BNL-71889-2003-JA

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AE International – North America

Atmospheric Environment 38 (2004) 4941–4956

ATMOSPHERIC ENVIRONMENT

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Ground-based and aircraft measurements of trace gases in Phoenix, Arizona (1998)☆

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Received 25 November 2003; accepted 28 April 2004

Abstract

In May and June of 1998, an extensive measurement campaign was fielded in the city of Phoenix and its environs. Measurements were made at ground sites and aboard the Department of Energy's G-1 research aircraft in an effort to understand the production of O_3 in this area. Diurnal variations in O_3 differed at the upwind Palo Verde, downtown Phoenix Super Site, and downwind Usery Pass surface stations. Air masses entering the metropolitan area had O_3 concentrations greater than 40 ppbv. Maximum O_3 concentrations near 100 ppbv were observed downtown at 14:00 local standard time; similar concentrations occurred much later in the day at the downwind site. One aircraft case study on 5 June, 1998 is presented to illustrate ozone production in the region. Calculated ozone production rate and efficiency varied from 1 to 7 ppbv h^{-1}, and 1–3 molecules of O_3 per molecule of NO_z, respectively, for this flight. Hydrocarbon apportionment, based upon ground site and aircraft measurements, establishes that biogenic species are not significant contributors to O_3 production in the Phoenix area. Therefore, carbon monoxide becomes a major contributor to OH reactivity as the more reactive anthropogenic hydrocarbons become depleted. The relatively low ozone production observed in this study is attributed to a low rate of radical production in the dry atmosphere.
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Keywords: Ozone; Ozone production efficiency; Biogenic hydrocarbons; Isoprene; Carbon monoxide; Nitrogen oxides

1. Introduction

The US Department of Energy Atmospheric Chemistry Program (DOE/ACP) and the Arizona Department of Environmental Quality (ADEQ) conducted a field program to investigate tropospheric ozone formation in the Phoenix, Arizona metropolitan area 15 May–15 June, 1998. The motivation was to extend the findings of the many studies that have focused on understanding O_3 production in the northeastern and southeastern regions of the United States (Solomon et al., 2000 and references therein). We anticipated that ozone formation rates and efficiencies in the Phoenix area would differ significantly from those observed in the eastern United States for a number of reasons. The mix of pollutants in the region is dominated by on- and off-road vehicle emissions; industrial and other point sources contribute less than in the eastern and southeastern United States (Table 1) (Maricopa Ozone Emissions Inventory, 1999). In fact, there are no coal-fired power plants in the Phoenix metropolitan area. Sparse vegetation cover in the southwest results in low emissions of biogenic

☆This research was performed under the auspices of the United States Department of Energy under Contract No. DE-AC02-98CH10886.

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doi:10.1016/j.atmosenv.2004.04.033

Table 1
Ozone season daily emissions for 1999[a]

Emissions	Sources				
	Biogenic	Point[b]	Area[c]	Onroad mobile	Nonroad mobile
VOC	49 tons day^{-1}, 14.5%	22 tons day^{-1}, 6.5%	91 tons day^{-1}, 27%	90 tons day^{-1}, 27 %	85 tons day^{-1} 25%
NO_x	10 tons day^{-1}, 4%	21 tons day^{-1}, 7%	23 tons day^{-1}, 8%	92 tons day^{-1}, 31%	147 tons day^{-1}, 50%
CO	None	7 tons day^{-1}, <1%	46 tons day^{-1}, 4%	634 tons day^{-1}, 51%	568 tons day^{-1}, 45%

[a] *Note*: Unless demographics changed dramatically during the course of the year it is expected that the 1999 emissions inventory would be identical to that of 1998.
[b] *Point*: Sources emitting 100 tons or more of VOC, NO_x or CO, and are located within 25 miles of the non-attainment area.
[c] *Area*: Stationary source in the non-attainment area that are too small to be defined as point sources but too numerous not to be counted.

hydrocarbons, which in other locations can contribute significantly to ozone formation (Chameides et al., 1988). In addition to these different emission profiles, complex terrain in the Phoenix urban area causes air flow reversals, and the contribution of these complex flows to multi-day episodes is unknown (Ellis et al., 2000). Another interesting feature, is the isolation of the Phoenix metropolitan area from other urban areas. Unlike the East Coast, this limits the amount of O_3 precursors available due to transport from other nearby cities that can contribute to production (Kleinman et al., 2000). Finally, the low humidity, high solar intensity and large boundary layer height characteristic of the region create processing conditions that are markedly different than those in the Eastern US. This study explores the composite effect of these differences on ozone production in the southwest.

The Phoenix study included a linked set of aircraft and surface measurements designed to characterize the chemical and meteorological processes leading to ozone episodes. ADEQ's network of surface monitoring sites was augmented by additional sites and enhanced monitoring capabilities for the duration of the study. Wind profilers were deployed to characterize the atmospheric structure in the region. The DOE G-1 research aircraft, equipped with a comprehensive array of instruments to determine atmospheric trace gas and aerosol composition, flew over the region to evaluate the vertical and horizontal distribution of these species. Flight plans were designed to sample the boundary layer in three different domains: upwind, source region and processed air downwind of the city.

This paper provides an overview of the field study, along with a summary of trace gas observations from the aircraft and diurnal trends at the surface. The vertical and geographical distribution of chemical species for aircraft flights are described and interpreted in the context of ozone formation. The reader is directed to related publications for additional details of the boundary layer meteorology (Fast et al., 2000; Doran et al., 2003), ozone production efficiency (Kleinman et al., 2002a) and photochemical age (Kleinman et al., 2003).

2. Experimental

2.1. Meteorological conditions

Meteorological conditions during the Phoenix 1998 field study have been summarized by Fast et al. (2000). The synoptic pattern was generally the same each day, with high altitude winds (>2 km MSL) from the WSW all day. Drainage winds from mountains north and east of the city caused surface winds to veer from east to west on most days. High temperatures and low water vapor content resulted in mid-afternoon mixed layer heights reaching 2.5–3 km, significantly higher than the 1.0–1.6 km measured in Nashville in July, 1995 (Nunnermacker et al., 1998).

2.2. Surface measurements

The Arizona Department of Environmental Quality (ADEQ, 1998) maintained a network of forty-two surface monitoring sites with different measurement capabilities during the study (Fig. 1). Twenty five of these sites housed ozone monitors, and some included basic meteorological measurements, i.e. temperature, wind speed, wind direction and relative humidity. Five special sites were outfitted with additional instrumentation to measure concentrations of O_3, CO, NO_y and SO_2. Three additional highly instrumented supersites also included measurement capabilities for volatile organic compounds (VOCs) and carbonyls; these are identified in Table 2 as Palo Verde (PV), downtown Phoenix Supersite (PXSS), and Usery Pass (USY).

Measurements were made according to standard EPA protocol with commercial TEI analyzers (Thermo Environmental Instruments Inc., Franklin, MA). Data from the TEI analyzers were acquired continuously at

all ground locations for 24 h d^{-1} during the entire study (15 May–12 June). Carbon monoxide was determined using a non-dispersive infrared gas filter correlation technique with a detection limit of 40 parts per billion by volume (ppbv) using a 5 min integration time. Ozone was determined with UV absorption, and SO_2 with pulsed fluorescence. NO was measured at surface sites using ozone chemiluminescence. In addition, NO_x measurements were made using an internal catalytic molybdenum (Mo) converter. Thus, the NO_x concentration measured at the ground sites is actually NO_y or some smaller fraction due to inlet line losses. At the super site (PXSS) this would be of minimal consequence since most of the emissions are NO and NO_2. However, at the other sites (PV and USY) the losses may be more significant. Detectors were spanned weekly and are audited on a quarterly basis for ADEQ. All samples inlets at the ground sites were located within the range of 0–10 m.

