9.4 OZONE PRODUCTION EFFICIENCY AT THE WILLIAMS TOWER

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1. INTRODUCTION

One of the monitoring sites established for the Texas 2000 Air Quality Study was on the 62nd floor of the Williams Tower Building in the Uptown Galleria area of western Houston (Figure 1). There were several reasons for establishing this site. At 830 feet above the ground, the 62nd floor is well above localized surface sources that often complicate the interpretation of observations from ground-level stations. And because the Williams Tower is at the western edge of the city (Figure 2), easterly flow was anticipated to result in sampling air that had recently passed over the major emissions of greater Houston, providing an integrated measure of the chemical mix coming from this highly industrialized area.

Observations from Williams Tower provide an excellent data set to evaluate a number of quantities related to the production of ozone. The first analysis we have done is to evaluate the efficiency by which ozone is produced in a parcel of air from the oxidation of NO_x

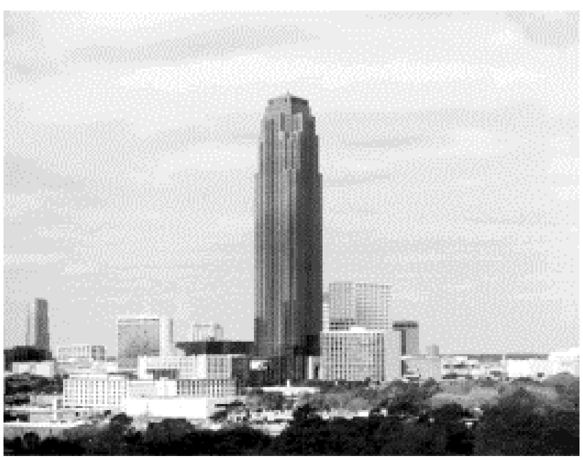

Figure 1. Williams Tower, looking to the southwest. Observations were taken from the top parapet.

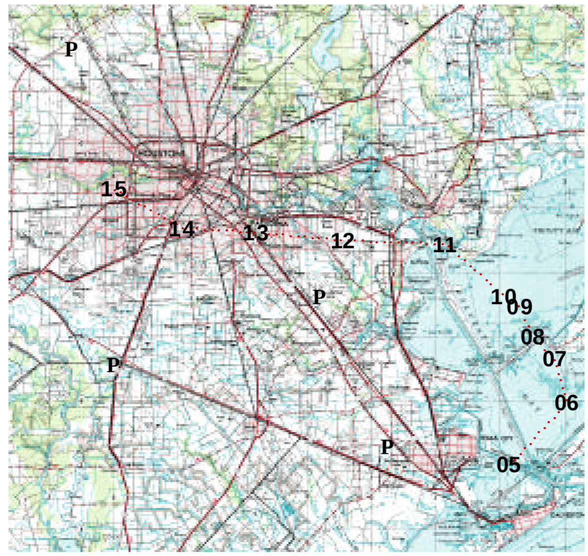

Figure 2. Map of the greater Houston area. The Williams Tower is at "15." Other numbers show local standard time along a back trajectory starting at 15:00 LST from the Williams Tower. Locations of the four radar wind profilers are indicated with "P."

(=NO + NO2) or, equivalently, the number of molecules of ozone produced per molecule of NOx. The oxidation of NOx results not only in the production of O_3, but also a variety of other compounds including PAN, HNO_3 and HONO. Because ozone production efficiency, or "OPE," is a measure of the anticipated efficacy of NO_x control strategies as part of broader emission reduction scenarios, it is of considerable practical interest. A small OPE is indicative of relatively inefficient chemical production of O_3 from volatile organic compounds (VOCs) and NO_x, whereas a large OPE indicates a comparatively efficient system.

Local emissions and meteorology can play a major role in defining the OPE. For this reason, estimates of OPE vary widely from place to place. Studies of urban plumes in the southeast United States suggest an OPE ~5–6, whereas in the drier climate of the southwestern United States, values are typically of order 3.

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It is important to note that OPE is a Lagrangian quantity; it applies to the changes resulting from chemical processes within a single parcel of air. For this reason we limit our analysis to periods of light winds and the relatively rapid onset of high ozone mixing ratios assuming that a single, albeit very large, air parcel is stationary over the Williams Tower, and that observed changes at this site during the selected study periods are predominantly a result of local chemical processes. Equivalently, we assume that the increases of ozone from one 15-minute period to the next under these conditions are a result of NO_x/VOC oxidation. During these intervals the loss of NO_x can be evaluated by the production rate of its oxidation products "NO_z," quantified as [PAN] + [HNO_3] + [HONO].

