



Trace-gas mixing in isolated urban boundary layers: Results from the 2001 Phoenix sunrise experiment

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Abstract

Measurements made from surface sites, from the 50 and 140 m levels (the 16th and 39th floors) of a skyscraper, and from an instrumented aircraft are used to characterize early morning profiles of CO, NO_y, and O₃ within the mid-morning summertime convective atmospheric boundary layer (CABL) over Phoenix, Arizona. Although mixing was anticipated to produce uniform values of these species throughout the CABL, this was found not to be the case. Background air advected into the upper levels of the boundary layer and entrained air from above appear to be the most likely cause for the lack of well-mixed trace gases. The results show that surface measurements may provide only limited information on concentrations of trace-gas species higher in the boundary layer.

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1. Introduction

Luke et al. (1998) reported results of a study to address the spatial and temporal representativeness of surface point measurements of trace gas concentrations. Their observations, made during overflights of surface air quality monitoring stations during the 1995 Southern Oxidants Study (SOS) in and around Nashville, Tennessee, found generally good agreement between surface and aircraft measurements under clear skies in the well-devel-

oped boundary layer. During periods when surface concentrations were changing rapidly and the boundary layer was evolving rapidly, the agreement was much poorer, a result that Luke et al. attributed to decoupling of the air aloft from the surface. Raga and Raga (2000) showed elevated peaks of ozone and particle concentrations in a thermodynamically well-mixed boundary layer over Mexico City.

Apart from these studies, direct observations of changes in the mixing ratio of key trace gases over the full depth of growing convective atmospheric boundary layers (CABLs) have been scarce. The extent to which reactive trace gases can be characterized as well mixed in the CABL is of considerable importance to modeling and the

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interpretation of observations made by air quality surface networks used for model evaluation. For these reasons, and for reasons of basic scientific interest, characterizing the behavior of chemical species within actively growing boundary layers is important for atmospheric chemists.

An earlier study in the Phoenix area, carried out during May and June of 1998 (Nunnermacker et al., 2004), using surface and airborne measurements was designed to study ozone formation in an urban plume at various points in its evolution during mid-morning through mid-afternoon. In contrast to the 1998 study, the 2001 “Phoenix Sunrise” campaign was designed to characterize the local nighttime accumulation of O₃ precursors, study their subsequent interactions the next morning as the nocturnal boundary layer began to break up, and examine the role of vertical mixing on the chemistry of the boundary layer during the morning hours. Doran et al. (2003) have presented a summary of meteorological observations from radar wind profilers, sodars, and radiosondes, and of chemistry observations made at the surface and from two levels of a building in downtown Phoenix during the 2001 campaign. They noted that the observations generally support a picture in which O₃ precursors trapped near the surface during the night are dispersed after sunrise, with subsequent vertical mixing determining the O₃ profiles in the first few hours after sunrise. However, this picture was found to be incomplete when, on several occasions, significant vertical mixing occurred over downtown Phoenix prior to sunrise and the associated heating of the surface layer (Shaw et al., 2005).

In this paper we present some features of vertical mixing of trace gases over Phoenix using a combination of observations to construct profiles of CO, NO_y, and O₃ from the surface to the top of and above the growing CABLs. We show that a thermodynamically well-mixed boundary layer, characterized by a nearly constant value of potential temperature with height, does not necessarily imply that profiles of trace gases, including slowly reacting species such as CO, will be well mixed. Although this behavior is well known to boundary-layer meteorologists for quantities such as water vapor mixing ratio, it appears not to be so widely recognized in the atmospheric chemistry community where the concept of “mixing depth” has been used to define the height to which the atmosphere is uniformly mixed (e.g., Finlayson-Pitts and Pitts, 2000).

2. Sampling strategy and overview of data collection

2.1. Observations from the Bank One building and DOE Gulfstream aircraft

Our analysis of mixing uses observations from the US Department of Energy’s Gulfstream I (G-1) aircraft, which made an extensive series of transects at various heights within and above the CABL; observations from two sites on the Bank One building in downtown Phoenix; and surface observations from the Arizona Department of Environmental Quality (ADEQ) monitoring network.

