophys. Res.*, 93, 8367–8377, 1988.

Ruiz Santoyo, M. E., K. Gerner, M. Y. Barbiaux Saldaña, and R. Seila, Hydrocarbon speciation in Mexico City: initial results, paper presented at 86th Annual Meeting and Exhibition, Air and Waste Manage. Assoc., Denver, Colo., June 13–18, 1993.

Russell, A. G., K. F. McCue, and G. R. Cass, Mathematical modeling of the formation of nitrogen containing air pollutants: Evaluation of an Eulerian photochemical model, *Environ. Sci. Technol.*, 22, 263–270, 1988.

Seila, R. L., W. Lonneman, and S. Meeks, *Determination of C_2 to C_{12} ambient air hydrocarbons in 39 U.S. cities, from 1984 through 1986*, Rep. EPA/600/S3-89/058, U.S. Environ. Prot. Agency, Washington, D. C., 1989.

Seiler, W., and J. Fishman, The distribution of carbon monoxide and ozone in the free troposhpere, *J. Geophys. Res.*, 86, 7255–7265, 1981.

Seinfeld, J. E., Urban air pollution; state of the science, *Science*, 243, 745–748, 1989.

Sexton, K., and H. Westberg, Nonmethane hydrocarbon composition of urban and rural atmospheres, *Atmos. Environ.*, 18, 1125–1132, 1984.

Singh, H. B., and P. L. Hanst, Peroxyacetyl nitrate (PAN) in the unpolluted atmosphere: An important reservoir for nitrogen oxides, *Geophys. Res. Lett.*, 8, 941–944, 1981.

Singh, H. B., and P. Zimmerman, Atmospheric distribution and sources of non-methane hydrocarbons, in *Gaseous Pollutants: Characterization and Cycling*, edited by J. O. Nriagu, pp. 177–235, John Wiley, New York, 1992.

Singh, H. B., W. Viezee, and L. J. Salas, Measurements of selected C_2-C_3 hydrocarbons in the troposphere: Latitudinal, vertical, and temporal variations, *J. Geophys. Res.*, 93, 15,861–15,878, 1988.

TUV, Air pollution control in the Mexico City metropolitan area: Emissions inventory for mobile sources, TUV Rheinland, Cologne, Germany, 1992.

United Nations, *Urban Air Pollution in Megacities of the World*, Blackwell, Cambridge, Mass., 1992.

Vega, E., D. Romero, M. Barbiaux, I. Garcia, and M. E. Ruiz, *Problematica de las particulas suspendidas en la atmosfera de la Ciudad de Mexico*, Tech. Rep. IMP/GCA-9505, Inst. Mex. del Petreleo, Mexico D. F., 1995.

Warneck, P., *Chemistry of the Natural Atmosphere*, Academic, San Diego, Calif., 1988.

Williams, M. D., M. J. Brown, X. Cruz, G. Sosa, and G. Streit, Development and testing of meteorology and air dispersion models for Mexico City, *Atmos. Environ.*, 29, 2929–2960, 1995.

Yamada, T., Numerical simulation of the night 2 data of the 1980 ASCOT experiments in the California geysers area, *Arch. Meteorol. Geophys. Bioclimatol.*, 34, Ser. A, 223–247, 1985.

Yamada, T., and S. Bunker, Development of a nested grid, second moment turbulence closure model and application to the 1982 ASCOT Brush Creek data simulation, *J. Appl. Meteorol.*, 27, 562–578, 1988.

D. R. Blake and F. S. Rowland, Chemistry Department, University of California, Irvine, CA 92715.

J. E. Bossert, W. E. Eichinger, S. Elliott (corresponding author), C.-Y. J. Kao, and W. M. Porch, Earth and Environmental Science Division, Geoanalysis Group, Los Alamos National Laboratory, Los Alamos, NM 87545. (e-mail: selliott@kokopelli.lanl.gov)

M. J. Brown, G. E. Streit, and M. D. Williams, Technology and Safety Assessment Division, Energy and Environmental Analysis Group, Los Alamos National Laboratory, Los Alamos, NM 87545.

F. Guzman and M. Ruiz Santoyo, Instituto Mexicano del Petroleo, Gerencia de Ciencias del Ambiente, Eje Central Lazaro Cardenas no. 152, 07730 Mexico D. F.

J. Keyantash, R. Lu, and R. P. Turco, Atmospheric Sciences Department, University of California, Los Angeles, CA 90024.

L. A. McNair and A. G. Russell, Department of Mechanical Engineering, Carnegie Mellon University, Pittsburgh, PA 15217.