5.5 OZONE PRODUCTION IN THE PHOENIX URBAN PLUME

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1. INTRODUCTION

In May and June of 1998, the Department of Energy's Atmospheric Chemistry Program conducted an aircraft and surface based field campaign in Phoenix, Arizona, with the overall goal of obtaining a mechanistic understanding of O_3 formation in the metropolitan area. Participants in the study included scientists from the Arizona Department of Environmental Quality, Argonne National Laboratory, Brookhaven National Laboratory, and Pacific Northwest National Laboratory.

On most days, afternoon O_3 levels in the Phoenix air basin were within 20 ppb of morning levels, indicating a relatively inactive photochemistry, despite ample sunshine and high NO_x levels. Maximum O_3 levels were about 100 ppb, in contrast to the situation later in the summer when there are usually violations of the Federal 1 hour 120 ppb standard. In this article we present a preliminary analysis of the DOE G-1 aircraft observations pertinent to understanding the slow rate of O_3 production in the Phoenix air basin. Comparisons will be made to other locations where higher levels of O_3 and more rapid O_3 production have been observed.

2. EXPERIMENTAL

The DOE G-1 aircraft conducted flights in the mid-morning after the surface based inversion had lifted and in the afternoon following most of the days O_3 production. Sampling was done upwind, over, and downwind of the center city. Two standard flight patterns accounted for most of the G-1 flight hours. Figures 1a and b, depict these patterns using the June 1 flights as an example. Both patterns include a vertical profile to an altitude of 3000 m and flight segments over downtown Phoenix. In the AM, sampling was done to the west of the city, while in the PM sampling was done to east where prevailing winds are expected to advect the cities emissions.

The Phoenix-Mesa metropolitan area, which occupies much of the top half of Figures 1a-b, has a population of 2.5 million people. Most of the emissions in this region are from surface or near surface sources, in particular those associated with motor vehicles.

Measurements made from the G-1 included, O_3, NO, NO_2, NO_y, speciated VOCs, CO, H_2O_2, organic peroxides, HCHO, aerosol parameters, actinic flux, and meteorological variables. Instrumentation is similar to that deployed on previous field campaigns. See Weinstein-Lloyd et al (1996) for a description of peroxides, Lee et al. (1996) for HCHO, Kleinman et al. (1996) for VOCs and Nunnermacker et al. (1998) for the remaining trace gasses. See also, the companion paper by Nunnermacker et al. (2000). Hydrocarbon samples were collected in canisters and analyzed at York University for C2-C12 compounds. Figures 1a-b show the locations of the AM and PM hydrocarbon samples that are used in the subsequent analysis. All samples shown in this figure (a subset of the total collected during the field program) are at altitudes below 1800 m and were within the boundary layer.

3. TRACE GAS OBSERVATIONS

In order to get a broad view of trace gas concentrations in the Phoenix air basin, we have calculated average values in several regions which are shown in Figures 1a and b. Averages have been calculated using the time periods which are coincident with the filling of hydrocarbon canisters. Typically, 10 HC canisters were filled on each flight. Locations were selected so as to get a representative sampling of different areas and also to capture events that were judged to be interesting on the basis of real time observations made from the G-1. This sampling strategy yields a bias towards high O_3, more polluted conditions.

For each sample we have averaged the trace gas concentrations over the approximately 30 s time period needed to fill a HC canister. An exception is made for CO, where the averaging time was extended by 1 minute in order to improve the signal to noise ratio for that measurement. If observations were not available during the 30 s averaging period, for example due to an instrument being in zero mode, the averaging time for

