

Phenomena that Influence High Ozone Concentrations in the Paso del Norte Area

98-WA69.05 (A857)

Clinton P. MacDonald, Paul T. Roberts, Hilary H. Main, and Timothy S. Dye

Sonoma Technology, Inc. 5510 Skylane Blvd., Ste. 101, Santa Rosa, CA 95403

James Yarbrough

U.S. EPA, Region 6, 1445 Ross Avenue, Dallas, TX 75202

ABSTRACT

This paper summarizes the results of analyses of meteorological and air quality data for the 1996 Paso del Norte Ozone Study. The purpose of these data analyses was to develop an understanding of the significant chemical and physical processes which lead to high concentrations of ozone in the Paso del Norte study region which includes El Paso, TX; Sunland Park, NM; and Juarez, Mexico. This analysis has shown that the high ozone concentrations are a result of slow convective boundary layer growth, reduced convective boundary layer depth, light surface winds, and high morning surface ozone precursor concentrations. Overlying meteorological conditions observed during high ozone episodes include an upstream aloft high pressure system, aloft warming, and weak surface pressure gradients. The analysis has also shown that aloft carryover of ozone and ozone precursors does not significantly contribute to the surface ozone concentration. Furthermore, hydrocarbon and NO_x data, although spatially limited, show that the system is most often NO_x rather than VOC limited.

INTRODUCTION

El Paso County fails to meet the National Ambient Air Quality Standards (NAAQS) for carbon monoxide (CO), particulate matter (PM-10), and ozone (O₃); it may also exceed the new proposed 8-hr ozone NAAQS and the new fine PM NAAQS. Adjoining Sunland Park exceeds the NAAQS for O₃ and PM-10. Juarez air quality exceeds Mexican ambient standards (which are similar to those of the U.S.) for O₃ and CO. Very high concentrations of PM-10 are also sampled in Juarez, and the Mexican ambient standard for total suspended particulates (TSP) is likely violated there as well. U.S. controls since the 1970s have significantly reduced volatile organic compound (VOC) emissions in El Paso, but this has not resulted in attainment of the ozone NAAQS in El Paso.

The U.S. and Mexico signed Annex V to the 1983 La Paz Agreement in 1989 and agreed to jointly monitor, gather emissions information, and model the airshed to determine which control strategies would most efficiently improve air quality. A U.S.-Mexico Binational Air Workgroup (formed in 1984) has sponsored several major field studies since 1989 to better understand the physical causes of the pollution and has sponsored the development of the first quality-assured air monitoring network in a Mexican border city. These bilateral data collection efforts continue.

An agreement between the U.S. Environmental Protection Agency (EPA) and the Texas Natural Resource Conservation Commission (TNRCC) in 1991 established 1999 as the target date for completion of all data collection and air modeling activities necessary to fulfill the Annex V

requirements. Much of the data collected prior to 1996 focused on PM-10 and CO, which have wintertime maxima in this airshed. Thus, a major field study was conducted during the summer of 1996 to provide data sufficient to support photochemical air dispersion modeling for ozone.

The objective of the data analyses was to develop an understanding of the significant chemical and physical processes which lead to high concentrations of ozone in the study region and to support modeling. The analyses provide an understanding of the phenomena which must be reproduced by the models and provide data and tools for model evaluation. They also provide a means of evaluating the quality of the field data which are used in the models and information on the appropriate boundary and initial conditions to use during the meteorological and photochemical modeling.

This paper presents a discussion of the data used in the analysis followed by a presentation of the phenomena that influence surface ozone concentrations. These phenomena include the contribution of aloft ozone and ozone precursors to daytime surface ozone concentrations, the growth of the convective boundary layer (CBL) and vertical mixing, and the horizontal dilution of ozone and ozone precursors by surface winds. The paper then discusses the overlying meteorology that controls the growth of the CBL and the strength of the surface winds under high ozone conditions. Finally, the paper presents the results of hydrocarbon data analysis used to determine VOC/NO_x ratios and to assess if ozone formation is NO_x or VOC limited. These results are then combined to form a conceptual model of ozone formation in the El Paso-Cuidad Juarez-Sunland Park area. Roberts¹ contains a full discussion of study details and findings.

Because the interpretative data analyses integrate large amounts of information to describe the evolution of pollutant concentrations in the region and the relevant physical and chemical processes that influence ozone concentrations, these analyses have focused on episode days and used a "case study" approach, rather than a "climatological" approach.

DATA AVAILABILITY

The data collected during the 1996 Paso del Norte Ozone Study used in this analysis include continuous surface and aloft monitoring of air quality and meteorological conditions. The field program also included noncontinuous measurements of aloft and surface air quality on selected Intensive Operations Period (IOP) days. IOP days were selected by forecasts for high ozone concentrations during the period from August 3, 1996 - September 21, 1996.²

Surface Data

Routine surface meteorological and air quality data were obtained directly from Areometric Information Retrieval System (AIRS), TNRCC, Los Alamos National Laboratory (LANL), New Mexico Environment Department, Western Regional Climate Center, El Paso City-County Health and Environmental Department, AeroVironment (AV), and Sonoma Technology, Inc. (STI). Figure 1 shows a map of the study area with the locations of the monitoring stations.

