

### 8.3 VERTICAL MIXING AND CHEMISTRY OVER AN ARID URBAN SITE: FIRST RESULTS FROM AIRCRAFT OBSERVATIONS MADE DURING THE PHOENIX SUNRISE CAMPAIGN

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#### 1. INTRODUCTION

The role of boundary layer mixing is increasingly recognized as an important factor in determining the concentrations of ozone and other trace gases near the surface. While the concentrations at the surface can vary widely due to horizontal transport of chemical plumes, the boundary layer is also characterized by turbulence that follows a diurnal cycle in height and intensity. Surface oxidant concentrations can therefore undergo significant changes even in the absence of photochemistry.

A central goal of the Phoenix 2001 Field Campaign was to study vertical mixing with the onset of convection and to quantify the effect of this mixing on chemistry within an urban boundary layer. As part of this study, a series of low altitude aircraft sampling flights were made over the Greater Phoenix area between June 16-30, 2001. The resulting observations, in conjunction with a series of surface measurements and meteorological observations, are being used to study the vertical transport and reactivity of ozone and ozone-precursors shortly after sunrise. Additional details of this campaign are given in Doran, et al. (2002).

It was anticipated that turbulence over Phoenix at night would be suppressed as a result of cooling of the boundary layer over the city. By sampling shortly after sunrise, we hoped to collect measurements above the residual nocturnal stable layer and to continue sampling through the developmental period of a convectively

active boundary layer. We report here on the first analysis of these observations, made from a Gulfstream-1 (G-1) aircraft operated by the U.S. Department of Energy.

#### 2. OVERVIEW OF MEASUREMENTS

The Gulfstream aircraft was instrumented to measure a number of basic meteorological and chemical variables (Table 1). The flight patterns over Phoenix, and a plan view of flight segments for the June 20 mission, are shown in Figures 1 and 2. A typical sampling mission consisted of a series of early morning loops around Phoenix. Although each segment was operationally defined by height above mean sea level (MSL) we report them as meters above the ground, using as base reference the altitude at downtown Phoenix, 350 m MSL. The G-1 left from Williams Gateway Airport (IGA), climbing to an altitude of ~470 m AGL. It first flew to Firebird Lake (FL), then north over Sky Harbor Airport (PHX), past Camelback Mtn. (CB) to Scottsdale (Sc). A spiral (sp) to 2700 m AGL was made in the vicinity of Scottsdale, after which the G1 descended to ~470 m AGL and continued to Glendale (Gl), then to South Mtn. (SM), Firebird Lake and north to Camelback Mtn. After completing this loop around the greater Phoenix area, a series of smaller loops at nominal altitudes of ~380 m AGL, 470 m AGL and 625 m AGL were made while flying between Camelback Mtn, Scottsdale, Glendale and back to Camelback Mtn.

Table 1. Summary of Instrumentation

Variable	Technique	Instrument	Sampling Interval
Ozone	UV absorption	Thermo Environmental Instruments (Model 49)	1 s (4 s update interval)
NO <sub>y</sub>	Heated Mo converter/chemiluminescence	BNL-constructed system	1 s
NO <sub>2</sub>	Photolysis/chemiluminescence	BNL-constructed system	
NO	Chemiluminescence	BNL-constructed system	1 s
CO	Non-dispersive IR	Thermo Environmental Instruments (Model 48)	20 s
CO	VUV fluorescence	Resonance Limited	1 s
Pressure	Aircraft static pressure port	Rosemount 102U2U/510BF	1 s
Altitude	Derived from pressure and temperature		