Observations were made from the 50 and 140 m levels (the 16th and 39th floors, respectively) of the Bank One building in downtown Phoenix (33.45N, –112.07E) between 16 and 30 June 2001. The observations made from the two levels of the Bank One building included O₃ (ultraviolet photometry), NO_y (chemiluminescence), and CO (non-dispersive infrared (NDIR) absorption). For the Bank One measurements, air was sampled through probes placed ~2 m outside the building through specially designed window ports. The NO_y monitors were modified by removing the catalytic converters from the instrument cases and adding wiring and plumbing extensions. The converters were positioned outside the building at the end of ~2 m extenders designed for this purpose. In this configuration, NO_y constituents are sampled directly into the converter, minimizing line loss of adsorptive NO_y constituents such as HNO₃. All data from the Bank One building sites were reported as 2-min averages. The ADEQ surface values of O₃ and CO were measured using UV and NDIR absorption, respectively. Details of the ADEQ instruments are available in Chapter 2 of ADEQ (2001). A summary of the instrumentation onboard the aircraft is given in Table 1.

Each research flight had the general flight plan illustrated in Fig. 1. The G-1 aircraft would depart from its base of operations, Williams Gateway Airport, at 0700 LST and enter the greater Phoenix area from the east side. To characterize the conditions just outside the central urban area the G-1 would first fly a single altitude lap at ~850 m above mean sea level (m MSL) along the path A–B–C–D–E–A–B, with a vertical profile done over the Scottsdale region northeast of downtown Phoenix between Points B and C. This was followed by a series of smaller laps around Points B–C–D changing between a low (~700 m MSL/~350 m

Table 1
Key trace-gas observations made from the aircraft and used in the analysis

Variable	Technique	Instrument	Precision
CO	NDIR absorption	Brookhaven National Laboratory (BNL) System	10–20 ppbV
Ozone	Ultraviolet absorption	Thermo-Environmental Instruments Model 49-100	1–2 ppbV
NO _y	Inletless-heated MO converter	BNL System	<100 pptV

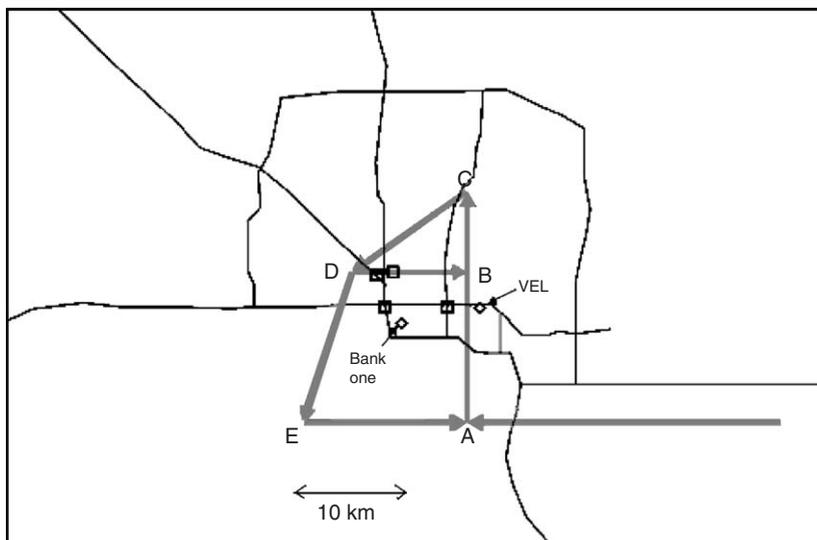


Fig. 1. Flight plan of the Gulfstream I aircraft over Phoenix (gray arrows), with key background features. The letters A–E that mark the vertices of the intersecting gray arrows are used as reference points for the flight patterns described in the text. The black lines are major highways in the area. The locations of the four ADEQ ozone monitoring sites used in this study (squares), the Vehicle Emissions Laboratory (VEL), and the Bank One building are also shown. Williams Gateway Airport is located off the map to the right.

above ground level (AGL)), medium (~ 850 m MSL/ ~ 500 m AGL) or high (~ 1000 m MSL/ ~ 650 m AGL) altitude at the beginning of each lap. Changes in altitude along B–C–D were made in the vicinity of Point B, and this B–C–D pattern was repeated until approximately 10:15 AM, when the G-1 started its return along the path D–E–A and east to Williams Gateway Airport. We matched each G-1 transect with the set of observations made at the corresponding times from the ADEQ ground sites and the two Bank One sites (see below).