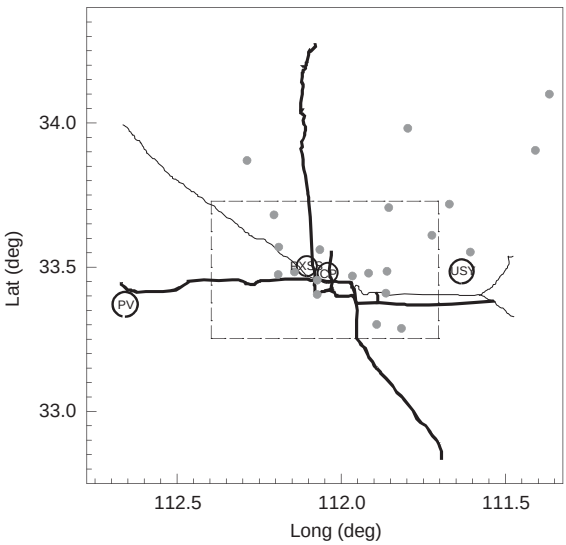

Fig. 1. Sampling area, showing city limits, location of surface sites and major roadways. Dashed line shows the high emission metropolitan area.

Modified VOC samplers (Model 910A, XonTech) with 6l stainless steel SUMMA type canisters were operated by ADEQ. Samples were cryogenically preconcentrated in a freeze-out loop and then analyzed using high resolution capillary gas chromatography with flame ionization or electron capture detection. VOC samples were taken three times per day (07:00, 11:00, 15:00 LST) for a period of 2 h.

Carbonyl compounds were measured at the supersites (see Table 2) using C18 Sep Pak cartridges treated with dinitrophenylhydrazine (DNPH) and phosphoric acid. High-pressure liquid chromatography with UV detection was used to determine the carbonyl compounds. Cartridges were collected for a 2 h period three times per day (as described for the VOC samples; except at Palo Verde (PV)—only once per day).

Hydrogen peroxide and total hydroperoxides were determined at USY using a continuous analyzer employing aqueous coil scrubbers for sample collection, followed by conversion to fluorescent products (Lee et al., 1990, 1994). Measurements were reported as hourly averages.

2.3. Aircraft measurements

2.3.1. Instrumentation

The DOE Grumman G-1 aircraft was equipped with an array of instrumentation to measure trace gases and meteorological parameters. Both research-grade and commercial instruments were deployed; some of the latter were modified to enhance sensitivity and/or improve response time. Table 3 summarizes the measurement capabilities for the Phoenix study. Detailed information about the instruments can be found in earlier publications (Hubler et al., 1998; Williams et al., 1998; Nunnermacker et al., 1998). With the exception of peroxides and carbonyls, trace gas data were acquired with 1 s resolution; 10 s averages of the data were used

Table 2
Intensive sites for the Phoenix study (1998)

Site	Latitude	Longitude	Elevation (ft) MSL[a]	Measurements	Purpose
PV	33° 20′	112° 50′	870	VOC, NO_y, O_3, carbonyls and surface meteorology	Background organic compounds
PXSS	33° 30′	112° 05′	1115	VOC, NO_y, O_3, CO, carbonyls and surface meteorology	Precursor concentrations in the source region
USY	33° 30′	111° 38′	2500	VOC, NO_x, NO_y, O_3, CO, PAN, peroxides, carbonyls and surface meteorology	Downwind (i.e. processed air O_3 precursors and oxidation products)

[a] Mean sea level.

Table 3
G-1 instrumentation

Species detected	Technique	Detection limits	Time response
NO	O_3 chemiluminescence	<10 pptv	1 s
NO_2	Same as NO with photolytic conversion	<50 pptv	4 s
NO_y	Same as NO with molybdenum converter at 350°C	<50 pptv	1 s
CO	Modified NDIR gas filter correlation[a]	~10 ppbv	1 min
O_3	UV absorption	2 ppbv	30 s
Aldehydes	HPLC/DNPH derivatization	10–20 pptv	3 min
H_2O_2, HMHP, MHP	PHOPAA/Fenton chemistry	60 pptv	1 min
Hydrocarbons	Canister collection/GC analysis	10–100 pptv	Post-flight analysis

[a] Dickerson et al. (1982).

for this analysis. The response time for peroxides was 1 min (Weinstein-Lloyd et al., 1998). Continuous 3-min average concentrations were reported for carbonyls (Lee et al., 1998).

2.3.2. Flight descriptions

The four-week program consisted of 23 flights in 15 days, including 8 days with both morning and afternoon flights (Table 4). Morning flights, $22\frac{1}{2}$ h in duration, were conducted between 08:00 and 12:00 LST. Fig. 2a shows the typical morning flight pattern: an upwind leg, west of Phoenix, to measure background conditions, a triangular pattern over the city to characterize initial conditions and source emissions, and vertical profiles to 3 km both upwind and over the city. Afternoon flights retraced part of the morning leg over the downtown area, and probed a region further east to sample the processed urban plume. Highest emissions were observed in the metropolitan area, indicated by the dotted lines in Fig. 2. Afternoon flights, conducted between 14:30 and 18:00, also included a vertical profile approximately 40 km east of downtown (Fig. 2b). The only exceptions were the 27th May morning flight, which included an extended upwind leg to sample background air, and the 6th June afternoon flight, which included an extended downwind leg.

Table 4
Flight summary

1998 Date	Flight pattern[a]	Start time–end time[b]
18 May	a	07:20–09:16
18 May	p	13:46–15:44
21 May	a	08:11–11:34
21 May	p	14:34–17:01
22 May	a	08:03–10:50
22 May	p	14:45–16:51
23 May	a	08:05–10:03
26 May	p	14:37–16:54
27 May	R[c]	07:56–11:03
28 May	a	08:04–11:04
28 May	p	14:38–16:50
29 May	a	08:04–11:20
30 May	T[d]	12:41–14:57
1 June	a	09:01–11:49
1 June	p	15:43–17:57
2 June	a	09:11–11:50
2 June	p	15:31–17:55
4 June	p	15:43–17:55
5 June	a	17:02–19:37
5 June	p	15:32–18:01
6 June	a	09:15–11:54
6 Jun	R[e]	15:33–20:20
9 June	p	15:36–18:19

[a] Flight paths are typical morning (a) or afternoon (p) patterns (see text).
[b] Local time (= UTC-7).
[c] Regional flight, all upwind of city.
[d] Test flight.
[e] Regional flight, all downwind of city.

3. Observations

3.1. Surface measurements

In this section, we discuss trends in trace gas measurements at PV, selected to characterize air upwind of the city, PXSS and Central Phoenix (CP) sites and USY, a downwind site east of downtown (see Fig. 1 for locations). Diurnal variations of ozone for the three regions between 15 May and 13 June are depicted in Fig. 3. The highest ozone concentrations were observed during the afternoons of 16th May, 24th May and 5th June at all three sites. In downtown Phoenix, reaction with NO and deposition reduced ozone in the nocturnal boundary layer (NBL) below the detection limit during most nights. Complete loss of O_3 was evident fewer than half of the nights at PV, and never at USY, presumably due to lower NO_x emissions at these sites. Nighttime boundary layer dynamics at mountain sites also play a role (Aneja and Li, 1992). Differences between the three sites are more easily seen in composite diurnal profiles of

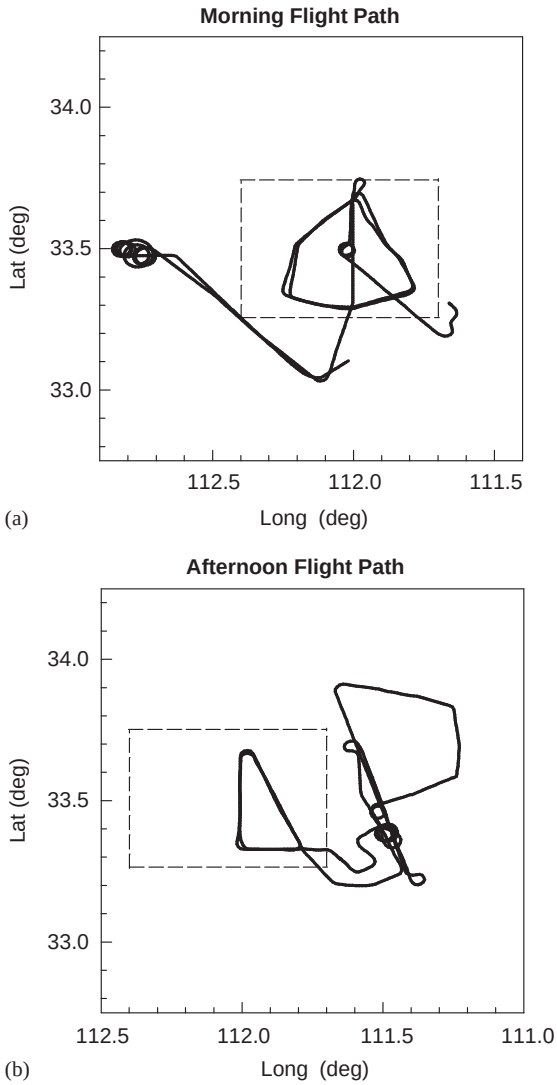

Fig. 2. Typical morning flight pattern (a) and afternoon flight pattern (b). Dashed line shows the high emission metropolitan area.