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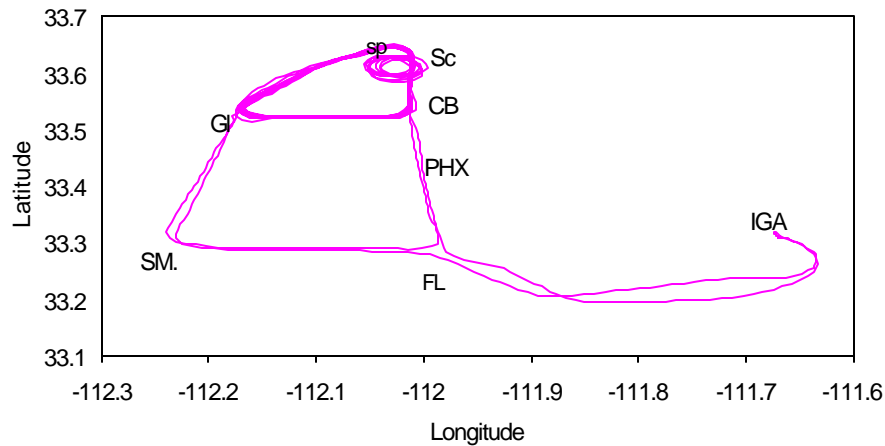


Figure 1. Flight path of June 20, and key landmarks. IGA = Williams Gateway Airport, PHX = Phoenix Sky Harbor Airport, CB = Camelback Mtn., Sc = Scottsdale, sp = spiral, GI = Glendale, SM = South Mountain, and FL = Firebird Lake. See text for details of flight path.

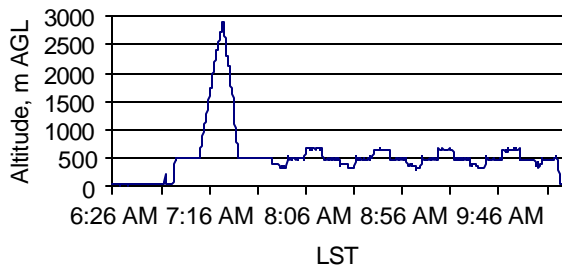


Figure 2. Altitude profile, morning flight, June 20.

### 3. FIRST RESULTS

We report here on features common to many of the missions, illustrating these features with data from the morning flight of June 20. The synoptic pattern on June 20 was characterized by high pressure over Arizona. The temperature before sunrise at Williams Gateway Airport was 31°C with northerly winds at 3 m s<sup>-1</sup>.

A recurring feature seen from the Gulfstream observations were the elevated values of ozone aloft (Figure 3). It was common to measure ozone levels towards the top of the spirals that were 50% greater than those observed at lower altitudes. In this example, values at 550 m AGL were 40 ppb, while values at 2300 m AGL were of order 65 ppb. Profiles of CO were also higher aloft, suggesting that this elevated layer of pollutant was a residual of auto emissions and photochemical processes, either local or advected from upwind sources.

Figure 4 shows two potential temperature profiles measured with radiosondes released at a site about

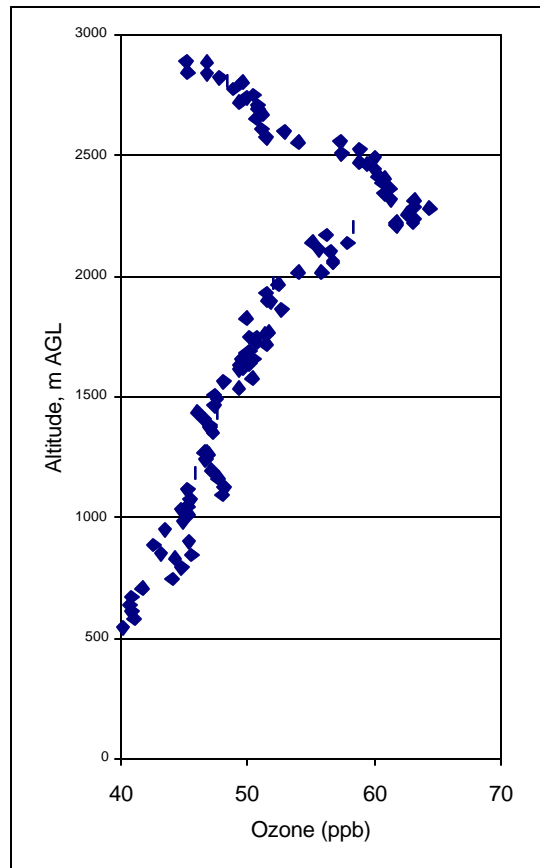


Figure 3. Profile of ozone, morning of June 20, at the location shown by the spiral shown in Figure 1, over northern Phoenix.