2. OVERVIEW OF MEASUREMENTS

Gas-phase and meteorological measurements made from the Tower included O_3, NO, NO_y (total nitrogen compounds), PAN, SO_2, CO, CH_2O, HNO_3, HONO, H_2O_2, volatile organic compounds, temperature, and moisture. The key species to be considered here are O_3 and NO_y. Ozone was measured using a commercial TECO 49 unit. NO and NO_y (total reacted oxides of nitrogen) were measured with a Thermo-Environmental 42S system. HONO and HNO_3 were measured using an API 365 mass spectrometer, and PAN was measured by gas chromatography. All values reported here are 15-minute averages.

3. FIRST RESULTS

A key set of supporting observations for these measurements came from four 915-Mhz radar wind profilers deployed throughout the Houston area. Relative to downtown Houston, these profilers were located to the northwest by Pacific Northwest National Laboratory at the Wharton Power Plant Site; to the southwest by NOAA's Environmental Technology Laboratory at the Houston SW Airport; to the southeast by Argonne National Laboratory at La Marque; and to the east by the Texas Natural Resources Conservation Commission at Ellington Field. The "Ps" in Figure 2 shows the locations of these profilers. The profiler observations were used to calculate back-trajectories from the Williams Tower. These calculations are time-dependent, constant altitude trajectories derived from the measured profiler winds between the lowest range gate and 200 m AGL.

The back-trajectory for the Williams Tower on August 21 at 15:30 LST is shown in Figure 2. The winds this afternoon were light and from the east. At mid-afternoon, air arriving at the Williams Tower had come from La Porte and the Houston Ship Channel. This east-to-west trajectory was part of the motivation for sampling at the Tower. Air sampled at the Tower had been over the greater Houston area for four hours (from 11 to 15:00 LST) preceding its arrival at the site.

On this day many surface monitoring stations throughout the Houston area reported ozone levels in excess of 125 ppb. The peak ozone mixing ratio observed at Williams Tower on this day was 205 ppb, observed at 15:00 LST. By way of contrast, a peak value of 164 ppb was observed at Bayland Park, a nearby surface-monitoring site operated by the Texas Natural Resources Conservation Commission. Although somewhat outside the scope of this particular paper, we note that ozone concentrations at the Williams Tower were frequently greater than concentrations measured at adjacent surface stations, particularly at night and early morning.

The time series of observed ozone and NO from the Williams Tower on August 21 during the daylight hours (Figure 3) showed several distinct features. The concentration of NO increased in the early morning, and reached a maximum that coincided with the start of heavy automobile emissions. Oxidant levels were low at the start of this period and increased until about noon. At this time the NO concentration dropped to ~1ppb.

From its definition, the ozone production efficiency within a parcel of air, over a time interval dt should be evaluated as

$$OPE = \frac{[O_3](t) - [O_3](t - dt)}{[NO_Z](t) - [NO_Z](t - dt)} \quad (1)$$

using the type of measurements shown in Figure 4. However, this calculation involves evaluating the ratio from two differences, hence it tends to amplify any noise in the measurements associated with instrument errors, short-term local variations in concentration, etc.

A more robust way to evaluate OPE comes from plotting $O_3(t)$ and $NO_z(t)$ on a common x-y plot. In such a figure, the values measured earlier in the time series of Figure 4 appear on the bottom left side, while the values measured later in this time series appear on the upper right side. The associated slope between points is a measure of OPE. Such a plot is shown in Figure 5.

The overall slope, and hence the overall estimate of OPE, based on the points in Figures 5, is 7, with the

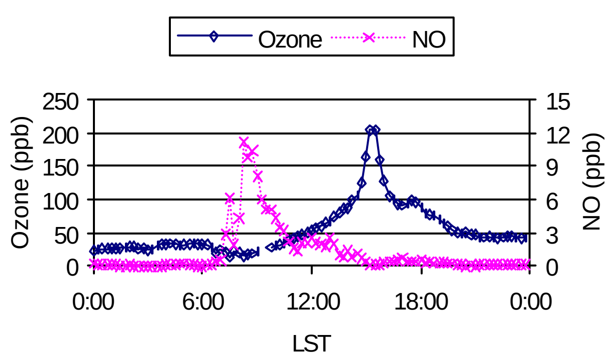

Figure 3. Time series of ozone and NO measured at the Williams Tower from pre-dawn to midnight, August 21-22.