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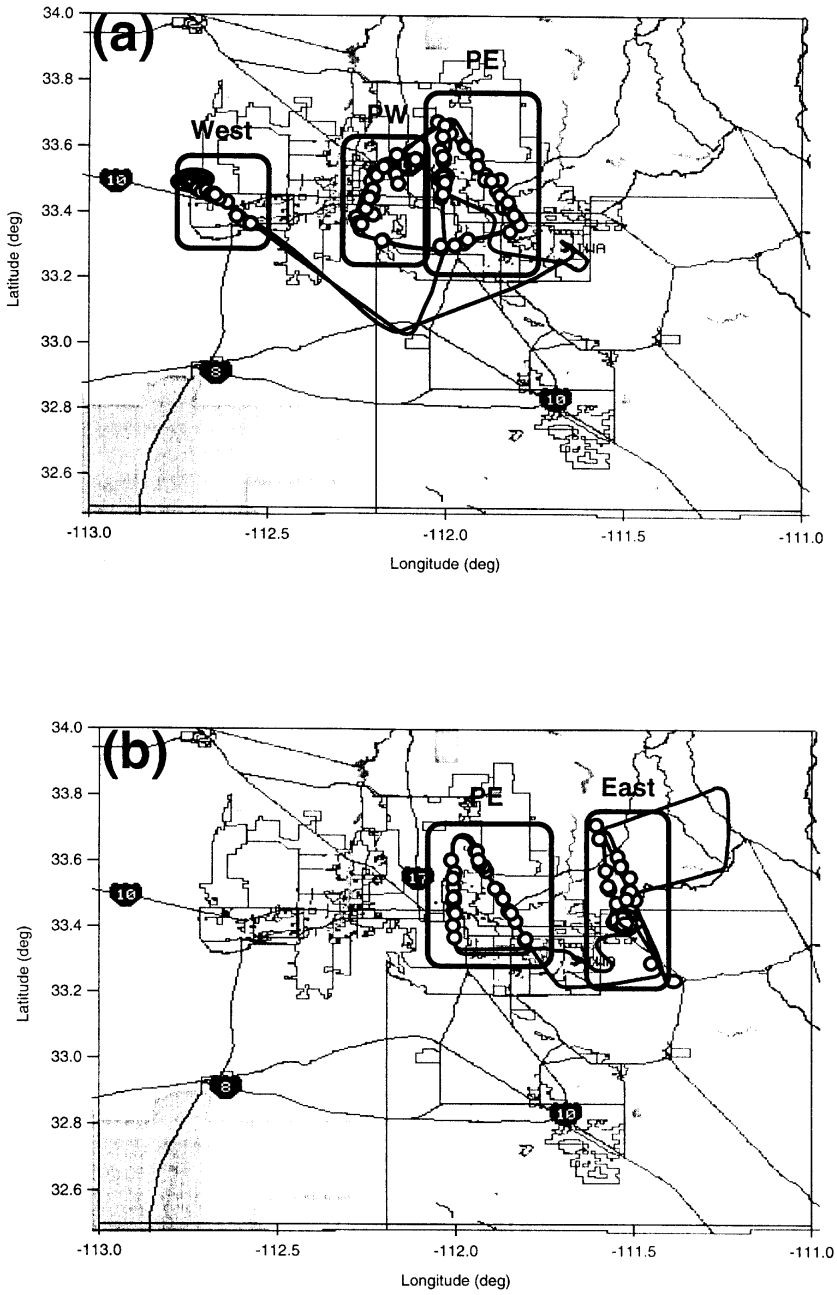

Figure 1. Map of the Phoenix air basin showing experimental areas in the (a) morning and (b) afternoon. Thick solid lines show the ground tracks of the DOE G-1 aircraft on June 1. Open circles indicate locations of hydrocarbon samples, from the whole field campaign, which are discussed in this study. Rectangular areas divide the hydrocarbon samples into subsets. Morning subsets are located to the west of the Phoenix Metropolitan area (West), and over the western and eastern parts of the Metropolitan area (PW and PE). Afternoon subsets are located over the eastern part of the Phoenix Metropolitan area (PE) and to the east of the Metropolitan area (East).

that instrument for that particular sample was extended by 1 minute. Missing HCHO data on several flights was estimated based on model calculations of its steady state concentration.

Table 1 shows average concentrations and physical parameters for 5 regions and time periods. Figures 2a and b provide a measure of the variability in these data sets by showing the percentile distributions for O_3 and NO_x/NO_y.