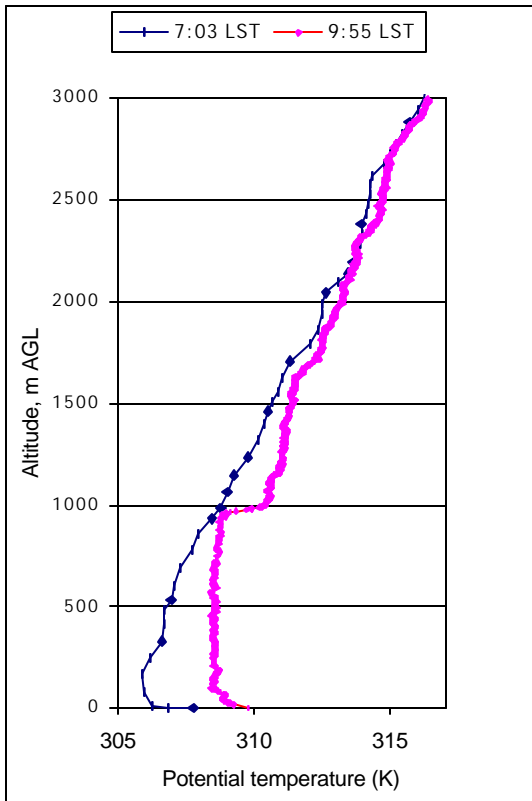


Figure 4. Profiles of potential temperature taken on the morning of June 20. Launch times are shown at the top.

1 km to the northeast of Sky harbor Airport (Figure 1). Around 0700 LST, approximately one hour before the G-1 began its series of sampling runs at three different elevations, a convective layer had begun to develop but its depth was less than 300 m at this time. We would expect that vertical mixing above this height would be suppressed, which is consistent with the observed stratification in the levels of  $\text{NO}_y$  and  $\text{O}_3$  discussed below. Over the next 3 hours the boundary layer grew so that by 1000 LST the mixed-layer was nearly 1000 m deep. This deepening is also consistent with the much more uniform profiles of  $\text{NO}_y$  and  $\text{O}_3$  observed by the G-1 near the end of their sampling run (see below).

We found that the chemical stratification observed in the early morning would frequently dissipate by mid-morning. Evidence of this feature is seen in Figures 5 and 6 where we have plotted  $\text{NO}_y$  and  $\text{O}_3$  as a function of time, and categorized each observation into one of three sampling altitudes, corresponding the lower altitudes in Figure 2 (300 to 350 m AGL, 475 to 525 m AGL, and 625 to 680 m AGL). Low altitude  $\text{NO}_y$  levels at 0754 LST had a mean value of 6.5 ppb in contrast to the corresponding values at the upper layer (625 to 680 m AGL) that were half this value (mean = 3 ppb). With the onset of mixing, the low altitude values were seen to decrease and the mean values at all layers converged to approximately 6 ppb by 1000 LST. A similar

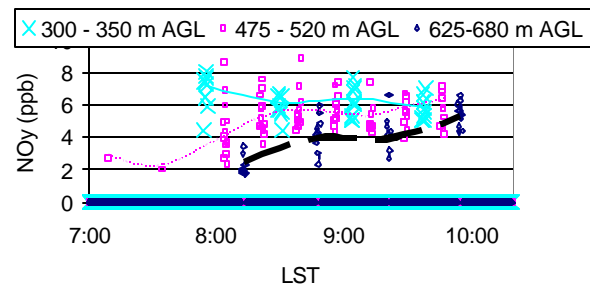


Figure 5. Time series of  $\text{NO}_y$ , June 20, partitioned by three altitudes. Lines represent fit to mean value at each altitude, showing convergence with development of mixed layer.