The routine data collected at most sites include O₃, NO_x, NO, temperature, and wind speed and direction. Some sites also collected CO, SO₂, relative humidity, solar radiation, pressure, and precipitation data. Routine hydrocarbon samples were collected at three sites as part of existing network operations. Nonroutine surface hydrocarbons and carbonyl data were also collected on several days during the field program at 12 of the 19 air quality/meteorological monitoring sites. Some survey samples were collected twice per day at various sites in Juarez and El Paso.

Aloft Data

As part of the 1996 Paso del Norte Ozone Study, aloft air quality and meteorological measurements were performed. Throughout the field study period, continuous measures of aloft wind and virtual temperature were made using radar wind profilers, Doppler acoustic sounders (SODAR), and radio acoustic sounding systems (RASS) (Figure 1). During the IOP period from August 3 to September 21, a total of 21 aircraft sampling flights were flown encompassing 16 days including August 11, 12, and 13, and 13 days in September. During the flights, the aircraft measured continuous O₃, NO, NO_y, temperature, dewpoint temperature, altitude, and position. Integrated grab samples for VOCs and carbonyls were also collected during most flights. Typically, the aircraft flew vertical spirals over designated sites, reporting vertical profiles of pollutant concentrations from just above the surface to about 1500 m agl. A hot air balloon was also flown in the El Paso-Juarez area to collect O₃, NO, NO_x, temperature, VOC and carbonyl grab samples, altitude, and position data. The balloon collected data on three mornings: September 9, 13, and 17. Ozone, NO_x, NO, and meteorological data were also collected at various locations in Juarez using a tethersonde. The tethersonde data were collected on August 12-14 and September 9, 13, 17, 18, and 21.

The aircraft and balloon monitoring flights were designed to provide information about boundary pollutant concentrations for use in models and to assess aloft vertical and horizontal pollutant gradients, mixed layer depth, the existence of elevated high pollutant concentration layers, and pollutant carryover potential. The flights were also used to provide information to determine possible local and regional aloft ozone and ozone precursor transport. Furthermore, because aloft data were collected near surface monitoring sites, comparisons between surface and aloft data were made to assess data validity and pollutant gradients between the surface and aloft air parcels.

IMPORTANT PHENOMENA

Analysis of surface and aloft air quality and meteorological data during two ozone episodes, from August 12 to 14, 1996 and from September 3 to 7, 1996, showed that the mixing depth growth rate and the surface winds are the primary physical phenomena that influence ozone concentrations in the area. Analysis has also shown that carryover of ozone from the prior day does not play a significant role in peak ozone concentrations. The following discussion presents the data analyses illustrating these phenomena and how these phenomena influence ozone concentrations, including a presentation of the synoptic features that control these mechanisms during the ozone episodes.

To understand how these phenomena influence ozone concentrations, days were compared that had similar weather, except for the feature being examined. In particular, days with similar wind patterns but different mixing depth growth rates (MGRs) were compared to examine the influence of mixing heights and MGR on peak ozone concentration. Likewise, to examine the effect of surface winds on peak ozone concentrations, days with similar MGR and mixing heights but different surface wind patterns were compared. In particular, on August 12 and 13, morning surface winds were light, but the MGRs were different. Whereas, on August 13 and 14, the MGR and mixing heights were similar, but the morning surface wind speeds were different. On August 12, 13, and 14, peak surface ozone concentrations reached 77, 137, and 87 ppb, respectively.

Before proceeding with the analysis, it is useful to define the major components of the Planetary Boundary Layer (PBL), which are the nocturnal boundary layer (NBL), convective boundary layer (CBL), and the residual layer (RL) as shown in Figure 2. The NBL forms at night when air near the surface cools. In response to this cooling, stable conditions reduce vertical mixing in the NBL, thus confining surface-based pollutants to the lowest several hundred meters. Starting shortly after sunrise, the CBL grows as thermals vertically mix heat, moisture, momentum, and pollutants. At sunset, these thermals decay and the stable conditions of the NBL return. Aloft at this time, a RL remains and initially has the characteristics of the recently decayed CBL.²

Carryover

Past ozone studies have shown that ozone and ozone precursors from previous days can contribute significantly to the following day's maximum ozone concentration. For example, data analyses for the 1990 San Joaquin Valley Air Quality Study concluded that residual ozone could account for 80 to 100 percent of the afternoon surface maximum ozone concentration on days with high ozone concentrations.³ Early morning aircraft air quality data were examined to explore potential ozone and precursor carryover in the Paso del Norte area.