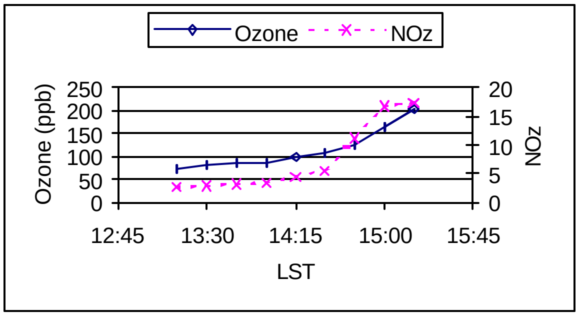

Figure 4. Enlargement of that part of the time series of NO_z and O_3 when both values were increasing, used to evaluate OPE.

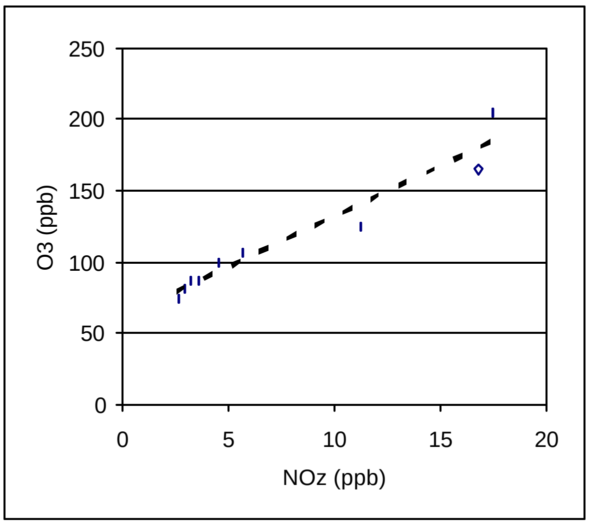

Figure 5. Scatter plot of Ozone and NO_z, using the values shown in Figure 4, from which OPE is evaluated during the period of peak photochemical activity August 21. The values on the lower left side were made earlier in the day whereas values shown in the upper right side represent observations later in the day. Dashed line is the best fit linear regression.

linear line of best fit used to calculate this slope having a correlation coefficient (r^2) of 0.93. Although not shown, most of the NO_z measured during this period of peak photochemical activity was in the form of PAN (with a maximum observed value of 15 ppb at 15:30 LST) and HNO_3 (with a maximum observed value of 3 ppb, also at 15:30 LST).

A second day with elevated ozone was measured throughout the greater Houston/Galveston area on September 6. The peak ozone reported from surface monitoring stations on this day was 150 ppb. Winds on the afternoon of September 6 were also light and had a more northerly component with the result that air at the Williams Tower came from north of the Houston Ship Channel (Figure 6). Although not shown here, the hourly ozone concentrations measured at Williams Tower were lower than those measured on August 21, with a peak ozone concentration of 110 ppb much earlier in the afternoon (at 13:34 LST) in contrast to the peak value of August 21, 204 ppb, measured at 15:30 LST.

The detailed time series from which we estimate OPE is shown in Figure 7, and the associated scatter plot of O_3 and NO_z is presented in Figure 8. The rate of increase in O_3 and NO_z were again relatively uniform throughout the day, allowing us to do a similar scatter plot analysis. For this case, we estimate the OPE ~12, with a correlation coefficient, r^2, of 0.99.

4. DISCUSSION AND FUTURE DIRECTIONS

We have presented an analysis of the ozone production efficiency in two air masses that had passed over the greater Houston metropolitan area on two separate days. These results, using preliminary observations from the Williams Tower, suggest OPE values, OPE ~ 7 on August 21, and OPE ~ 12 on September 6) somewhat larger, but certainly comparable, to estimates made for other sites. The days selected for analysis had relatively smooth increase in O_3 and NO_z during the time of peak photochemical activity, and were also characterized by light easterly flow with high regional levels of ozone. In doing this analysis, we have assumed that a) all sampling was within the same parcel of air over 15-minute time intervals, and b) all changes were associated with local photochemical processes, e.g., the change in NO_z associated with dry deposition of HNO_3 was relatively small compared to other processes.