O_3, CO, and NO_y (Fig. 4). Features of these profiles are discussed below.

3.1.1. Upwind

Median ozone at PV showed a broad peak between 12:00 and 16:00 LST, with a maximum of 58 ppbv. The decrease in O_3 to a minimum of 20 ppbv at 06:00 LST coincides with a peak in NO_y reaching 11 ppbv. While southwesterly synoptic winds place PV upwind of the source region, surface winds were slow and had a S/SE component during the night and early morning hours. The anticorrelation of NO_y with O_3 suggests that O_3 was titrated by local NO_x emissions, and that the PV site is influenced by local sources during the night, perhaps the nearby highway. Concentrations of NO_y were at or below the detection limit of 0.4 ppbv during the rest of the day.

3.1.2. Downtown Phoenix

Diurnal variations downtown are illustrated in Fig. 4 for the CP site; other downtown locations exhibited similar patterns. Median ozone concentration peaked at 60 ppbv in the afternoon (15:00), similar to PV. Overnight, much higher NO_x emissions resulted in extensive titration of ozone until 06:00. Values of NO_y as high as 400 ppbv and of CO as high as 5 ppmv were observed near midnight, possibly due to a very low nocturnal boundary layer. While the median peak in NO_y and CO emissions indicates an early morning rush hour starting at 06:00 LST. This is at about the same time as sunrise and the break up of the nocturnal boundary layer. As is evident by the corresponding increase in O_3 concentration which can be attributed to a combination of photochemical production and downward transport of ozone from air aloft (see G1 observations) (Berkowitz et al., 2002a,b). Hourly average sulfur dioxide values, measured at four downtown locations, were always below 9 ppbv (detection limit = 1 ppbv). Since there are no significant sources of SO_2 in the region, SO_2 data were not analyzed further.

3.1.3. Downwind

On most afternoons, the USY site was downwind of the source region. A striking observation at this site was the relatively high concentration of ozone (median 50 ppbv) during the overnight period that represents regional background, because this site lies above the nocturnal boundary layer at night. Median ozone remained high during the early morning hours, and increased gradually in the afternoon to 60 ppbv at ~16:00. In contrast to PV and CP, the pattern of maximum concentration did not track that of median concentration at USY. For example, excursions in NO_y at 14:00 (top of the whiskers in Fig. 4), were not reflected in the median. The maximum O_3 at this site also occurred several hours later than the median, and approximately 2 h later than at CP. Although median ozone rose to 60 ppbv in the afternoon at all three sites, the maximum ozone at USY, which lies directly in the path of the urban plume under typical afternoon wind conditions, was on average 11 ppbv higher than at CP. These observations are consistent with transport of pollutants from downtown during the afternoon.

3.2. Hydrocarbon abundance and reactivity at the surface

Hydrocarbon canisters were collected by ADEQ at upwind, downtown and downwind monitoring sites (PV, PXSS, and USY) allowing us to examine geographic and temporal differences in VOC abundance and OH

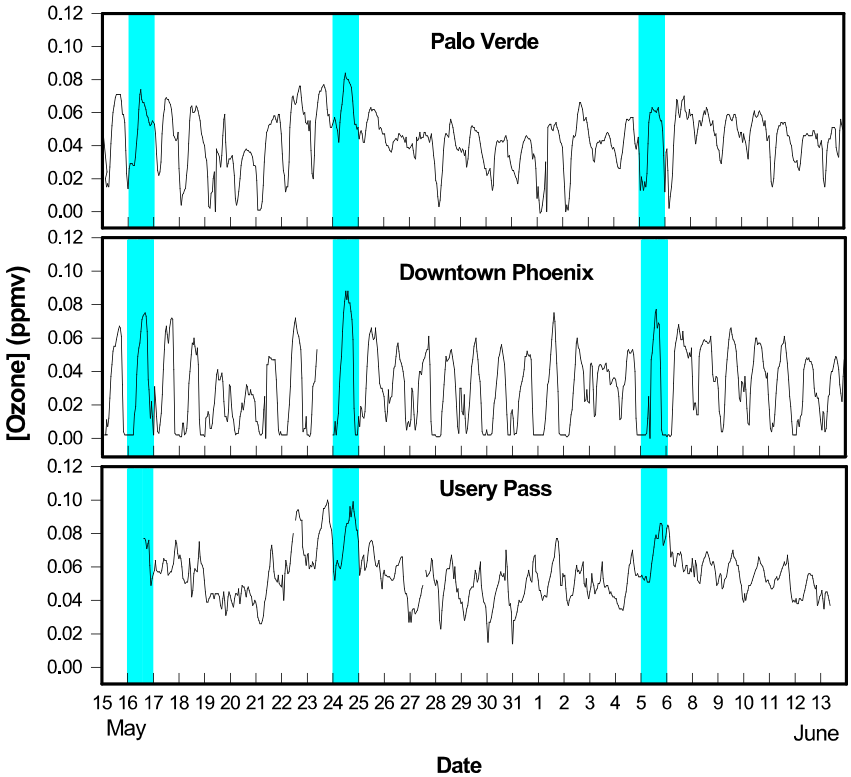

Fig. 3. Ozone time series for the entire sampling period at PV, PXSS, and USY. Shading indicates high O_3 days.

reactivity. Average concentrations of anthropogenic and biogenic compounds at these sites for morning (07:00) and afternoon (15:00) sampling periods are given in Table 5. OH reactivity is calculated by summing the product of concentration (as ppbv) and OH rate constants for individual VOCs in each category. The biogenic category consists of isoprene, alpha-pinene, beta-pinene, and limonene. The downtown site is located in a heavily trafficked area, impacted primarily by emissions from vehicles and other non-industrial sources. Photochemical age calculations performed for aircraft samples collected over downtown as well as downwind indicate that the composition of the aircraft samples is consistent with the downtown surface observations modified by the select removal of reactive species according to OH kinetics (Kleinman et al., 2003). This finding is consistent with emission inventory data indicating low levels of industrial emissions in the Phoenix air basin. The downtown propane observations, however, are not consistent with any of the aircraft measurements. Many of the PXSS afternoon samples contain several hundred ppbv of propane, whose origin is uncertain. Possible sources include an undocumented local point source or leaks from propane fueled vehicles. As the propane observations are unique to this area, they are not included in our analysis. In any event, propane only contributes about 10% to the total reactivity of the PXSS samples.

Concentrations and reactivities are low except at the downtown site. For comparison a CO concentration of 200 ppb has an OH reactivity of about $1\,s^{-1}$. Biogenic compounds do not contribute a significant fraction of total carbon but because of their high reactivity account for 16–37% of total OH reactivity at PXSS and USY. These very reactive compounds make a lesser contribution to OH reactivity at mid-boundary layer altitude, as indicated in a following section where aircraft data are presented.