The East samples are from a region which is generally downwind of the city and where, according to surface observations, peak O_3 levels often occur. In 16 samples, O_3 levels averaged only 75 ppb, with a maximum value of 92 ppb. These samples have an average NO_x to NO_y ratio of 22% indicating that they have achieved most of their O_3 forming potential (Olszyna et al., 1994). There were 10 samples taken early in the morning to the west of the city providing an estimate of the background O_3 level which is the starting point for the current days photochemistry. A comparison with the East data set indicates an average O_3 difference of 20 ppb. As might be expected from the O_3 distribution shown in Fig. 2, this value can be smaller or larger on a given day. Samples taken on the western side of the city in the AM show high concentrations of primary pollutants; average NO_y and CO concentrations were 23 and 300 ppb, respectively. These are relatively fresh emissions as indicated by an average NO_x to NO_y ratio of 65%. On most days temperatures were high, there was little cloud cover, and winds were moderate.

Our task is to explain the relatively low values of O_3 found to the east of the city in spite of a large nearby source region. Without doubt many of the explanatory features will be meteorological having to do with the very high boundary layer height (approximately 3km in the afternoon) and the complex wind circulations in the Phoenix air basin. However, in this article we will focus entirely on chemical factors, in particular those related to the 20 ppb O_3 that can be attributed to same day photochemistry.

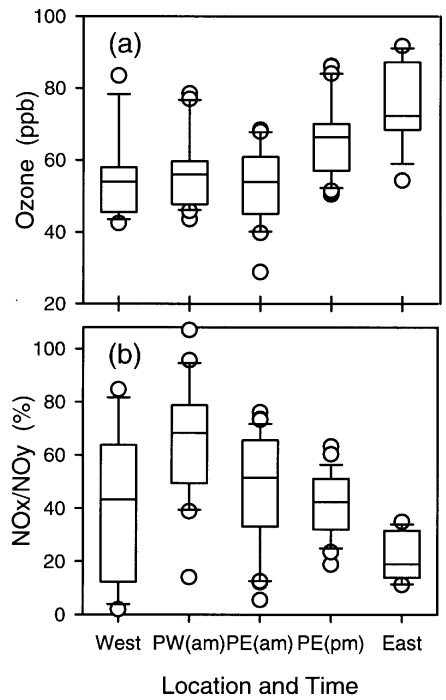

Figure 2. Percentile distributions of observed values for (a) O_3 concentration and (b) NO_x to NO_y ratio. Box covers interquartile range, between 25 and 75 percentiles. Whiskers are at 10 and 90 percentile. Line in box is median. Circles are values outside of 10-90 percentile range. Data subsets are for the regions defined in Figure 1a-b. West, PW(am), and PE(am) are data collected during morning flights. PE(pm) and East are data collected during afternoon flights.

4. CALCULATIONS

Constrained steady state photochemical calculations (Kleinman et al., 1998) have been performed for each of the hydrocarbon samples shown in Figs. 1a and b, provided that a "full set" of other trace gas information was available. Calculations use the RADM2 chemical mechanism (Stockwell et al., 1990) with a description of isoprene oxidation from Paulson and Seinfeld (1992). Photolysis rates for this set of calculations were obtained from a radiative transfer program (Madronich, 1987) applied to climatological conditions with zero cloud cover.

A steady state solution consists of the concentrations of rapidly reacting species; namely OH, HO_2, speciated RO_2, and NO_2 which are in equilibrium with the observed mixture of VOCs, CO, NO, O_3, HCHO, H_2O_2, and ROOH. Time of day, altitude, and H_2O concentration are also model inputs. In addition to concentrations, output variables include the primary rate of radical formation (Q), the rate of O_3 production ($P(O_3)$), and other variables reflecting chemical pathways and the sensitivity of O_3 production to changes in the concentration of NO_x or VOCs. Calculated variables are included in Table 1.

Table 1. Average Values of Measured and Calculated Quantities by Region and Time Period

Parameter	Region[1]				
	West	PW(am)	PE(am)	PE(pm)	East
Observed# samples[2]	10	20	39	28	16
Time (LST)	9:08	10:29	10:16	15:40	6:19
Alt (m)	898	827	996	987	1204
Dew Point (˚C)	0	1	0	-1	-3
O_3 (ppb)	56	57	57	66	75
NO_y (ppb)	4.6	23	13	10	8.7
NO_x/NO_y (%)	39	65	47	41	22
CO (ppb)	170	301	216	181	176
HCHO[3] (ppb)	1.3	2.1	1.6	1.7	1.4
Isoprene (ppt)	3	44	51	48	27
Anthropogenic HC(ppbC)	8.3	45	24	19	12
Calculated # samples[4]	7	16	31	23	13
Q (ppb/h)	0.7	1.4	1.1	0.9	0.6
$P(O_3)$ (ppb/h)	2.2	3.9	4.5	4.5	2.9
L_N/Q	0.56	0.95	0.82	0.89	0.64

[1] Regions are defined in Figures 1a and b.
[2] Total number of samples in region and time frame. Number of samples with valid concentration measurements will in general be less.
[3] Combination of measured and calculated steady state values.
[4] Number of samples with requisite measurements for calculation.

