

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

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1. INTRODUCTION

We report here on combined meteorological and chemical trace-gas observations made from two levels of a skyscraper in downtown Phoenix, Arizona. These observations were made as part the U.S. Department of Energy's Phoenix Sunrise Campaign in June 2001. The focus of this campaign was to study the early morning chemical and meteorological transition period as an urban atmosphere develops from a stable to a convective state. The measurements to be presented here were designed to evaluate changes to the concentration of NO_x, VOCs, PAN and other photochemically active species at sunrise concurrent with the onset of mixing and chemistry. The Bank One observations were one component of an extensive set of meteorological observations and supporting air chemistry measurements designed to characterize the vertical structure of the lower urban atmosphere (Figure 1), as described in Doran, et al. (2002). Additional measurements were

available above the surface through a series of aircraft observations taken at approximately 300, 500, and 700 m AGL. Thus, the Bank One building provided two intermediate sampling levels within a much larger network of observations.

The motivation for this campaign developed from studies in other urban areas that found peak ozone values above the surface layer appeared to play an important role in governing the surface ozone concentrations in the early morning. The conceptual model for the design of our field campaign hinged on the development of a nocturnal stable layer via cooling at night. Phoenix was selected as a study site because of its heavy pre-dawn traffic, which is a common occurrence as workers schedule their days to avoid high daytime temperatures. As a result of this traffic we expected to find a rich mixture of emissions trapped close to the ground (below 200 m AGL) at sunrise. This rich mixture would be decoupled from air aloft at sunrise, which was expected to have its own unique chemical mix. With the

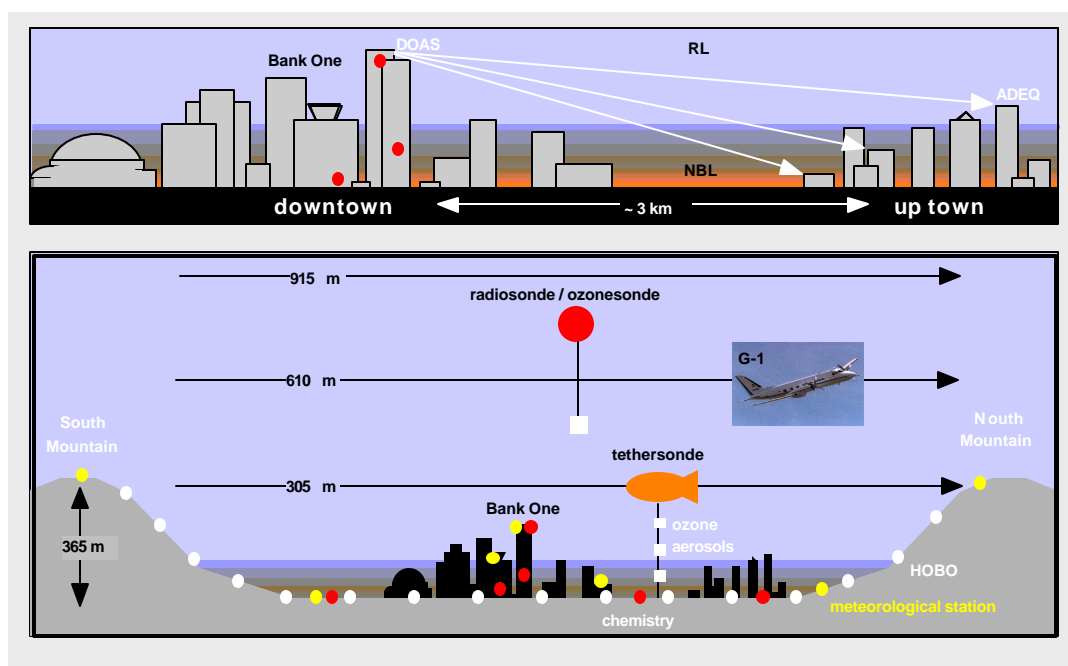


Figure 1. Experimental design of the Phoenix Sunrise Experiment.

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onset of sunrise and surface warming, these two layers would mix together, diluting surface pollutants into a deeper layer, and bringing air aloft down to the surface.