Anthropogenic concentrations and reactivities decrease from morning to afternoon due to diurnal variations in emissions and to the deepening of the boundary layer. However, changes due to emissions are relatively small compared with the several-fold growth of the mixed layer between 07:00 and 15:00. In order to determine how the reactivity changed, determinations of the intrinsic reactivity were made (Table 5). One determination of the intrinsic reactivity is the ratio of anthropogenic OH reactivity to ppb carbon; the other is the ratio of ethylene to acetylene concentration. The latter ratio is of two compounds that are emitted almost exclusively in vehicle exhaust. Ethylene reacts with OH radical almost an order of magnitude faster than

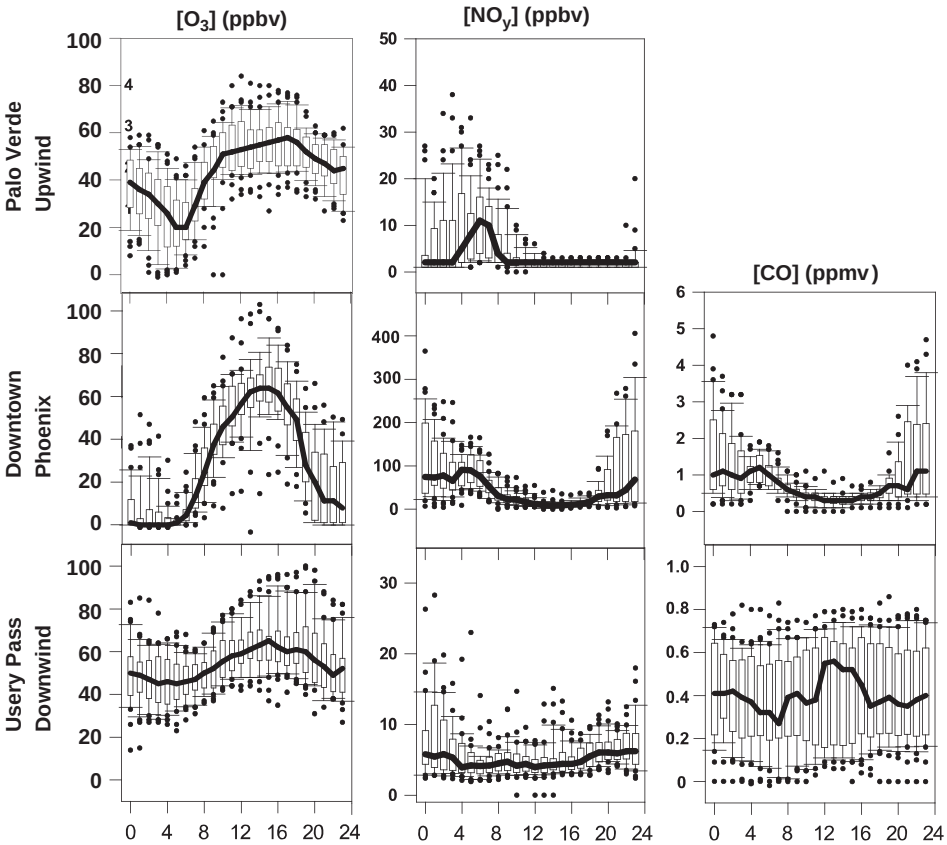

Fig. 4. Composite diurnal profiles of O_3 and NO_y at the PV surface sites. Composite diurnal profiles of O_3, CO, and NO_y at the CP and USY surface sites. Rectangles enclose the central 50% of data and 10th and 90th percentile range is depicted by whiskers. Medians are shown by heavy lines and maximums are shown by filled circles.

acetylene. Exposure of emissions to atmospheric photochemistry will therefore decrease the $[C_2H_4/C_2H_2]$ ratio. Table 5 indicates that the afternoon samples are selectively depleted in ethylene, indicating that the reactivity decreased due to photochemistry. However, according to the OH reactivity to ppbC ratio, which reflects a more diverse range of emission types, changes in intrinsic reactivity from morning to afternoon are small and in the case of PXSS was greater in the afternoon. The intrinsic reactivity could be affected by diurnal emission trends, for example by increased evaporative rates during a hotter afternoon, as well as by photochemistry.

3.3. Carbonyl and hydroperoxide measurements

Carbonyl measurements for three surface sites from 18th May through 9th June are shown in Table 6. Formaldehyde, acetaldehyde and acetone are distinctly elevated downtown in comparison with upwind and downwind sites, while methyl ethyl ketone concentrations are similar upwind and downtown, but significantly lower downwind. Aircraft formaldehyde measurements also show high concentrations in the source region (Table 6). Average formaldehyde concentrations for surface sites and aircraft agree well except for downtown samples in the morning, when the average surface concentration was twice that seen on the G-1. However, the ratio of formaldehyde (HCHO) to VOC concentration is greater in the air than on the ground. In general, the downtown G-1 samples are more dilute than downtown surface samples, but have a greater proportion of oxidation products (Kleinman et al., 2003). Formaldehyde and NO_y concentrations were reasonably well correlated ($r^2 = 0.6$) during downtown G-1 transects, suggesting vehicles as both a primary source for formaldehyde (Altshuller, 1993) and as a secondary source due to the oxidation of VOCs (which are co-emitted with NO_y).

Total hydroperoxide was measured at only one surface station, USY, between 28th May and 9th June. At this site, mixing ratios remained below 0.5 ppbv, and did not exhibit any discernable diurnal trend. On individual aircraft flights, median total hydroperoxide

Table 5
Average hydrocarbon concentration and OH-reactivity

Site	Time of day	Anthropogenic[a]				Biogenic[b]	
		Concentration (ppb C)	OH Reactivity (s^{-1})	k_{OH}/[ppb C]	[Ethylene]/[Acetylene]	Concentration (ppb C)	OH reactivity (s^{-1})
PV	a.m.[c]	18	0.71	0.038	0.87	0.20	0.063
	p.m. (up wind)	13	0.57	0.42	0.64	0.10	0.025
PXSS	a.m.	198	10.4	0.052	0.82	5.5	2.0
	p.m.[d]	122	8.4	0.069	0.68	7.0	2.7
USY	a.m.	27	1.5	0.057	0.59	1.0	0.42
	p.m.	14	1.3	0.055	0.51	1.9	0.76

[a] All volatile organic compounds except aldehydes, biogenics and carbon monoxide.
[b] Biogenics include: isoprene, alpha-pinene, beta-pinene, limonene. Methyl vinyl ketone and methacroline were not included.
[c] PV a.m. biogenic does not include one sample with a very high limonene concentration.
[d] PXSS p.m. biogenic does not include 2 samples with very high limonene concentrations.

Table 6
Average concentrations (in ppbv) of carbonyl compounds at Phoenix ground sites

Site	Time of day	Formaldehyde	Acetaldehyde	Acetone	Methylethyl ketone
PV	a.m.	1.21 ± 0.53	2.66 ± 0.3	4.03 ± 0.94	0.83 ± 0.07
PXSS	a.m.	3.44 ± 1.03	3.05 ± 0.6	7.02 ± 1.7	0.80 ± 0.20
	p.m.	2.01 ± 0.61	2.85 ± 0.47	6.59 ± 2.43	0.75 ± 0.42
USY	a.m.	0.74 ± 0.47	1.86 ± 0.49	3.90 ± 2.68	0.37 ± 0.33
	p.m.	0.78 ± 0.36	2.07 ± 0.29	3.11 ± 1.99	0.37 ± 0.24

varied from 0.9 to 2.9 ppbv within the boundary layer. Average contributions to the total were 59% hydrogen peroxide, 33% from methylhydroperoxide (MHP), and 8% from hydroxymethyl hydroperoxide (HMHP). For comparison, Nashville, TN exhibited higher concentrations of total hydroperoxide in the boundary layer (median = 5.2 ppbv) during the 1995 Southern Oxidant Study, with H_2O_2 representing 48% of the total and MHP 33%. HMHP represented 19% of the total, consistent with the greater abundance of its precursors, ozone and biogenic alkenes (Weinstein-Lloyd et al., 1998).

We present hydroperoxide measurements, segregated into upwind, source and downwind regions, in Fig. 5. The four days depicted in the figure are the only days during the program for which hydrogen peroxide data for each region is available for both morning and afternoon flights during a single day. On each morning flight, H_2O_2 was lower over the city than in background air. Afternoon H_2O_2 in the source region was lower than in the morning, and decreased still further downwind, consistent with inhibition of photochemical peroxide production in Phoenix and loss of H_2O_2 in incoming air masses as they traverse the source region. These

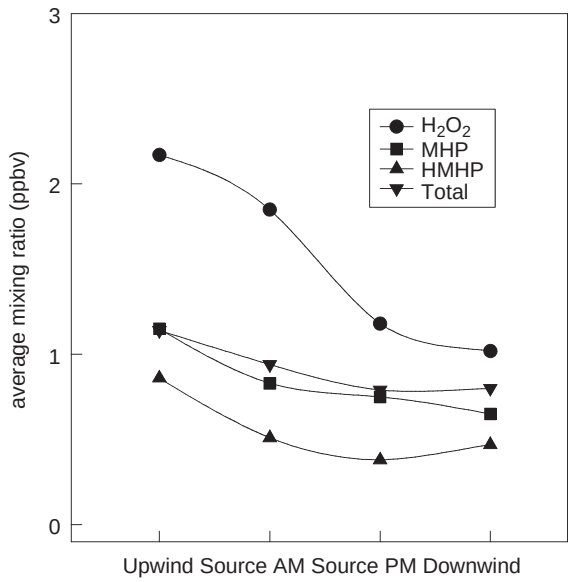

Fig. 5. Daily average hydroperoxide trend for upwind, source, and downwind regions. All samples collected below 2 km. Data taken from 4 days containing both morning and afternoon flights.

conclusions are supported by photochemical calculations presented in a later section.