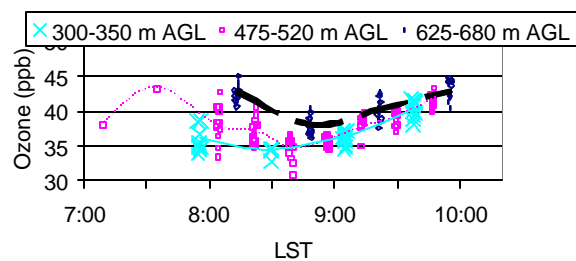


Figure 6. Time series of  $\text{O}_3$ , June 20, partitioned by three altitudes bins. Lines represent fit to mean value at each altitude, showing convergence with development of mixed layer.

pattern of convergence was observed for  $\text{O}_3$  (Figure 6), but in this case, the values near the surface were less than those aloft, with both sets of observations converging to a common value by 1000 LST, consistent with the growth of the boundary layer as seen in Figure 4.

The highest values of  $\text{NO}_y$  during the first part of the flights were found near the surface, in contrast to higher values of  $\text{O}_3$  that were found aloft early in the morning. The production of ozone is typically associated with an increase in the total reacted oxides of nitrogen; a positive correlation between these species is a common indicator of photochemical activity. However, as shown in Figure 7, an inverse correlation was frequently found during the morning flights over Phoenix as would be expected if ozone was being removed through its reaction with  $\text{NO}$ . Frequent reductions in ozone were observed as the aircraft sampled directly over freeways and other traffic-filled streets of Phoenix, suggesting that the observed pattern of high- $\text{NO}_y$ /low- $\text{O}_3$  near the surface and low- $\text{NO}_y$ /high- $\text{O}_3$  aloft was a result of  $\text{NO}$  removing ozone near the surface followed by this  $\text{O}_3$ -depleted air being mixed upward.

Past studies of the circulation patterns in Phoenix (Fast, et al., 2000) have shown that heating of the higher terrain north of Phoenix regularly produced thermally driven circulations from the south in the late

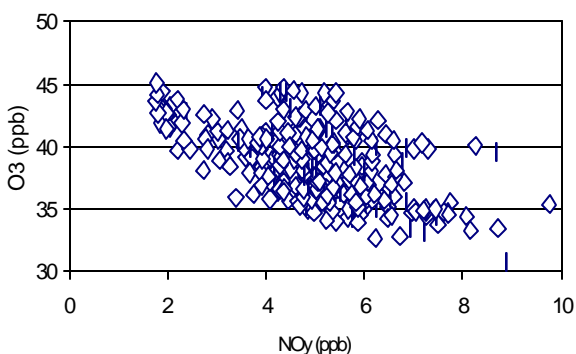


Figure 7. Scatter plot of  $O_3$  and  $NO_y$ , showing the inverse relation frequently observed during the morning aircraft sampling, and suggesting the removal of ozone by NO from auto emissions being mixed upward into the atmosphere, is still a significant process through mid-morning.

morning and afternoon, carrying the urban ozone plume to the north. A somewhat different feature was observed during the early morning measurements noted here, probably because the thermal circulations occurring during this more recent campaign had not yet started during the sampling times of the G-1. Rather than finding high ozone to the north of the city, we regularly found high values of  $NO_y$  directly over the major transportation corridors (e.g., in the vicinity of Sky Harbor Airport). A key component of morning  $NO_y$  is  $NO_x$  ( $= NO + NO_2$ ), tying it to automotive emissions. It seems unlikely this pattern would be observed later in the day with the onset of the thermally driven winds.

#### 4. SUMMARY AND FUTURE DIRECTIONS

A typical flight began with sampling in the residual boundary layer of the preceding afternoon, showing a

large vertical gradient in both chemical and meteorological species. With the development of the convective boundary layer, these gradients disappeared, and a more uniform value was found at all altitudes in the more slowly reacting species. Ozone levels were typically observed to be greatest aloft during the early morning hours, with values typically twice those found near the surfaces.  $NO_y$  was inversely related to ozone at the start of the flights, as would be expected from the  $O_3 + NO$  reaction, suggesting the upward mixing of  $NO_x$ -rich air with the downward transport of  $NO_x$ -poor,  $O_3$  rich air. The timing of the development of the convective boundary layer, as measured by the weakening of chemical stratification, appeared to be related to the intensity of the residual nocturnal stable layer.

#### 5. REFERENCES

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#### 6. ACKNOWLEDGMENTS

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