Sampling at two levels of a skyscraper was an ideal way to quantify this process. Measurements were made 24 hours a day, 7 days a week during the period from June 16-30. Observations made during the early morning hours at the 39th floor (~139 m AGL) were expected to be made above the nocturnal stable layer, while measurements made at the 16th floor (at ~73m AGL) would be within this layer at sunrise. We decided not to sample directly at street level so as to avoid contamination from idling vehicles or other very localized sources. As the day developed, we anticipated that observations from the 16th floor would measure changes associated with dilution as the mixed layer became deeper. In contrast, observations from the 39th floor were anticipated to characterize the chemistry above the nocturnal stable layer and the chemistry associated with the subsequent upward mixing of surface emissions.

2. OVERVIEW OF MEASUREMENTS

The observations made from the Bank One Building, and the organizations making these observations, are listed in Table 1.

One instrument unique to this field campaign was a differential optical absorption spectroscopy (DOAS) system. This system uses a technique that identifies and quantifies trace gases with narrow band absorption structures in the near UV and visible wavelength region in the open atmosphere. The advantages of DOAS are

the unequivocal and absolute identification of the trace gases, as well as the fact that trace gas concentrations are determined based solely on the absorption cross section. The DOAS system used in Phoenix consisted of a 500 W Xe-arc lamp as a broadband light source. The light from this lamp was fed into a double Newtonian telescope that sent and received a highly collimated light beam that was reflected back via a set of retroreflectors located on adjacent buildings. The spectral recording is made by a spectrograph-detector system connected to the telescope by a quartz fiber mode mixer. To study the vertical distribution of trace gases we mounted the telescope on the 39th floor of the Bank One. The three arrays of retroreflectors were mounted at a distance of 3.4 km at heights of 10 m, 40 m, and 120 m from the tops of other buildings in the uptown of Phoenix (Figure 1, upper panel). We alternated the direction of the telescope between the three arrays, resulting in a trace gas profile every 20 min. The following trace gases were measured (average detection limits, in parentheses, are given as 10^{10} molec. cm^{-3}): O_3 (5.5), NO_2 (0.35), SO_2 (0.18), HCHO (0.73), HONO (0.13), and NO_3 (0.01).

3. FIRST RESULTS

Figure 2 shows the time series of carbon monoxide, NO and ozone observed on the 16th and 39th floors of the Bank One Building, measured on the morning of June 26. The peaks observed between 0700 and 0800 LST were associated with the morning rush hour. Mixing ratios on both the lower and upper flow approached 1 ppm, although somewhat

Table 1. Observations from the Bank One Building

| Instrument/Measurement | 16th Floor | 39th Floor |
|--|------------|------------|
| Aerosol light scattering (b_{scat}) TSI 3563, 3 wavelengths; MRI-1550 | BCO | BCO |
| O_3 (TECO 49) | BCO | BCO |
| Temperature | BCO | BCO |
| Dewpoint temp. (GE 1011B) | BCO | BCO |
| Pressure | PNNL | PNNL |
| NO/NO_y ThermoEnvironmental 42S | BCO | BCO |
| PAN | BCO | BCO |
| Nitric and nitrous acid (API 365 MS) | BCO | |
| CO NDIR | BCO | BCO |
| Formaldehyde | BCO | |
| VOCs: Automated Canister Sampling System | ANL | ANL |
| Aerosol Samplers | ASU | |
| Elemental Aerosols | LUC. | |
| DOAS | | UCLA |
| NO_3 | | UAF |

Note: ANL = Argonne National Laboratory; ASU = Arizona State University; BCO = Battelle Columbus Operations; LUC = Loyola University at Chicago; PNNL = Pacific Northwest National Laboratory; UAF = University of Alaska at Fairbanks; UCLA = University of California at Los Angeles.