The low, medium and high altitude sampling strategy over the path B–C–D in Fig. 1 was developed from a simple conceptual model. It was anticipated that the top of the CABL would initially be at an altitude lower than that at which the G-1 could sample. At some later time, depending on the growth rate of the boundary layer, the G-1 would begin to successively sample slightly above the CABL, in the entrainment zone, and eventually

within the CABL. Combining aircraft measurements at three altitudes with observations from the 50 and 140 m levels of the Bank One building would let us construct profiles of trace gases within the developing boundary layer as the boundary layer grew to encompass the various measurement levels of the Bank One building and the aircraft.

2.2. Evaluation of mixing layer depths

We determined the depth of the convective boundary layer from wind profiler data using the method described by Angevine et al. (1994). This method makes use of the relation between the mean structure of the boundary layer and its scattering properties for electromagnetic radiation. The strength of the signal returned to the radar (backscatter) for a given transmitted power is determined by the intensity of small-scale variations of refractive index in the air, usually expressed as the

refractive index structure parameter C_n^2 . This is directly related to temperature and water vapor fluctuations which, for convective conditions, are most intense at the surface and in the inversion that caps the convective boundary layer. Because the signal-to-noise ratio (SNR), which is a measure of the return signal strength to internal system noise, is routinely recorded by wind profilers, it provides a convenient method for determining boundary layer depth. Our approach was to plot time–height cross-sections of the range-corrected SNR for a day of interest and then use digitizing software to manually select the height of maximum SNR as a function of time. This is the practical approach used by Angevine as well (pers. comm.). Selected estimates of boundary layer depths derived from the profiler measurements were found to compare very well with independent measures of boundary layer depths obtained from radiosondes launched from same location as the radar wind profiler.

Our analysis of the G-1 observations will focus only on those periods when the G-1 was between points D and B in Fig. 1. There are three reasons for this focus. First, this region is the leg closest to the Bank One building. As a result, combining measurements made by the aircraft over this segment of the flight path with measurements made from the Bank One building results in a profile that is more representative of a column of air than would be the case if the combined observations were farther apart. Second, this section of the flight path is over relatively uniform terrain. The mean elevation between points D and B is 359m MSL, with minimum and maximum elevations of 344 and 382m MSL, respectively. Because of the relatively small variation in the elevation, our (approximately) constant MSL altitude flight tracks were also (approximately) constant AGL altitude paths, making the measurements easier to compare with radiosonde and profiler observations. Finally, as a result of the relatively uniform terrain along this leg of the flight path, mixing layer heights evaluated from the profiler at the Vehicle Emissions Laboratory are likely to be representative of the mixing layer heights along the path D–B, and we assume this is true in our analysis.

While the surface observations from the ADEQ network and, frequently, the observations from the Bank One building were within the growing convective boundary layer by 0730 LST, the highest sampling altitude of the G-1 was usually not in the boundary layer until ~0830 or 0900 LST. The total