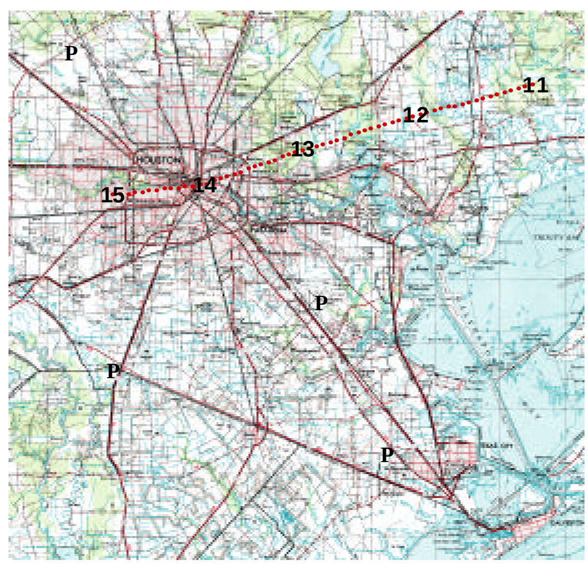

Figure 6. As in Figure 2, for September 6, 15:00 LST.

The preliminary OPE values reported here are comparable or only slightly greater than values reported elsewhere; we find this somewhat surprising given the very high ozone mixing ratios frequently measured throughout the Houston/Galveston region. However, before making any final conclusions, we plan to carry out the analysis presented to other suitable periods during the Texas 2000 Air Quality Study. In addition, we are planning two major refinements to this study.

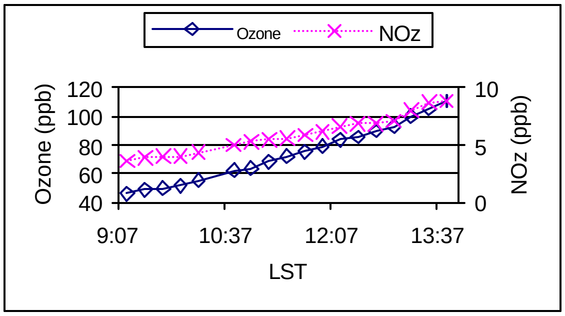

Figure 7. As in Figure 4, for September 6.

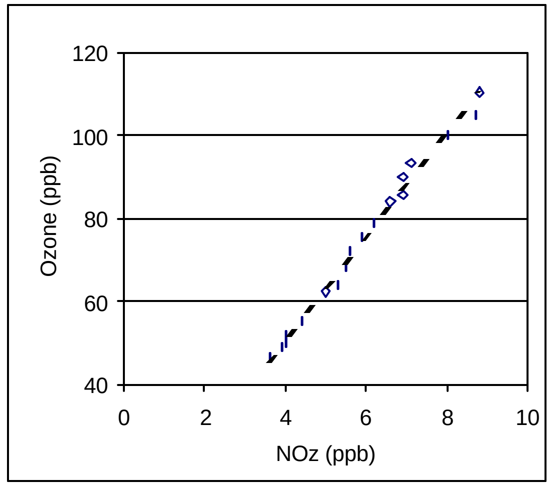

Figure 8. As in Figure 5, for September 6

First, we anticipate using a photochemical box model to evaluate a number of quantities associated with the production of ozone at the Williams Tower, using the observations from this site to initialize the model. An automatic by-product of these calculations will be a theoretical estimate of the instantaneous ozone production efficiency, evaluated directly from the ratio of the numerical derivatives of d[O_3]/dt and d[NO_z]/dt.

The second refinement to this work will build around the previously noted point that ozone production efficiency is a Lagrangian quantity that applies to chemical changes within a single parcel of air. Evaluating OPE per its basic definition should be done by comparing the O_3 and NO_z within a parcel at one location against values measured in the same parcel at a later time and different location. Such Lagrangian measurements are usually very difficult to make in the field given the uncertainties of parcel movement. However, the trajectory fields coming from the profiler measurements made during the Texas 2000 Air Quality Study may allow for such an evaluation by using observations made at surface sites in the vicinity of the Houston Ship Channel (La Porte, Deer Park) with measurements taken several hours later at the Williams Tower. These two sets of numbers may yield an estimate of OPE based on the fundamental definition of this quantity.

5. ACKNOWLEDGMENT

We gratefully acknowledge the support of the Texas Natural Resources Conservation Commission in working with us to set up the Williams Tower site. We are also very appreciative of the work by Chris Doran (DOE/PNNL), Wayne Angevine (NOAA/ETL), Tim Martin (DOE/ANL), and Dan White (TNRCC) for providing us with the profiler observations used in our back trajectory calculations. A large part of the scientific support for the observations made from Williams Tower came from the U.S. Department of Energy's Atmospheric Chemistry Program. Pacific Northwest National Laboratory is operated for the U.S. Department of Energy by Battelle Memorial Institute under contract DE-AC06-76RLO 1830.