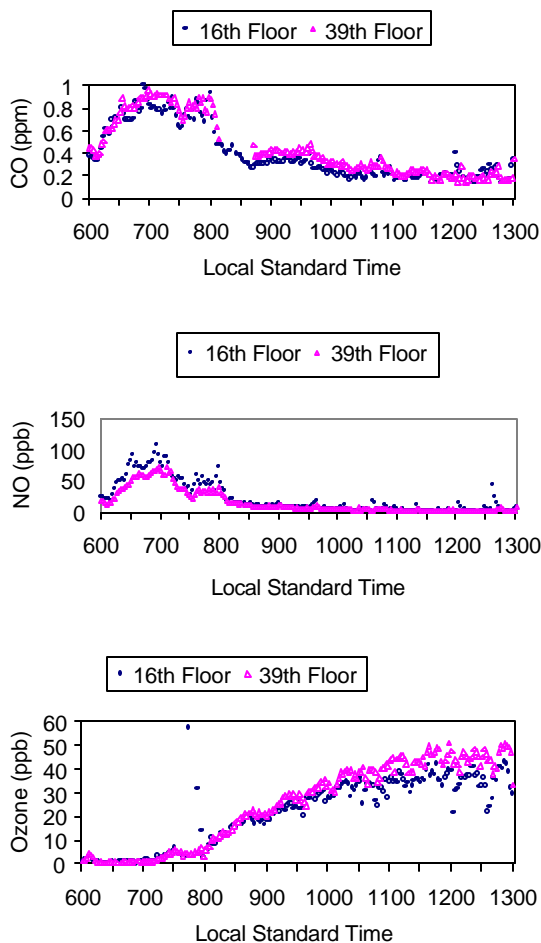


Figure 2. Time series of carbon monoxide, NO, and ozone on the 16th and 39th floor on June 26, 2001 between 0600 and 1300 LST.

surprisingly, the 39th floor detected higher values than those measured at the 16th floor. The greater value of CO aloft was found for both for the maximum value detected (at close to 1 ppm) and some hours after the maximum, between 0800 and 1100 LST. This gradient may be due to the horizontal transport of a CO-enriched air mass that did not mix down to the 16th floor.

NO is also associated with the morning rush hour of June 26. Following this morning spike the values quickly fell to lower levels. In contrast to the pattern previously noted for CO, greater values of NO were observed near the ground. This pattern is consistent with the emissions of NO at the ground by traffic and an upward mixing of these emissions. The maximum NO mixing ratios were observed at close to 0700 LST at both the lower and upper floors. Ozone at this time was measured to be less than 10 ppb, consistent with the reaction sequence $\text{NO} + \text{O}_3 \Rightarrow \text{NO}_2 + \text{O}$. We think this reaction, in addition to turbulent mixing, is also part of the explanation for the greater ozone values measured

at the 39th floor between 1030 and 1300 LST (Figure 3). There is a significant difference between the mixing ratios at these two levels, with the values aloft typically more than 10 ppb greater than the values near the ground.

Figure 4 shows the mixing ratios measured on the three DOAS light paths before sunrise and during the daytime hours of June 17. All trace gases show strong gradients throughout the night. At around 0730 LST the gradients disappeared and the mixing ratios along the three light paths followed each other closely. The simultaneously measured temperature profiles (Figure 5) also

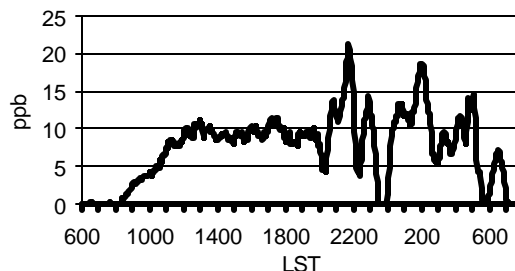


Figure 3. Time series of the difference in ozone at the 39th floors and the 16th floor, June 26, 2001. Positive values imply the values on the 39th floor were greater than those below. Note that the horizontal scale extends from 0600 LST on June 26 to 0800 LST on June 27.

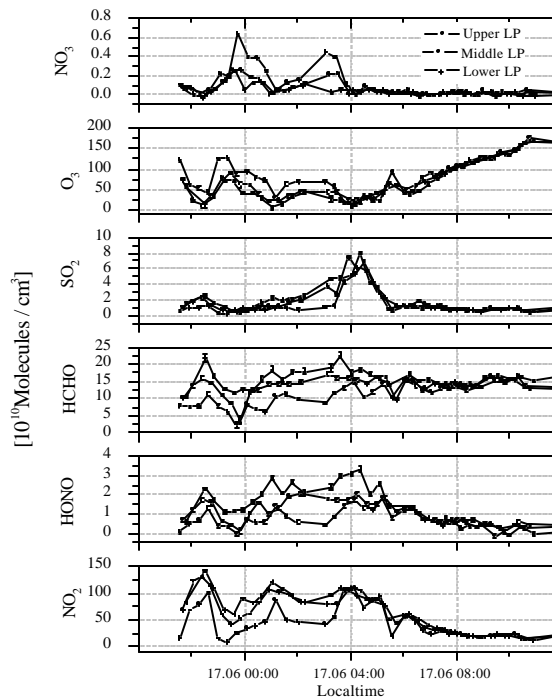


Figure 4. DOAS results for the morning of June 17. Time stamps are dd.mm hh:mm LST.