Comparisons of all early morning aircraft spirals show similar aloft ozone concentrations on all days examined. This includes days when peak ozone concentrations were no greater than 70 ppb, a day when ozone reached 137 ppb, and several days when peak ozone concentrations were between 70 and 137 ppb. Predawn morning aircraft flights on high ozone days showed relatively low aloft ozone concentrations ranging from 45 to 65 ppb, only 5 to 25 ppb above natural background concentrations. Likewise, morning aircraft flights on low ozone days showed ozone concentrations ranging from 45 to 65 ppb. Figure 3 shows an early morning aircraft spiral near Ciudad Juarez Airport (CJS) on the episode day of August 13. CJS is located about 10 km south of Downtown El Paso. This plot shows the vertical profile of ozone, NO_y, NO, temperature, and dew point as observed by the aircraft at about 0445 MST. This vertical pollutant profile is representative of vertical pollutant profiles on other low and high ozone days for early morning flights. Above the NBL at 1250 m msl, ozone concentrations range from 50 to 65 ppb. From the top of the NBL to the surface, ozone concentrations decrease rapidly due to apparent titration by fresh NO emissions emitted in and confined to the NBL.

Like ozone, comparisons of all early morning aircraft spirals on low and high ozone days show no discernible difference in aloft NO_y or NO above the residual layer. NO_y and NO concentrations above the residual layer were typically around 2.0 ppb and 0.2 ppb, respectively. NO and NO_y concentrations within the residual layer and in the NBL were higher, with maximum concentrations near the surface where sources are located. As shown in Figure 3, the NO_y concentrations in the NBL range from 8.0 ppb near the surface to about 2.0 ppb at the top of the NBL (1250 m msl). A similar NO profile is also observed within the NBL; the NO concentrations range from approximately 1.0 ppb at the surface to 0.2 ppb at the top of the NBL. The decrease of NO_y and NO through the NBL is indicative of slow mixing of NO_y and NO from emission sources beneath the NBL. The fresh surface emissions in the NBL are significantly constrained on August 13 as indicated by the short, sharp rise in NO_y concentration and the short, sharp drop in ozone within the NBL. This is likely a result of the strong nocturnal inversion observed on August 13.

Based upon the similar aloft ozone and NO_y concentrations between days with high and low peak surface ozone concentrations and the relatively low aloft ozone and NO_y concentrations, it appears that aloft carryover was not a major contributing factor to high ozone concentrations measured at the surface.

Although it is likely that aloft carryover of pollutants does not play a major role in peak ozone concentration, the observed aloft NO, NO_y, and ozone concentrations should be used to set appropriate initial and boundary conditions for photochemical models. Above the NBL up to about 3000 m msl, ozone concentrations are about 45 to 65 ppb; NO_y concentrations are about 1.0-2.0 ppb; and NO concentrations are about 0.1-0.2 ppb.

Mixing Depth Growth Rate

The growth and depth of the mixed layer is critical for understanding the day-to-day differences in ozone concentrations. Previous work² showed that exceedance days typically had slower daytime boundary layer growth than non-exceedance days. The results presented below examine these observations in the El Paso-Cuidad Juarez-Sunland Park area.

Radar wind profiler (RWP) reflectivity data can be used to infer mixing depths. To estimate mixing depths from RWP data, the returned signal strengths are used to estimate the refractive index structure parameter (C_n^2). Both theoretical and empirical studies have shown that C_n^2 peaks at the inversion located at the top of the CBL, due to warm, dry, aloft air entraining into cooler and moister air below the inversion². Generally, C_n^2 measured by boundary layer profilers will not resolve low-level inversions associated with the top of the NBL when such inversions are less than about 200 to 300 m agl. Consequently, T_v data collected by RASS are used, coupled with surface T_v measurements, to provide estimates of the depth of the NBL.

To investigate the role that the evolution of the CBL has on surface ozone concentration, hourly mixing depths at the El Paso Downtown (ELD) profiler site were estimated for the August 12-14 and September 3-7 periods. These hourly mixing depths were produced using a combination of radar profiler, RASS, and aircraft data. Comparisons of the mixing depths estimated at ELD with two other sites in the area showed similar CBL evolution and thus gave us confidence in the results. From these hourly mixing depths, daily morning MGRs from 0600 to 1200 MST were calculated for each day and compared to peak ozone concentrations in the downtown area. The 1200 MST cutoff time was chosen because it was the most frequent time that the maximum ozone concentration occurred. Because horizontal transport by surface winds can negate or accentuate the effect of the MGR on ozone concentration, mornings with significant surface winds (including August 14, September 3, and September 5) were considered separately from the following mixing height analysis.

Review of the ozone exceedance of August 13 showed that the mixed layer at the downtown ELD site grew much slower compared to August 12, when ozone concentrations were lower. This is important because the slower MGR resulted in reduced vertical mixing of morning emissions so that chemical reactions may have occurred in the presence of higher ozone precursor concentrations on August 13. This may have been one factor that led to higher peak ozone concentrations.