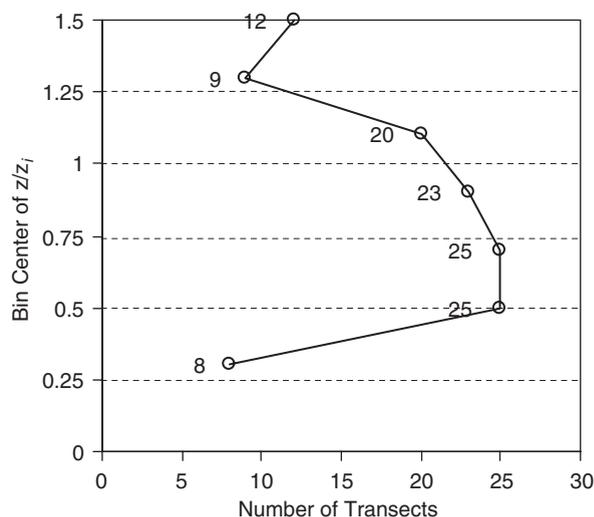


Fig. 2. Profile of the number of G-1 transects made along the path D–B (Fig. 1) as a function of intervals of z/z_i , where z is height above ground and z_i is the height of the top of the boundary layer at the time of the transect.

number of aircraft transects within the CABL was thus a function of the height of the boundary layer at the time of each sampling interval. As a result, different levels of the CABL had different sample sizes (Fig. 2).

3. Results

3.1. Processing

We have analyzed the vertical profiles of CO , NO_y and O_3 in terms of the fractional depth of the mixing layer, z/z_i , where z is the altitude above ground at the time at which the observations were made and z_i is the height of the boundary layer at the same time. For example, measurements reported at altitudes of $z/z_i = 0.5$ correspond to the middle of the developing boundary layer, regardless of the time of day or the actual depth of the CABL. For profile display purposes, measurements were binned into the z/z_i intervals given in Table 2. Also shown in Table 2 is the percentage contribution to the total observations within each z/z_i bin made from each measurement location. The surface ADEQ sites provided all observations for $z/z_i = 0.0$, the 16th floor of the Bank One building provided most of the observations for $0.01 \leq z/z_i \leq 0.2$ and the 39th floor provided most of the observations for $0.2 \leq z/z_i \leq 0.6$. The G-1 was the sole source of observations for $z/z_i > 0.8$.

Table 2

Height bins, z/z_i , where z is height above ground and z_i is the height of the mixed layer, used to summarize observations and the percent contribution to each bin from the indicated measurement platform

Height range	Plotted at $z/z_i =$	ADEQ/surface (%)	16th floor (%)	39th floor (%)	G-1 (%)
$1.4 < z/z_i \leq 1.6$	1.5	0	0	0	100
$1.2 < z/z_i \leq 1.4$	1.3	0	0	0	100
$1.0 < z/z_i \leq 1.2$	1.1	0	0	0	100
$0.8 < z/z_i \leq 1.0$	0.9	0	0	0	100
$0.6 < z/z_i \leq 0.8$	0.7	0	0	12	88
$0.4 < z/z_i \leq 0.6$	0.5	0	0	64	36
$0.2 < z/z_i \leq 0.4$	0.3	0	8	81	11
$0.01 < z/z_i \leq 0.2$	0.1	0	77	23	0
$0.0 < z/z_i \leq 0.01$	0	100	0	0	0

Platforms making the greatest contribution to each height range are shown in bold font.

Because we were interested in the relative magnitudes of mixing ratios at various heights in the boundary layer rather than their actual magnitudes, we have also normalized all G-1 mixing ratios by the corresponding median values found at the 16th floor of the Bank One building for each time interval during which the G-1 was sampling along the path D–B. For example, if the G-1 was at point D at time t_D and at point B at t_B , then the median of the observations taken at the 16th floor between t_D and t_B was the normalization value. The result of this normalization is to remove day-to-day variations associated with very high or very low concentrations. We chose to normalize by values at the 16th floor rather than at the surface for several reasons. First, because surface stations are more likely to be strongly influenced by proximity to local sources, they can show a very high degree of station-to-station variability, and this was found to be true in the data records from the ADEQ network (not shown). Second, surface stations can often lie within or close to the roughness sublayer of the urban environment in which they are located, and applications of boundary layer scaling in such circumstances is not appropriate. Finally, while CO and O₃ values are available from the ADEQ network, NO_y values are not.