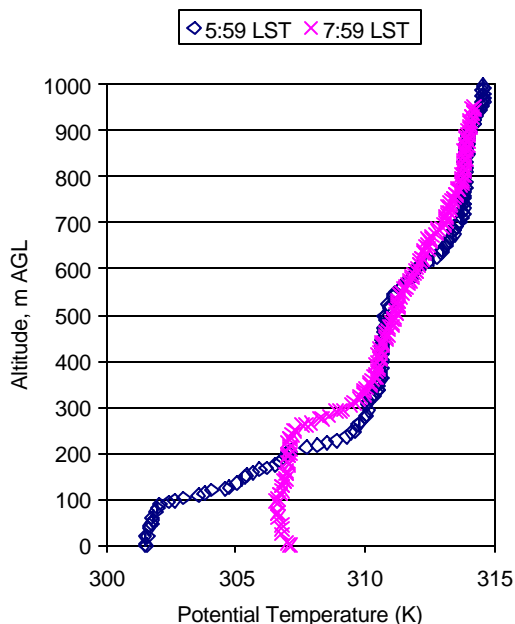


Figure 5. Temperature profile, showing the development of well-mixed layer during the morning of June 17, corresponding to the observations presented in Figure 4. Launch times are shown at the top of the figure.

detected a strong surface inversion before sunrise and then, with the onset of vertical mixing in the lowest 150 m of the atmosphere at 0730 LST, we measured the disappearance of the gradients. The simultaneous measurement of gradients of meteorological and chemical parameters is expected to greatly enhance our understanding of how chemical processes start at sunrise in an urban environment.

4. DISCUSSION AND FUTURE DIRECTIONS

Within the context of urban air quality, the buildup of ozone precursors in nocturnal boundary layers has been recognized for decades but relatively little attention has been given to quantifying how accumulations of ozone precursors in the nocturnal boundary layer affect chemical processes the next morning. Over flat, open terrain the effect on mid-afternoon chemistry may be relatively small but in basins and valleys the effect can be larger. Similarly, in the morning hours before the mixed layer has grown significantly, one can expect that

the effects of the nocturnal buildup will be important. For a sufficient description of the vertical distribution of pollutants prior to sunrise, one needs not only the concentrations of the critical species but both their horizontal and vertical spatial distribution.

We have presented a small set of the observations recently made from the Bank One Building in Phoenix, Arizona, during a field campaign that took place last summer. While each day will likely pose its own unique features, the first examination of the data here suggests a) the vertical extent of the boundary layer before sunrise is below 200 m and the concentrations of trace gases are very sensitive to the stability of the atmosphere, as shown by the observed gradients. Capturing these processes with an air quality model will require a very high degree of vertical resolution. b) Typically at night, and sometimes during the day, we would see lower concentrations of ozone at the ground, as expected from the titration of O_3 with NO . On June 26 this difference throughout much of the day was of order 10 to 15 ppb. It is not clear if this is a local effect associated with street canyons, or representative of what actually occurs over the entire city and environs. c) DOAS observations highlight the relationship between the gradient structure of reactive trace gases and meteorology at night.

Much work remains to be done with this data including simply examining the daily values. A much bigger task will be to synthesize the type of results, such as those presented here, with the associated meteorological observations and related chemical measurements made throughout the Phoenix area during this study.

5. REFERENCES

Doran, J. C., C. M. Berkowitz, and J. D. Fast. 2002. "The Phoenix 2001 Field Campaign: Evolution of Oxidants During the Morning Transition Period." To be presented at the Fourth Conference on Atmospheric Chemistry, January 2002, Orlando, Florida.

6. ACKNOWLEDGMENT

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