5. OZONE PRODUCTION

Distinguishing features of the Phoenix area are that biogenic emissions are low and that the atmosphere is very dry. Dew points are about 0˚C, at 800-1000 m altitude. Isoprene concentrations average less than 51 ppt. Both of these factors contribute to a low rate of radical production and O_3 formation.

The largest source of radicals in the boundary layer is normally photolysis of O_3 producing O^1D which can react with H_2O yielding 2 OH radicals. Water vapor concentrations are several fold lower than in the eastern U.S., limiting radical production from this route. HCHO is usually the second largest source of free radicals, accounting for 1/4 to 1/3 of the total. Following the analysis of Lee et al. (1998), we ascribe the low concentrations of HCHO in the Phoenix area to the near absence of the biogenic precursor, isoprene. Typical midday (i.e., 09:00-15:00) values for Q calculated for moderately polluted conditions in Nashville and NYC are 2-5 ppb h^{-1}. For comparison purposes we have re-calculated Phoenix radical production rates for a solar intensity appropriate to 14:00, arriving at values between 1.2 and 1.5 ppb h^{-1}, roughly a factor of 2 or more lower than in the other locations.

As discussed by Daum et al. (1999) in a study of oxidant formation in Nashville, the O_3 production rate in a high NO_x environment is given by

$$P(O_3) = Y\, Q\, k_1[HC]/\, k_2[NO_2] \qquad (1)$$

where Y is the average number of peroxy radicals formed from an OH + HC reaction, Q is the radical production rate, k_1 is an average rate constant for reaction of OH with hydrocarbons (including CO), and k_2 is the rate constant for reaction of OH with NO_2. That the Phoenix area exhibits high NO_x chemistry is demonstrated by the values of L_N/Q (the fraction of radicals removed by reactions with NO_x) given in Table 1. For air parcels evolving from a downtown source-like composition to the composition observed in the East, L_N/Q varies between 0.95 and 0.64. While Equation (1) is meant to apply in the limit that L_N/Q approaches 1, it should still be a reasonable representation over much of the range between 0.95 and 0.64. Equation (1) shows that the O_3 produced in the East samples was produced under conditions where the rate of production is proportional to the radical formation rate (Q) and also proportional to HC reactivity ($k_1[HC]$). Consequently, O_3 production rates will be low in Phoenix due to low water vapor concentrations affecting Q; and due to low biogenic emissions affecting Q through HCHO, and affecting VOC reactivity directly.

The photochemical calculations confirm the prediction of a low O_3 production rate in Phoenix. Table 1 shows that $P(O_3)$ varies between 3 and 5 ppb h^{-1} in the PW, PE, and East regions. Sensitivity calculations using a solar intensity appropriate for 14:00 yield a $P(O_3)$ between 4 and 8 ppb h^{-1}. These values are a factor of 2 or so lower than occur for "comparable" mid-day moderately polluted conditions in Nashville and NYC (Daum et al., 1999; Kleinman et al., 1999).

In order to quantify the effects of our calculated O_3 production rate on the total amount of O_3 formed downwind of Phoenix, it is necessary to take into account the time available for chemical processing and the amount of dilution that occurs while O_3 is being formed. At this stage of our analysis we can only offer a qualitative observation based on experience in other regions that an O_3 production rate of 4-8 ppb h^{-1} (at 14:00) is not going to produce a very high downwind O_3 concentration. The fact that O_3 standard violations occur later in the summer when the humidity, is higher is consistent with our argument that O_3 production is limited by the formation of free radicals, which in turn is limited by water vapor concentration as well as biogenically derived HCHO.

6. ACKNOWLEDGEMENT

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