3.4. General observations from aircraft studies

The relatively consistent meteorological conditions in Phoenix, coupled with repeated flight patterns around the metropolitan area, allowed us to characterize geographic patterns of trace gas abundances during the field program. We illustrate the influence of the source region by segregating flight data into four subsets: upwind and source region during morning flights and source region and downwind during afternoon flights (see Fig. 2). Summary statistics for the four subsets appear in Table 7, and general observations are described below.

Concentrations of CO, NO_x and NO_y in the source region and downwind were significantly elevated in comparison to upwind. We consistently observed elevated accumulation mode aerosols and NO_y as the aircraft crossed major roadways in the source region. Roadways parallel to the flight track often produced plumes extending tens of kilometers, broadened by surface level winds that shifted gradually during the day (see below). Median afternoon temperatures were only slightly higher than morning (21.9°C vs. 20.5°C), but water vapor concentration was more than 20% higher in the shallower morning boundary layer. Wind patterns changed significantly between morning and afternoon flights, with flows generally from the south to southeast in the early morning, becoming progressively more westerly during the afternoon. High wind speeds on most afternoons prevented the accumulation of photochemical products in the region. In the source region, peak afternoon concentrations of O_3 exceeded morning concentrations by approximately 10 ppbv, and were not substantially higher on the downwind legs.

4. Discussion

4.1. Comparison of hydrocarbon distribution for PXSS, USY, and the G-1

The distribution of hydrocarbon reactivity (i.e., the product $k_i[\mathrm{VOC}]_i$) for 8 sampling days (26 May–6 June) is illustrated in Fig. 6. Source contribution was calculated based on hydrocarbon concentration and reactivity for aircraft data and the downtown (PXSS) and downwind (USY) surface sites where simultaneous measurements of CO and VOCs were available (Nunnermacker et al., 1998). Aircraft data for the region over PXSS during morning flights and the downwind region near USY during afternoon flights were selected in order to compare aircraft to ground measurements, and to observe changes in apportionment with time. PXSS samples were taken at 07:00, before the mixed layer was fully formed, and showed the highest reactivity and largest fraction of anthropogenic VOCs. Pollutants from the source region undergo aging and dilution in the growing boundary layer during the average 2 h transport time to USY, resulting in a threefold decrease in reactivity. The larger contribution of CO at USY reflects depletion of the more reactive hydrocarbons. Reactive hydrocarbons in downtown aircraft samples are depleted in comparison with surface samples. This is

Table 7
Summary statistics for G-1 flights

Species	Upwind (a.m.)		Source (a.m.)		Source (p.m.)		Downwind (p.m)	
	Median	Max	Median	Max	Median	Max	Median	Max
O_3 (ppbv)	51	84	54	101	62	95	65	96
NO_x (ppbv)	0.5	9.2	4.6	47	3.0	20	1.1	4.9
NO_y (ppbv)	3	13	11	61	7	30	5.4	16
NO_x/NO_y	0.24	0.69	0.49	0.80	0.41	0.55	0.17	0.27
CO (ppbv)	133	324	187	535	174	583	155	326
H_2O_2 (ppbv)	1.1	2.8	0.8	2.6	0.8	1.4	0.7	1.2
MHP (ppbv)	0.7	1.7	0.7	2.3	0.5	2.5	1.0	2.3
HMHP (ppbv)	0.1	0.6	0.2	0.6	0.1	0.8	0.1	0.7
HCHO (ppbv)	1.10	2.22	1.76	3.74	1.66	3.54	1.41	2.11
PCASP (cm^{-3})	233	808	333	1166	275	1224	222	1045
H_2O ($g\,kg^{-1}$)	4.45	7.54	4.38	7.58	3.60	6.10	3.38	5.24
Relative humidity (%)	27	62	24	64	18	38	18	44
Temperature (°C)	20.8	25.4	22.4	26.7	23.3	31.6	21.0	31.1
Wind direction (deg)	142	356	144	359	234	359	225	334
Wind speed ($m\,s^{-1}$)	2.3	7.4	3.0	11	4.1	10.8	5.5	14.1

Values above are calculated for all data points obtained at altitude <2 km.

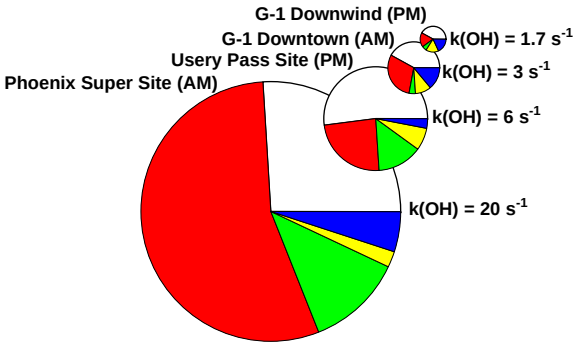

Fig. 6. Hydrocarbon distribution in Phoenix for specific categories: nonmethane hydrocarbons, carbon monoxide, isoprene, methane and formaldehyde. Data shown for PXSS and USY surface sites, and for aircraft samples obtained on flight legs over the source region and USY. Diameter of circle scaled to OH reactivity, i.e., Σk_i[VOC] for that location. NMHC = red; White = CO; Green = isoprene; Yellow = CH_4; Blue = HCHO.

partially due to dilution, as they were taken somewhat later in the morning, and partially to reaction with OH. Hydrocarbon reactivity in downwind aircraft samples has declined further and, as in the ground site observations, CO has become the major contributor. The percent contribution of biogenic species to hydrocarbon reactivity is low in all samples, in contrast to observations in the southeastern US. For example, by comparing samples from the two cities with approximately the same total OH reactivity (5–6 s^{-1}) biogenic hydrocarbons contributed ~25% of the reactivity in the Nashville urban plume, in comparison to ~10% in the Phoenix urban plume as determined from samples taken on the G-1 (Kleinman et al., 2002b). Due to differences in sampling sites and the height of the boundary layer during downtown measurements a direct comparison of reactivities between Nashville and Phoenix is difficult to make. It is also interesting to note that concentrations of isoprene were highest in the Phoenix downtown area and substantially lower in the surrounding areas (Table 5). This is also quite different from observations made in Nashville where high isoprene was more likely to be found outside of the metropolitan area (Nunnermacker et al., 1998). Thus, the contribution of biogenic hydrocarbons to O_3 production is not an important factor in the Phoenix air basin.

4.2. CO/NO_y relationship

CO and NO_x are co-emitted from vehicular sources that dominate the Phoenix emission inventory. CO and NO_y show a linear relationship for G-1 transects over the source region on morning flights. The average slope for six flights, 7.4 ± 1.0 ($r^2 \geqslant 0.70$), was somewhat lower than the value of 9–10 observed in earlier studies in automotive source regions (Parrish et al., 1991; Kleinman et al., 1998), but agrees with more recent values of 6.3 ± 0.9 made in Nashville, TN in 1999 by Parrish et al. (2002). These authors note that emission controls have resulted in a steady decline in CO to NO_x ratios and that measurements show a rate of decrease faster than indicated by EPA emissions inventories. During the 2001 Phoenix experiment, data collected for downtown morning flights gave a CO vs. NO_y slope of 7.8 ± 0.9, essentially the same as that obtained in 1998 (Berkowitz et al., 2002a,b). These values also are consistent with CO vs. NO_y slopes of 6.3 ± 0.8 during early morning rush hours, measured at a downtown building during the Phoenix 2001 experiment (Spicer, 2001). CO vs. NO_y slopes could not be determined for downtown surface sites in 1998 because data were provided only as hourly averages.