Figure 4 shows time-series plots of mixing depth at the ELD profiler site for August 12-14. Table 1 shows the daily morning MGRs from 0600 to 1200 MST and the peak ozone concentrations in the downtown area for August 12-14 and September 4-7. As shown in Table 1

and Figure 4, the MGRs on August 13 were significantly slower compared to August 12. At the downtown site (ELD) the MGR was 150 m/hr on August 13 compared to 380 m/hr on August 12. The slow MGR on August 13 likely resulted in higher ozone concentrations by increasing pollutant concentrations from surface emissions as indicated by the 0600 to 1000 MST average downtown CO, NO_x, and NO concentrations. The average 0600 to 1000 MST downtown CO concentrations were 1229 ppb on August 12 compared to 2358 ppb on August 13. Significantly higher NO_x and NO concentrations were also observed on the morning of August 13 compared to August 12. The slower growth rates combined with the higher precursor concentrations may partially account for the high ozone (137 ppb) observed at Chamizal (ECH) on August 13, whereas the quick increase in the mixing depth and lower precursor concentrations may account for the modest ozone peak (77 ppb) on August 12.

Besides the MGR playing a major role in peak ozone concentration, analysis has shown that the depth of the mixed layer during the evolution of the PBL may also be important. Like August 13, slow MGR was also observed on September 4. The MGR at ELD on September 4 was similar to the MGR on August 13 (Table 1). However, peak ozone concentrations were 19 ppb lower on September 4 than on August 13. The lower ozone concentrations on September 4 compared to August 13 may be partially attributed to the deeper midmorning mixed layer on September 4. Although both August 13 and September 4 exhibit similar MGR between 0600 and 1200 MST, the 0900 MST mixing depth on September 4 was about 250 m deeper than the mixing depth on August 13 at the ELD site. The more confined volume before 0900 MST on August 13 could result in chemical reactions occurring in the presence of higher ozone precursor concentrations on that day.

The difference in the peak ozone concentration between August 13 and September 4 may also be partially attributed to slightly stronger surface winds on the morning of September 4 than on August 13. Slightly stronger surface winds did not allow precursors to accumulate as much on September 4 as on August 13, thereby decreasing their concentrations and ultimately, the resulting ozone concentrations.

Thus, slow MGR combined with shallow mixing depths results in high ozone concentrations for two reasons. First, when the MGR is slow and the mixing depth shallow, ozone precursors are confined to a smaller volume than with faster MGRs and a deeper mixed layer. The smaller volume increases precursor concentrations for a given emissions input. Higher precursor concentrations resulted in higher ozone concentrations. Furthermore, slow MGRs mean that ozone chemistry took place under high precursor concentrations. Higher precursor concentrations are observed on August 13 (slow MGR day) compared to August 12 (fast MGR day).

Dispersion (non-accumulation of emissions)

Although slow MGRs played a significant role in producing high ozone concentrations, high ozone concentrations did not occur under conditions of moderate-to-strong morning surface winds. When surface winds were moderate-to-strong, ozone precursor emissions were dispersed horizontally, which decreased their concentration. On windy days, lower peak ozone concentrations with broader horizontal extent occurred because photochemistry occurred under low precursor concentrations. Note that when dispersion is referred to, it means the nonaccumulation of pollutants in source regions due to advection of the pollutants by surface winds.

As mentioned above, August 14, September 3, and September 5 all had relatively strong morning winds. Of these three days, August 14 and September 5 had slow MGRs. The mixing growth rate at ELD on August 14 was only 120 m/hr, 30 m/hr slower than on August 13. However, the peak downtown ozone concentration on August 14 was only 79 ppb compared to 137 ppb on August 13. Likewise, the mixing growth rate at ELD on September 5 was only 150 m/hr, the same as on August 13. The peak downtown ozone concentration on September 5 was only 60 ppb. Given the potential for surface carryover from August 13 to August 14 and from September 4 to September 5, combined with slow MGR on both August 14 and September 5, it becomes evident that dispersion of pollutants by wind plays a significant role in the low peak ozone concentrations on August 14 and September 5.

Dispersion of ozone precursor emissions by moderate morning winds was made evident by the relatively lower NO_x and NO concentrations near downtown source areas and relatively higher concentrations in downwind areas. Contrarily, on stagnant mornings, higher NO_x and NO concentrations were confined to the downtown area with lower concentrations observed at rural sites. On the light wind day of August 13, morning NO_x concentrations of about 200 ppb were observed at source regions whereas, on the windy day of August 14 morning NO_x concentrations of about 80 ppb were observed at source regions. Also, on the morning of August 13, the non-source site Desert View Elementary School (NDV) had NO_x concentrations of about 20 ppb; whereas, on the morning of August 14, downwind of the source area at NDV, NO_x concentrations of 40 ppb were observed. On September 5 spatial characteristics in NO_x concentrations were similar to those on August 14. This again reinforces the effect of dispersion on ozone precursor concentrations.

The effect of dispersion on pollutant concentrations is also apparent in the observed CO concentration patterns. On August 13, high CO concentrations were observed in the downtown area and lower concentrations were observed away from source areas. Like NO_x concentration patterns, on the windy day of August 14, lower morning CO concentrations were observed near downtown source areas and higher concentrations were observed in downwind areas compared to the light wind day of August 13.