The data from the various platforms were collected with a variety of sampling and reporting intervals. Most of the G-1 data were sampled at a rate of 1 s^{-1} , the Bank One building measurements were averaged over 2-min intervals, and the ADEQ values are averages reported once per hour. To avoid normalizing the G-1 or ADEQ data with a rapidly varying quantity, the Bank One data were additionally processed with a symmetric first-order recursive low-pass filter. Each data series x_n at the

Bank One Building was first filtered in the forward direction using $y_n = (1 - a)x_n + ay_{n-1}$. Here, $a = \exp(-\Delta t/\tau)$, Δt is the time interval between successive data values x_n , and τ was set to 600 s (Bendat and Piersol, 1971). Working in reverse, a second series was defined by $y_{n-1} = (1 - a)x_{n-1} + ay_n$, and the two series were then averaged to produce the low-pass data series used for further analysis.

While the G-1 trace gas data were normalized by the median of the filtered Bank One values interpolated to the median time of each D–B flight segment as described earlier, the hourly ADEQ values were normalized by the low-pass 16th floor Bank One building values interpolated to the hourly reporting interval for the ADEQ network. The normalized profiles of G-1 data presented in the next section were then derived from the many individual, normalized measurements made within the vertical layers listed in Table 2 for all CO, NO_y, or O₃ observations made when the G-1 was sampling between points D and B (Fig. 1). The sample size for each layer thus ranges from several hundred to several thousand individual measurements.

3.2. Vertical profiles

Fig. 3 shows the normalized profile of carbon monoxide. CO is a relatively long-lived chemical species in urban areas that is a common byproduct in automotive exhaust. It is a good tracer of urban air because it has an atmospheric lifetime of many days. Several features are readily apparent from this profile. First, the surface values (from the four ADEQ surface stations) are considerably greater than the values reported at the 16th floor of the Bank One building, indicating a pronounced

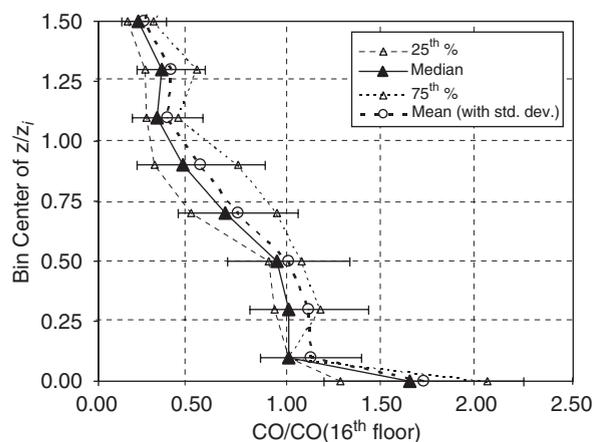


Fig. 3. Profiles of CO normalized by the corresponding measurement of CO made at the 16th floor of the Bank One building. Each point in this figure was derived from observations made within bins of z/z_i (Table 2), with bin centers indicated on the vertical axis. These values include concurrent measurements made from the surface ADEQ sites identified in Fig. 1, the Bank One 16th and 39th floors, and the G-1 measurements between points D and B. Also shown are the 25th and 75th percentile values of each bin and the corresponding median and mean values (with standard deviations shown by horizontal bars).

vertical gradient below $z/z_i \approx 0.1$ that probably reflects the influence of strong local surface sources of CO. Second, for $0.1 \leq z/z_i \leq 0.5$, the CO mixing ratios were relatively constant with values very close to those measured at the 16th floor of the Bank One building. Finally, from $z/z_i > 0.5$ to the top of the CABL, at $z/z_i = 1$, CO decreased nearly linearly toward values measured above the CABL, which in turn averaged about a third of the values measured at the 16th floor (40 m AGL). It is clear that the CO profile was well mixed only through the lower half of the CABL.

The corresponding profile for NO_y is presented in Fig. 4. NO_y is a lumped quantity defined as the sum of all nitrogen compounds in an oxidation state of +2 or greater: $\text{NO}_y \equiv \text{NO} + \text{NO}_2 + \text{PAN} + \text{HNO}_3 + \text{NO}_3^-$ (particles) + $2\text{N}_2\text{O}_5$ + other reactive N compounds (Finlayson-Pitts and Pitts, 2000). Because many of the component species oxidize to one another, it, like CO, is a relatively well conserved compound over a few hours. NO_y was not measured at the surface ADEQ sites, so no values were available at $z/z_i = 0$. As a result, we can make no statement about near-surface gradients of NO_y .