CO to NO_x emission ratios for Maricopa County for 1988–1999 are shown in Fig. 7 (http://www.epa.gov/air/data/index.html). The regression line through the EPA data indicates a decreasing trend of approximately 3% yr^{-1}. Aircraft measurements for 1998 and 2001, and downtown surface data for 2001 fall along the EPA regression line and agree well with the decreasing emission ratio for CO to NO_y. Within experimental uncertainty, the CO/NO_y ratio from measurements is consistent with emission inventory data for Maricopa County.

4.3. Constrained stationary state calculations

Despite high concentrations of ozone precursors, afternoon ozone concentrations in Phoenix were only moderately higher in the afternoon than in the morning. We performed constrained stationary state (CSS) calculations (Kleinman, 2002b) to probe the factors that limit ozone production in this region in comparison to other urban areas. Calculations were based on RADM2 chemistry, augmented by Paulson and Seinfeld's isoprene oxidation mechanism and photolysis rates from Madronich's radiative transfer program. Concentrations of VOCs, CO, NO_x, O_3, HCHO, H_2O_2 and ROOH were constrained by aircraft observations. Calculations were performed for each time period during which a hydrocarbon canister sample was available. Hydrocarbon sampling locations (approximately 10 per flight) were chosen to represent different parts of the study region, and to capture events that appeared to be interesting based on real-time aircraft observations. We note that this sampling strategy yields a bias toward high-O_3 conditions. Trace gas concentrations were obtained by averaging data for the approximately 30 s time periods that coincided with canister hydrocarbon sampling. The averaging time was

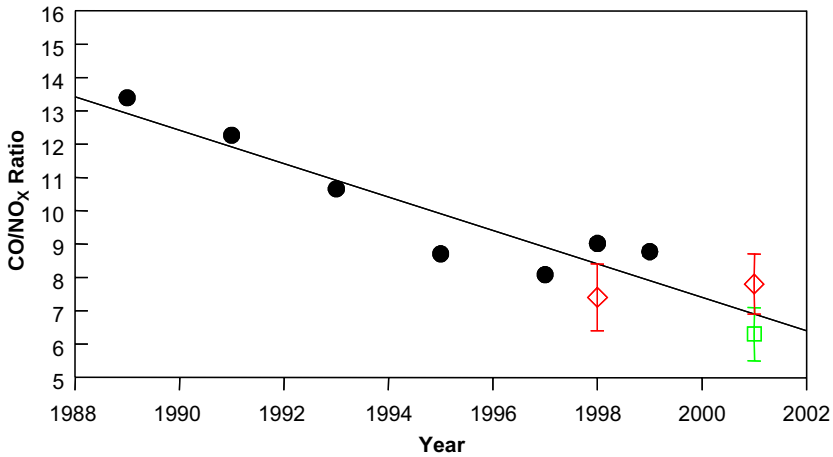

Fig. 7. CO/NO_y from EPA emissions, G-1 flights (1998 and 2001) and downtown (2001): red diamonds = G-1, flights and green square = downtown site.

Table 8
CSS calculations mean values

Parameter	Region			
	Upwind	Source a.m.	Source p.m.	Downwind
$P_{peroxide}$ = peroxide production rate (ppb h^{-1})	0.14	0.04	0.05	0.09
Net $P_{peroxide}$ (ppb h^{-1})	−0.06	−0.17	−0.20	−0.08
Q = radical production rate (ppb h^{-1})	0.62	1.14	1.57	0.48
%HCHO = fraction of radical produced from HCHO photolysis	0.26	0.32	0.35	0.37
% O_3 = fraction of radical produced from O_3 photolysis	0.57	0.52	0.40	0.40
P_{O3} = ozone production rate (ppb h^{-1})	1.76	4.22	5.21	2.38
Net P_{O3} (ppb h^{-1})	1.35	3.68	4.71	2.01
L_N/Q = fraction of radicals removed as HNO_3	0.44	0.85	0.87	0.48
n	9	49	26	24

All points are alt <2 km.

extended for 1 min in some cases to make up for missing or noisy data. These calculations yielded 108 data points for 20 flights. Results were segregated into subsets described earlier: upwind points early in the morning west of the city, the source region in the morning and in the afternoon, and downwind east of the city in the afternoon. Mean values of the calculated variables for these four areas are given in Table 8. The net instantaneous O_3 production rate (production minus loss) was only 3.7 ppb h^{-1} during the morning flight over the source region, where concentrations of NO_x and reactive VOCs are highest. This is a consequence of the dry atmosphere, which results in a low value (0.6 ppb h^{-1}) for Q, the rate of radical production from the photolysis of O_3, followed by reaction of $O(^1D)$ with H_2O. Approximately one-third of the radicals arise from photolysis of HCHO in the source region and downwind.

Another consequence of the dry atmosphere is inefficient production of peroxides. If NO_x concentrations were zero, peroxide formation would be stoichiometrically limited to be half of the radical production rate (i.e. 0.3 ppb h^{-1} at a Q of 0.6 ppb h^{-1}). Calculated peroxide production (H_2O_2 + MHP) is ~0.1 ppbv h^{-1} both upwind and downwind, but only at ~0.05 ppbv h^{-1} in the high-NO_x source region (Table 8). High NO_x concentrations effectively move radicals from peroxide—to NO_z—forming pathways. Slow chemical removal of NO_x by reactions with radicals, helps keep NO_x concentrations high. These processes, along with losses from dilution and deposition, explain the decrease in H_2O_2 concentrations illustrated in Fig. 5. The CSS calculations suggest that low water vapor significantly limits photochemical ozone production in Phoenix, a conclusion that is explored further in the case study below.

4.4. Case study—5th June

One of the highest ozone days during the Phoenix program occurred on Friday, 5th June, when unusually weak winds furnished the potential for enhanced ozone production as precursor concentrations built up in the area.

The day began with high background ozone, illustrated by surface network measurements in Fig. 8. Outside the congested downtown area, where ozone was removed by reaction with NO, concentrations averaged 55 ppbv at 08:00. On the aircraft vertical profile between 800 and 2500 m, we observed a uniform O_3 concentration of 60 ppbv upwind at 09:50 and again over the source region at 11:30 (Fig. 9). Ozone at the surface began to increase with the breakup of the nocturnal boundary layer, with most sites reaching ~60 ppbv by noon. In the source region, surface O_3 peaked at 77 ppbv at 15:00, while downwind sites peaked at higher concentrations early in the evening. For example, ozone at the USY site reached 86 ppbv at 18:50. Low wind speeds ($0.5\,m\,s^{-1}$) would result in a transport time of 4–10 h between the source region and the nominally downwind site. Thus, we can attribute the increase in ozone in the source region and downwind ($\Delta O_3 \approx 17$–26 ppbv, respectively) to local production and transport during the afternoon.

Portions of the flight tracks above the downtown area, upwind sites at PV, and downwind sites near USY were used for comparison with surface observations. The G-1 flight path over downtown Phoenix in the morning crossed numerous fresh pollutant plumes (i.e., NO_y >