The effects of dispersion on ozone and ozone precursors can be summarized as follows. On light wind days, the morning precursor “cloud” has high NO_x, NO, and CO concentrations and is confined to the source region, as observed on August 13, resulting in high ozone concentrations. On days with moderate wind, the wind disperses the source “cloud” and maximum precursor concentrations are lower, but more widely distributed, as observed on August 14, resulting in lower ozone concentrations. On days with high ozone concentrations, the midday ozone “cloud” with the highest ozone concentrations is confined to the source region, or slightly downwind (Figure 5). On days with lower ozone concentrations, maximum ozone concentrations are lower, but more widely distributed (Figure 6).

Synoptic Weather

Having shown that the MGR and surface winds play significant roles in peak ozone concentration, it was necessary to determine the possible mechanisms that control these phenomena. Previous work for the NARSTO-Northeast⁴ showed that slower daytime boundary layer growth was caused by an increase in aloft stability. It also showed that the increase in aloft stability was a result of aloft warming due to a combination of warm air advection and

subsidence. The results presented below examine these mechanisms in the Paso del Norte area.

It was suspected that a strengthening of the nocturnal or subsidence inversion likely caused slower MGRs and lower midmorning mixing heights in the Paso del Norte area. To explore this theory, RASS virtual temperature data, surface temperature data, and the MGRs were examined. Synoptic charts were also examined for the possible causes for a strengthening of the inversion, including warm air advection aloft, strong subsidence aloft, or surface cooling. It was also suspected that the upper-level forcing which influences surface pressure gradients was also responsible for changes in surface flow patterns. To explore this theory, synoptic charts of surface winds were analyzed.

A comparison of the RASS virtual temperature data on the fast-mixed layer growth day of August 12 to the slow-mixed layer growth days of August 13 and 14 shows differences in aloft temperature and early morning aloft-surface temperature gradients. Figure 7 shows the 0600 MST virtual temperature profiles on August 12, 13, and 14 at ELW. The ELD data were not used because of incomplete temperature profiles. As shown in Figure 7, the aloft virtual temperatures on August 12 were cooler than on August 13 and 14. On August 12, the peak aloft temperature was 24.4°C, warming to 25.7°C on August 13 and to 27.7°C on August 14. This warming aloft from August 12 through 14 was also observed on the synoptic charts. On August 12 at 0600 MST, the 850 mb observed temperature was approximately 25°C, warming to 30°C on August 13 and 14. More importantly, the difference in surface temperature and maximum aloft temperature (representing the strength of the inversion) also increased during this period from 6.5 °C on August 12, to 8.7 °C on August 13, and finally to 9.7°C on August 14. Surface data shows that this increase in inversion strength was a result of aloft warming rather than surface cooling. The stabilization of the aloft air from August 12 to 14 likely caused the daily growth rate of the mixed layer to slow each day through the period.

Besides the growth of the mixed layer being controlled by aloft warming, it is also controlled and driven by the surface heat flux, the amount of energy available for heating the air in the PBL. However, the surface heat flux was nearly identical on August 12, 13, and 14. Again, as discussed above, the temperature sounding was warmer on August 13 compared to August 12, and warmest on August 14. Therefore, the same heat flux would produce a later breaking of the nocturnal inversion and a longer time to reach a given altitude on August 14 compared to August 13, and on August 13 compared to August 12. For example, to mix surface air to 600 m on August 14, it takes 15 percent more sensible heat flux than on August 13, and 25 percent more sensible heat flux than on August 12, ignoring the effects of mechanical mixing. The data suggest that the aloft warming and resulting stability were the major factors controlling growth rates on these days.

Analysis of the synoptic charts showed that the aloft warming was a result of the intensification and movement of an upper-level ridge of high pressure. On August 12, the aloft high pressure was located northwest of El Paso over eastern Utah. On August 13 and 14, the high pressure broadened and intensified slightly. The broadening and intensification of the high pressure resulted in a sinking motion over El Paso. As the air sinks, it adiabatically warms. Warm-air advection is another way to warm the aloft air, but no definitive temperature advection is observed on the synoptic charts. Although data were not available to prove warming due to sinking motion, it is a reasonable explanation given the synoptic pattern.

Analysis of the upper-level high-pressure ridge and surface pressure gradients on August 12 through 14 shows that the upper-level dynamics likely play a role in the surface winds. With the broadening and movement eastward of the upper-level ridge on August 12 through 14, surface pressure gradients, although weak, changed in accordance with atmospheric dynamics. On August 12, the aloft high pressure ridge was located well to the north and light surface pressure gradients existed over El Paso. As the high broadened on August 13, surface pressure gradients became flat under the broad high pressure; as a result, surface winds were near stagnant on August 13. On August 14, with the center of the high-pressure system pushing further eastward to a location north of El Paso, surface pressure rose slightly to the east of El Paso, while dropping moderately to the west of El Paso. As a result, the surface winds on August 14 increased significantly from August 13, blowing from the east and southeast.

Other meteorological conditions associated with ozone episodes include surface temperatures greater than 90°F and a diurnal temperature variation greater than 25°F. The high diurnal temperature variation is indicative of the strength of the inversion and is likely to be associated with suppressed CBL growth and reduced mixing of pollutants.