For $0.01 \leq z/z_i \leq 0.5$, NO_y was also found to be relatively uniform, having values close to those measured at the 16th floor of the Bank One building. For $z/z_i > 0.5$, this species was found to

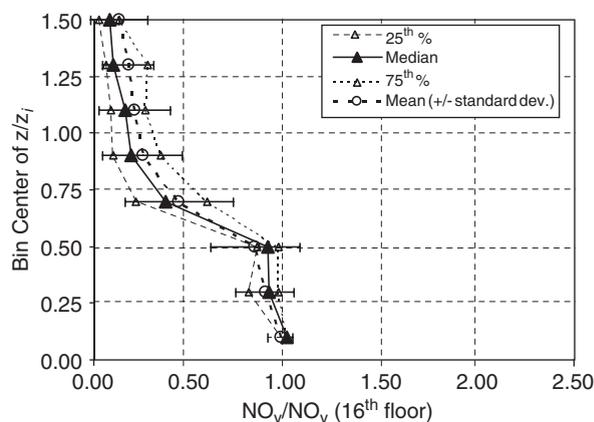


Fig. 4. As in Fig. 3, for NO_y normalized by values measured at the 16th floor of the Bank One building. No surface observations were available for NO_y .

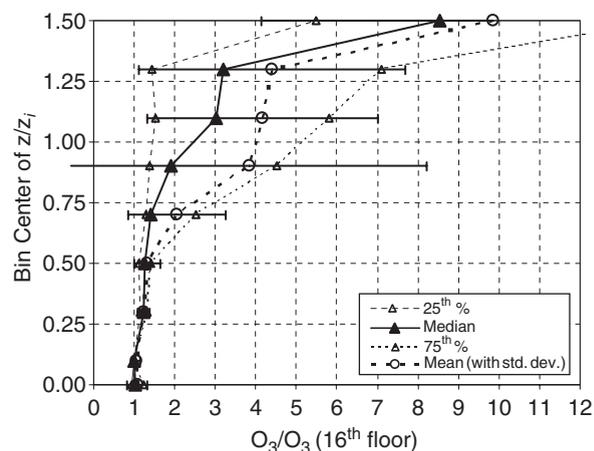


Fig. 5. As in Fig. 4, for O_3 normalized by values measured at the 16th floor of the Bank One building.

decrease, converging to values measured above the CABL. The values of NO_y above the boundary layer are roughly 10% of those within it. Like CO, this profile is also well mixed through only the lower half of the CABL.

Fig. 5 shows the composite profile of normalized O_3 . O_3 is the most reactive trace gas to be considered. It is formed through a complex series of photochemical reactions involving hydrocarbons and $\text{NO}_x (= \text{NO} + \text{NO}_2)$ and destroyed at night via the $\text{O}_3 + \text{NO}$ reaction and via deposition to the ground and other surfaces. O_3 shows a relatively uniform value for $z/z_i \leq 0.5$. Unlike CO, there is little indication of a surface gradient of O_3 . Also in contrast to CO and NO_y , O_3 values were largest above the CABL. Consistent with these much larger

ozone levels aloft, O_3 increased with height for $z/z_i > 0.5$. Values for $z/z_i > 1$ were several times greater than those measured at the 16th floor. It is again evident that this profile is well mixed only for $z/z_i < 0.6$.