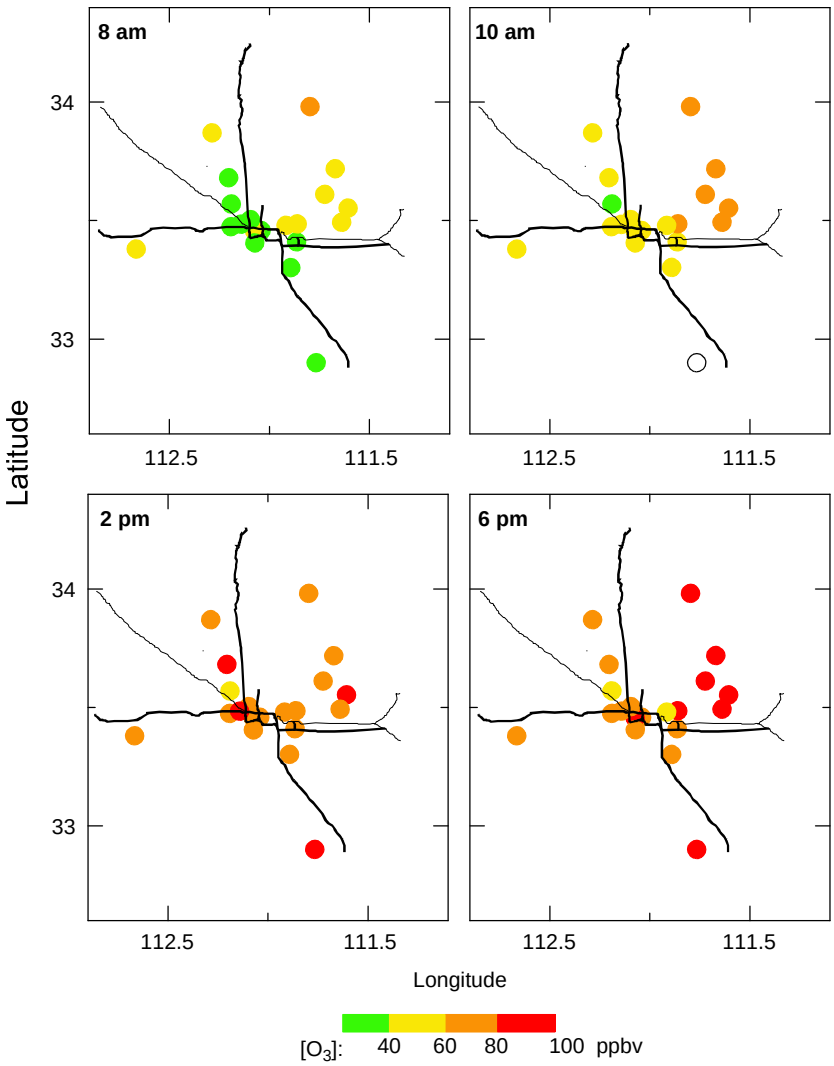

Fig. 8. Ozone concentrations observed at ground sites on 5 June, 1998.

10 ppbv and median NO_x /NO_y = 0.61), shown in color in Fig. 10. Based on location (over major highways), these plumes appear to be emissions from major traffic corridors. A correlation between PCASP and NO_y, was

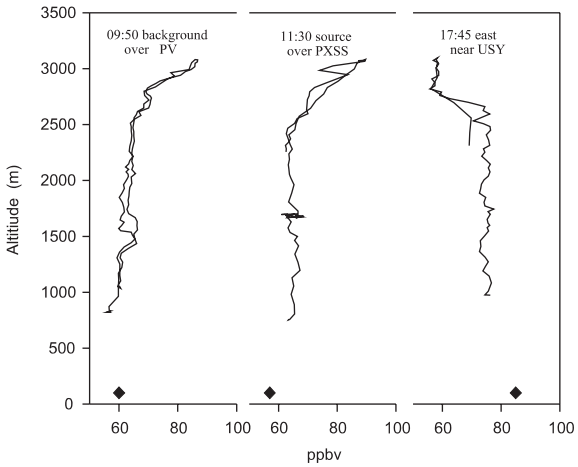

Fig. 9. Vertical profiles of trace gases observed on 5 June, 1998: At 09:50 a sounding was taken on the upwind flight leg near PV, at 11:30 a sounding was taken over PXSS and at 17:45 a sounding was taken near USY. Diamonds indicate ground site concentrations.

also observed in these plumes, as shown in Fig. 11. By afternoon, plumes had grown to cover most of the source region, and the median ratio of NO_x to NO_y had decreased to 0.40 due to aging of the stagnant air mass since the morning flight. The efficiency of ozone production (OPE), i.e. the number of oxidant molecules (O_3 + NO_2) formed per molecule of NO_z produced, is shown in Fig. 12 for the source region in the afternoon. The slope of the regression line is 1.4 ($r^2 = 0.6$), consistent with values obtained in other high-NO_x regions where radical removal occurs primarily by reaction with NO_x (Daum et al., 2000a; Sillman, 2000). Fig. 12 also shows that OPE for the downwind G-1 transect has increased to 3.7 ($r^2 = 0.84$). It is interesting to note that at this point the air has been processed (NO_x / NO_y = 0.21) and the system is under low-NO_x conditions. The trend toward higher OPE at low NO_x is a general feature of O_3 production in Phoenix (Kleinman et al., 2002a and elsewhere; Gillani et al., 1998; Ryerson et al., 2001). We note that the OPE obtained later in the day should be considered an upper limit because we have not corrected for loss of NO_y as the plume aged.

Instantaneous O_3 production rates in the source region varied between 1.3 and 6.7 ppb h^{-1}, with a mean rate of 4.6 in the morning and 2.8 in the afternoon

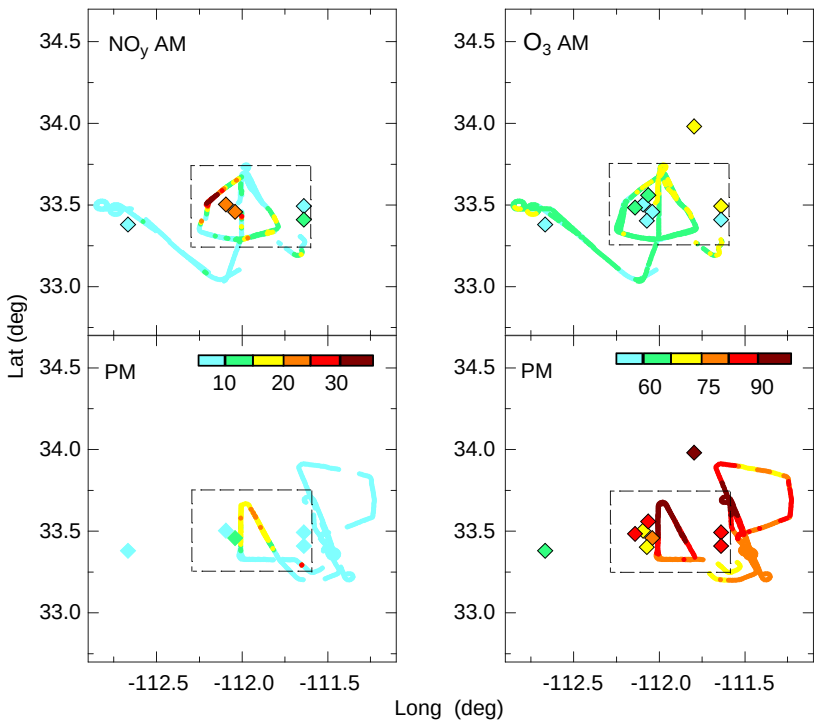

Fig. 10. Flight path for morning and afternoon flights on 5 June, 1998. Trace gas observations on specific flight legs discussed in the text. NO_y and O_3 concentrations along the flight track depicted in color. Ground based measurements indicated by diamonds. Dashed line shows the high emission metropolitan area.

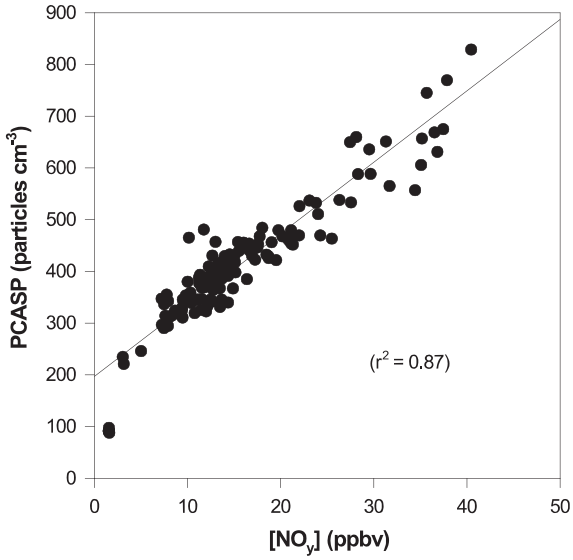

Fig. 11. Correlation of NO_y with PCASP during the afternoon flight on 5 June, 1998. Only boundary layer data for this flight are included.