ASSESSMENT OF NO_x AND VOC LIMITATIONS

We assessed available morning nonmethane hydrocarbons (NMHC) to NO_x ratios to determine NO_x and VOC limitations. Data for this analysis were limited spatially and may not be representative of ozone formation potential in the entire El Paso-Juarez-Sunland Park area. The ratio of NMHC to NO_x in the morning is an important parameter for photochemical systems. The ratio characterizes the efficiency of ozone formation in NMHC-NO_x-air mixtures. In general, environmental chamber experiments and photochemical model calculations both show that at low early morning NMHC/NO_x ratios (less than 5 ppbC/ppb), ozone formation is slow, inefficient, and VOC-limited. Furthermore, at high NMHC/NO_x ratios (above about 10), ozone formation is limited by the availability of NO_x rather than by NMHC. This means that reductions in NMHC emissions when the NMHC/NO_x ratios are high do not significantly influence ozone formation. Knowledge of NMHC/NO_x ratios is important for selecting appropriate emission control strategies. Note that the NO_x measured at the surface in this field study is the sum of NO, NO₂, and a poorly defined fraction of other NO_y species.

The distribution of morning (0600-0800 MDT) NMHC/NO_x ratios observed during the 1996 field study at the canister sites is shown in Figure 8. Data, rather than IOP days only, were included in the plots to provide a more robust data set. Most of the sites showed NO_x limitations with the exception of Campbell which showed hydrocarbon limitations. The data show that 77 percent of the ratios were above 10, with most falling between 10 and 30, and extreme values of 4.5 and 77. The figure also shows the distribution of ratios for all sampling time periods. Again, 74 percent of the ratios were above 10, with extreme values of 1.5 and 1940. Therefore, the system is most often NO_x limited, and NO_x controls would aid in ozone reduction.

Figure 9 shows the NO_x and NMHC concentrations by site for the early morning sampling period. The data are labeled by site. Regression lines are shown for Campbell ($R^2=0.77$), 20/30 Club ($R^2=0.87$), Advanced Transformer ($R^2=0.44$), and Winn Road ($R^2=0.65$) with inverse slopes (NMHC/NO_x) of about 9, 16, 37, and 11, respectively. The Campbell site is located in downtown El Paso, an area dominated by motor vehicle emissions. The 20/30 Club site is located in downtown Juarez and is also dominated by motor vehicle emissions. The Advanced

Transformer site is located in an industrial section of Juarez. The Winn Road site is a suburban site in El Paso located near a highway. Table 2 lists the median concentrations and ratios for the 0600-0800 MDT sampling period for each site. The plots and median values show that the hydrocarbon concentrations at Advanced Transformer and 20/30 Club were higher than at other sites while NO_x concentrations were higher at Campbell. Figure 10 shows the median ratios at 0600, 0800, 1000, 1200, and 1600 MDT at each location. These data further illustrate the large spatial and temporal differences in the NMHC/NO_x ratios observed during the study. Ratios were relatively unchanged with time of day at 20/30 Club and Campbell, while large increases with time of day were observed at Advanced Transformer, Turf Road (a suburban/rural site in El Paso), and Winn Road sites.

CONCEPTUAL MODEL AND CONCLUSIONS

Based on the analysis results and observations discussed in this report, we have developed a simple conceptual model of high ozone concentration episodes in the Paso del Norte area. A conceptual model is a description of the important phenomena and characteristics which produce high ozone concentration episodes. The purposes of developing a conceptual model are to summarize the current state of knowledge regarding ozone episodes, to provide a basis for testing and evaluating specific hypotheses, and to provide a basis for evaluating meteorological and photochemical models and model results. The conceptual model can also be used to help design additional field measurements and to improve episode forecasting.

The conceptual model for the Paso del Norte area includes information on typical synoptic meteorological conditions, plus the air quality and meteorological characteristics during various episodes. We have identified a number of conditions which occur during ozone episodes, as summarized below.

Typical Meteorological Conditions:

- 500 mb ridge over or just west of the El Paso area
- Weak surface gradients
- Stagnant or weak early-morning surface winds
- Maximum surface temperature of at least 90°F
- Diurnal temperature variation of at least 25°F
- Slow mixing growth rates and light surface winds are associated with high ozone; fast mixing growth rates are associated with low ozone concentrations. In addition, on high ozone days, higher surface precursor concentrations are observed; this may also be attributed to the stronger nocturnal inversion associated with the slow growth of the mixed layer and shallower mixing depths. The data suggest that aloft warming and the resulting increase in stability was the major factor influencing the growth rate of the mixed layer.
- Fast winds do not allow ozone precursors or ozone to accumulate and low ozone concentrations result.

Air Quality Characteristics:

- Early-morning surface CO, NO, and NO_x concentration peaks in the source regions of

El Paso and Juarez.