4. Discussion and summary

Deardorff (1980) explained how feedback mechanisms tend to keep the vertical gradient in potential temperature, $\partial\theta/\partial z$, small in the mixed layer. A significant positive θ gradient (e.g. $> 1 \text{ K km}^{-1}$) would keep convective elements from moving very far upward from the surface because of the negatively buoyant restoring force. Conversely, a negative gradient would result in enhanced mixing that in turn would bring potentially warmer air from aloft downward, stably stratifying the air and stopping the convection. However, he notes that “No such direct feedback mechanism exists for the other mean properties...” such as water vapor mixing ratio, and similar considerations apply to trace gases. There are a number of mechanisms that can result in non-zero vertical gradients of these quantities. One such mechanism is differential horizontal advection, which can occur when wind speeds or directions aloft differ significantly from those near the surface. Stronger winds in the upper boundary layer can bring in air from more distant and relatively pristine areas surrounding Phoenix, compared to weaker winds near the surface that would bring in air from within the Greater Phoenix metropolitan area. Another mechanism is entrainment, in which relatively clean air from above the CABL can be mixed downward across the interface between the CABL and the free atmosphere, producing the entrainment zone previously noted. Both of these mechanisms would tend to produce the results shown in Figs. 3–5.

Entrainment of clean air from above and differential horizontal advection would not be expected to play a major role in cities such as Nashville or Atlanta. Air coming into those areas is typically heavily burdened with elevated values of CO , NO_y , and other pollutants (Chameides and Cowling, 1995). In contrast, Phoenix is relatively isolated from outside sources of pollution so that incoming air should be relatively pollution-free most of the time. Of course this need not always be the case given the presence of power plants to the north and agricultural burning to the south. Nonetheless, clean background air was, in fact, regularly

measured by the G-1 during its initial flight over path A–B–C–D–E–A–B and its initial sounding over Scottsdale. Raga and Raga (2000) attribute elevated peaks of O_3 in the thermodynamically well-mixed boundary layer over Mexico City to an interplay between aerosol particles, solar radiation, and photochemistry rather than advection. While their explanation is less likely for Phoenix (where no similar correlation was observed between aerosols and O_3), the lack of well-mixed ozone profiles in otherwise thermodynamically well mixed boundary layers is similar to what was observed in our study.

Another possibility is discussed by Wyngaard (1984), who presented modeling results showing that a sharp peak in surface emissions of a conservative scalar quantity like CO , such as might be associated with morning rush hour traffic, could result in significant vertical gradients of this species during the period of peak emissions. This also seems unlikely to be a significant mechanism in our observations because the vertical gradients over Phoenix persist for some time after both the morning rush hour and the breakup of the inversion that tends to trap CO near the surface in the morning. It is possible that during the early-to-mid-morning hours the CABL was growing too rapidly to allow thorough mixing over its full vertical extent. Simple scaling arguments suggest that characteristic times required for vertical mixing could be comparable to the times over which the boundary layer depth changes significantly. However, we found no consistent differences in the shapes of profiles constructed from data on days with slow-growing CABLS compared to days with faster growing CABLS.

Finally, we have also considered the possibility that the vertically non-uniform mixing ratios of the trace gas species might be caused by some chemical mechanism. This also seems unlikely because photochemical activity associated with the $VOC/NO_x/O_3$ cycles was negligible during the sampling period of the aircraft. Evidence for this was found in a scatter plot (not shown) of O_3 mixing ratios as a function of NO_y during the post-dawn to mid-morning aircraft sampling period. Such scatter plots made during periods of photochemical activity show a strong positive linear correlation (see, for example, Zaveri et al., 2003 and references therein), and have been interpreted as a measure of the efficiency by which O_3 is produced from its VOC and NO_x precursors. No such correlation was found

in our data. Moreover, a long-lived chemical species such as CO should not be significantly affected by chemical processes over the sampling periods relevant here.

We do not have sufficient information to definitively identify which of these various mechanisms is responsible for the lack of well-mixed profiles of CO, O₃, and NO_y over the Phoenix area. The evidence suggests that the most likely contributing causes are a combination of differential advection and entrainment of background air into the upper portions of the boundary layer. Thus, in the Phoenix region and possibly in other relatively isolated urban areas, surface measurements may provide only limited information on the concentrations of trace gases that can be expected higher in the boundary layer. Appropriate caution should therefore be exercised in using surface information to estimate values higher in the CABL.

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