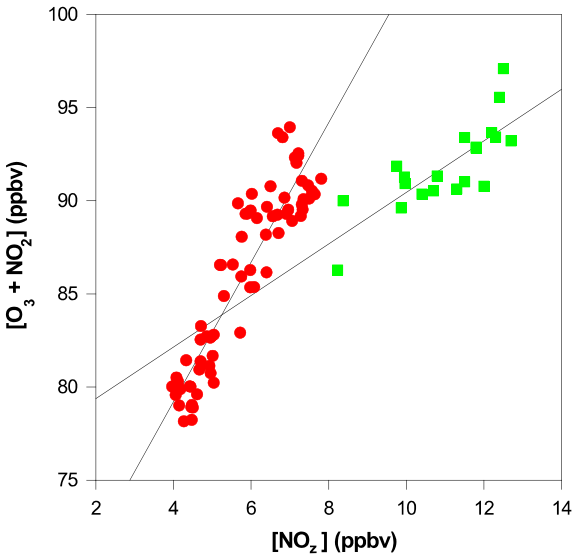

Fig. 12. Correlation of O_3 with NO_z during the afternoon flight on 5 June, 1998. Only boundary layer data for this flight are included. The OPE_x for the downtown transect was 1.4 (r^2 = 0.6) (squares) and for the downwind (USY) transect was 3.7 (r^2 = 0.8) (circles).

(Fig. 13). The G-1 traversed the triangular path over the source region once at 10:33–11:26 and again from 16:05 to 16:36. During this 5.5 h interval, average ozone increased from 62 to 83 ppbv. This observed O_3 increase of 3.8 ppb h^{-1} is within the range of the calculated rates. At the USY surface site, ozone concentrations were of

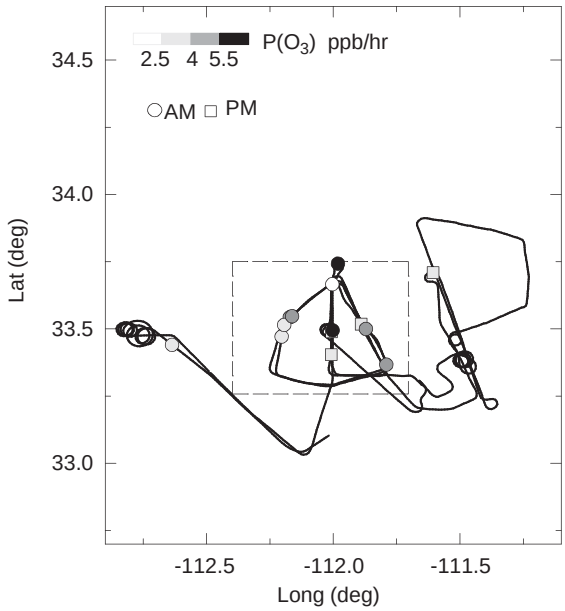

Fig. 13. CSS calculated ozone production rates during the 5 June, 1998 flight. Both morning and afternoon flights are included. Dashed line shows the high emission metropolitan area.

the order of 58 ppbv at 07:00, characteristic of background air, as discussed earlier. By 18:30, ground O_3 concentrations had reached a maximum of 86 ppbv. The observed change in ozone concentration during this period is approximately 2.3 ppbv h^{-1}, in good agreement with the calculated afternoon value.

4.5. Comparison of photochemistry in Downtown Phoenix vs. Nashville

Conditions on 5th June were similar to stagnation events in Nashville that generated ozone maximums during the 1995 Southern Oxidant Study (Valente et al., 1998; Daum et al., 2000a). We take advantage of this feature to compare details of ozone production between Phoenix and Nashville (Fig. 14). The Phoenix metropolitan region had a range of ozone production rates from 3 to 6.7 ppb h^{-1} and an ozone production efficiency between 1 and 3 for the urban plume. CSS calculations were performed for a G-1 flight in Nashville that occurred under approximately the same solar irradiance and ozone concentration. Data were further selected to have similar ratios of hydrocarbon to NO_x reactivity, $k_1[HC]/k_2[NO_2]$, ensuring that the hydrocarbon and NO_x mix was similar for the two regions. Ozone production efficiency is proportional to $k_1[HC]/k_2[NO_2]$ because this ratio represents the rate at which OH reacts with hydrocarbons (producing O_3) divided by the rate at which OH reacts with NO_2 (removing NO_x). Note that this ratio is independent of radical production

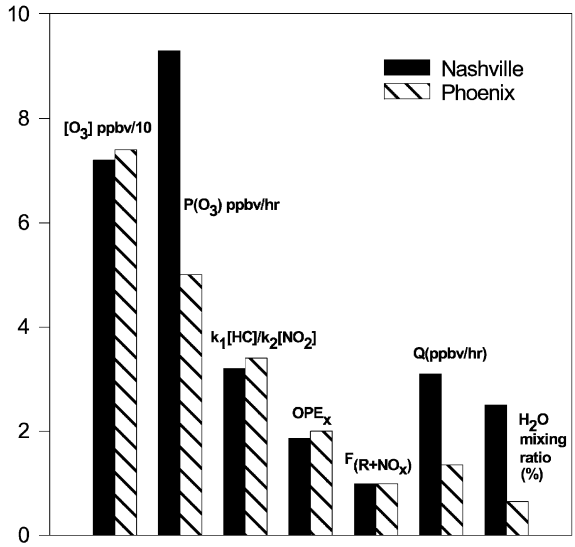

Fig. 14. Comparison of the CSS parameters for Nashville (1995) and Phoenix (1998).

rate. As a result, ozone production efficiencies, OPE_x, were ~ 2 ppb O_3/ppb NO_x for both Phoenix and Nashville. The fifth set of bars, representing the fraction of radicals removed as nitric acid ($\sim 90\%$), confirms that the two cities were both in the hydrocarbon limited regime. Ozone production rate, $P(O_3)$, versus the quantity $Q\{k_1[HC]/k_2[NO_2]\}$ was linear, also indicating that ozone production was hydrocarbon limited (Daum et al., 2000b). $P(O_3)$ in Phoenix is approximately 5 ppb h^{-1}, significantly lower than observed in Nashville. For this subset of data, selected to ensure similar NO_x to VOC - OH reactivity, the explanation for a lower ozone production rate cannot arise from a difference in the amount of ozone produced from a molecule of NO_x, (i.e., from a difference in chain length in the two cities). Rather, the dry atmosphere makes initiation of the process occur more slowly in Phoenix compared to Nashville. In particular, the water vapor mixing ratio in Phoenix is only 25% of that in Nashville, leading to a radical production rate Q, that is only 40% as large. This translates into a much lower ozone production rate in Phoenix, as illustrated in the figure. The significant difference is the rate of radical production Q, which was twice as high in Nashville, a direct result of the higher water vapor mixing ratio. Further comparisons of ozone photochemistry in these cities can be found in the paper by Kleinman et al. (2002b).

5. Conclusions

- Ratios of CO to NO_y observed downtown and on the G-1 indicate that the trace gas mix in Phoenix is dominated by vehicle emissions. This ratio agrees with the decreasing trend in emissions published by EPA.
- Hydrocarbon distributions for both aircraft and ground sites established that biogenic compounds do not contribute greatly to ozone production in Phoenix. Anthropogenic hydrocarbons are the biggest contributor for both ground site and aircraft measurements with CO becoming more important as the plume ages.
- Ozone production in Phoenix is VOC limited based upon model calculations and is similar to one case observed in Nashville (1995). In general, Nashville had more days when ozone production was NO_x limited.
- The efficiency of ozone production in Phoenix (1998) was similar to that obtained in Nashville (1995). Ozone production rates were lower in large part because low humidity depresses the radical production rate.

Acknowledgements

The authors gratefully acknowledge the ground and flight crew of the DOE G-1 for another safe and successful field mission. Special thanks to the Arizona Department of Environmental Quality and all of the ground-site personnel who kept the stations operating around the clock. We would also like to thank Carl Berkowitz of PNNL and Chet Spicer of Battelle for providing us with CO and NO_y data from their 2001 Phoenix field study. This paper has been authored with support from the Office of Biological and Environmental Research under Contract number DE-AC02-98CH10866. JWL acknowledges support from DOE Grant DE-FG02-98ER62586 and NSF ATM94-14108. The US Government retains nonexclusive, royalty free license to publish or reproduce the published form of this contribution or to allow others to do so, for US Government purposes.

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