- On days with high ozone concentrations, the morning precursor “cloud” has high concentrations and is confined to the source region. On days with lower ozone concentrations, higher wind speeds disperse the source “cloud” and maximum precursor concentrations are lower, but more widely distributed.
- On days with high ozone concentrations, the midday ozone “cloud” with the highest concentrations is confined to the source region, or slightly downwind. On days with lower ozone concentrations, maximum ozone concentrations are lower, but more widely distributed.
- Aloft ozone concentrations on nights preceding days with high ozone concentrations (and on early mornings of these days) were significantly lower than the maximum ozone concentrations, with aloft ozone concentrations of about 45-65 ppb. Thus, ozone carryover did not have a major influence on ozone exceedances, but may have contributed as much as 20 ppb to the surface ozone concentration.
- Aloft ozone precursor concentrations on nights preceding days with high ozone concentrations (and on early mornings of these days) were significantly lower than the maximum surface precursor concentrations; with aloft NO_y of about 1-2 ppb, aloft NO of about 0.1-0.2 ppb, and aloft NMHC of about 25-55 ppbC.
- NMHC/NO_x at most of the hydrocarbon sampling sites showed NO_x limitations, with the exception of Campbell which showed hydrocarbon limitations.

ACKNOWLEDGMENTS

This work was funded by the U.S. Environmental Protection Agency (EPA). The EPA Work Assignment Manager, James Yarbrough of EPA Region 6, provided extensive advice and guidance during this project. In addition, we would like to extend our appreciation to the many field and data processing personnel whose hard work made this study possible, including those from the EPA, Instituto Mexicano del Petroleo, Los Alamos National Laboratory (LANL), STI, AeroVironment, Desert Research Institute, University of Texas at El Paso, University of Utah, New Mexico State University, Texas Natural Resource Conservation Commission (TNRCC), El Paso City-County Health and Environmental District, Direccion Municipal de Ecologia - Ayuntamiento de Juarez, and the New Mexico Environment Department (NMED). The members of the Technical Review Group (TRG) also provided comments on our plans and activities. The TRG consisted of the following individuals: Jim Price, TNRCC, Ed Michel, TNRCC, Pete Breitenbach, TNRCC, Chris Kennedy, TNRCC, Cecilia Williams, NMED, Victor Paramo, SEMARNAP-INE, Jose Trevino, Chihuahua, Oscar Ibanez, Ciudad Juarez, Jesus Reynoso, El Paso City-County Health and Environmental District, Rich Scheffe, EPA-OAQPS, Quang Nguyen, EPA-Dallas, J.T. Lee, LANL, Clay Heskett, LANL, Steve Ziman, Chevron Corporation. STI MF# 1784

REFERENCES

1. Roberts, P.T.; MacDonald, C.P.; Main, H.H.; Dye, T.S.; Coe, D.L.; Haste, T.L. Analysis of meteorological and air quality data for the 1996 Paso Del Norte ozone study. Final Report prepared for the USEPA, Region 6 Dallas, TX, by Sonoma Technology, Inc. Santa Rosa, CA

under subcontract to Science Applications International Corporation Mclean, VA, STI-997330-1754-FR, September 1997.

2. Dye, T.S.; Lindsey, C.G.; Anderson, J.A. Estimates of mixing depths from "boundary layer" profilers. In *Preprints of the 9th Symposium on Meteorological Observations and Instrumentation, Charlotte, NC, March 27-31, 1995* STI-94212-1451.
3. Blumenthal, D.L.; Lurmann, F.W.; Roberts, P.T.; Main, H.H.; MacDonald, C.P.; Knuth, W.R.; Niccum, E.M. Three-dimensional distribution and transport analyses for SJVAQS/AUSPEX. Final report prepared for San Joaquin Valley Air Pollution Study Agency, Sacramento, CA by Sonoma Technology, Inc., Santa Rosa, CA, Technical & Business Systems, Santa Rosa, CA, and California Air Resources Board, Sacramento, CA, STI-91060-1705-FR, February 1997.
4. Dye, T.S.; Roberts, P.T.; MacDonald, C.P. Mixing depth structure and evolution as diagnosed from upper-air meteorological data collected during the NARSTO-Northeast study. Paper No. 5A.6 presented at the *10th Joint Conference on the Applications of Air Pollution Meteorology, Phoenix, AZ, January 11-16, 1998* (STI 1749).

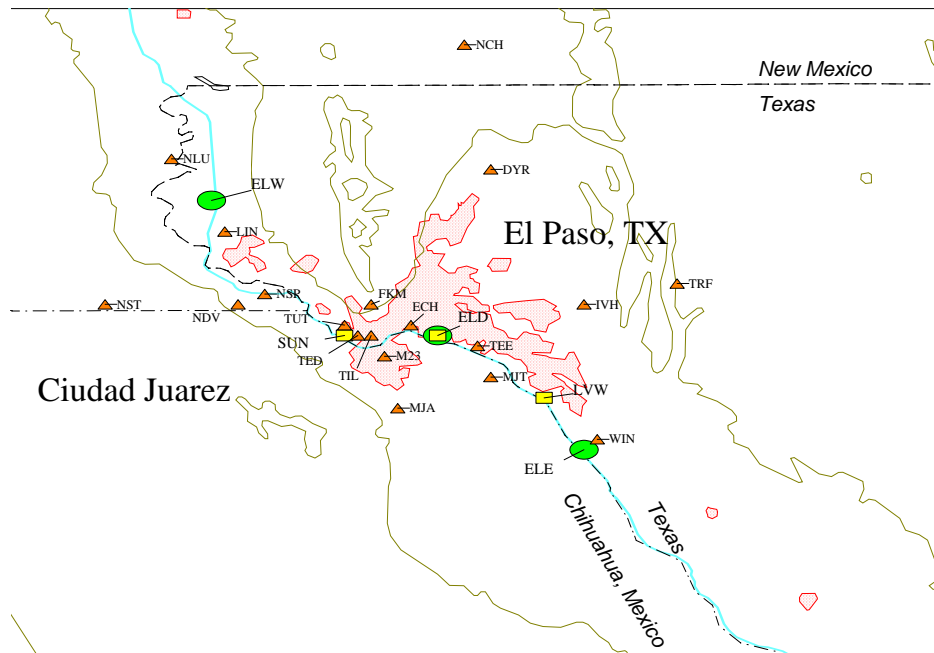
Table 1. Mixing depth growth rates (m/hr) for 0600 through 1200 MST at ELW, ELE, and ELD on August 12 through August 14 and September 4 through September 7.

Site	Aug. 12	Aug. 13	Aug. 14	Sept. 4	Sept. 5	Sept. 6	Sept. 7
ELW	320	80	220	120	130	130	120
ELE	370	50	50	60	80	100	80
ELD	380	150	120	100	150	130	120
Average of all sites	357	93	130	93	120	120	107

Table 2. Median NMHC/NO_x ratios and median concentrations measured during the 0600-0800 MDT sampling period at the canister sites.

Site	NMHC (ppbC)	NO _x (ppb)	NMHC/NO _x
20/30 Club	762	60.1	12.9
Advanced Transformer	1680	44.3	34.7
Campbell	469	92.0	5.6
Franklin Mtn	209	9.1	26.7
Sunland Park	266	13.0	18.4
Turf Road	180	8.8	21.5
Winn Road	683	50.7	14.0

Figure 1. Locations of radar profilers with RASS and surface met (circles), surface met and air quality stations (triangles), and sodars (squares) during the 1996 Paso del Norte Ozone Study.



Note: Surface meteorological stations were also located at the ELW, ELD, and ELE sites.

Figure 2. Schematic of the Planetary Boundary Layer (PBL) which shows the Nocturnal Boundary Layer (NBL), the Residual Layer (RL), and the Convective Boundary Layer (CBL). Vertical arrows show the height to which surface air is mixed.

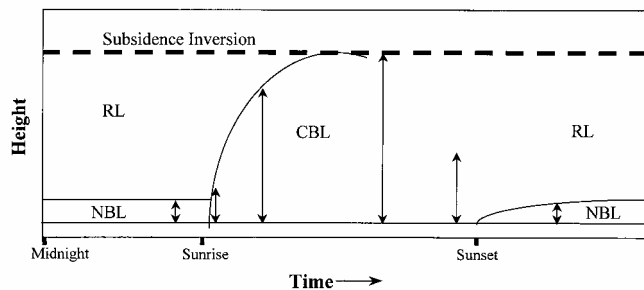


Figure 3. Aircraft spiral at Juarez Airport from 0446 to 0458 MST on August 13, 1996.

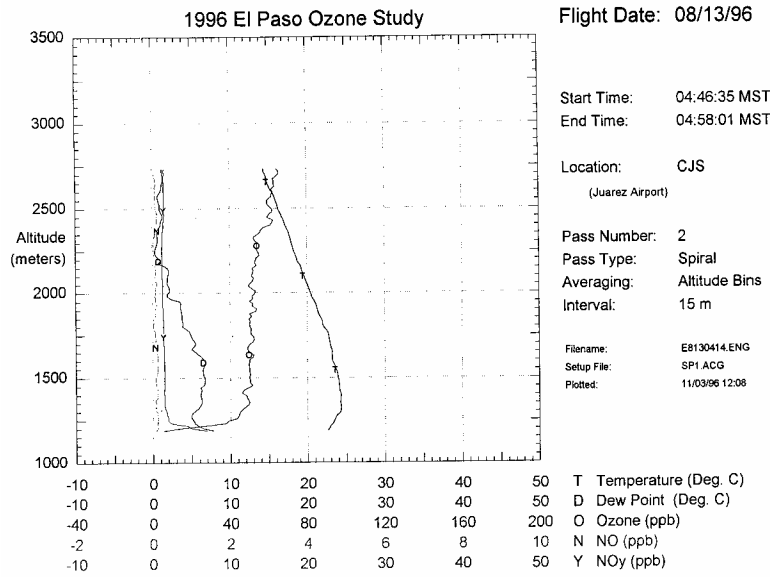


Figure 4. Surface-base mixing heights at ELD on August 12-14, 1996.

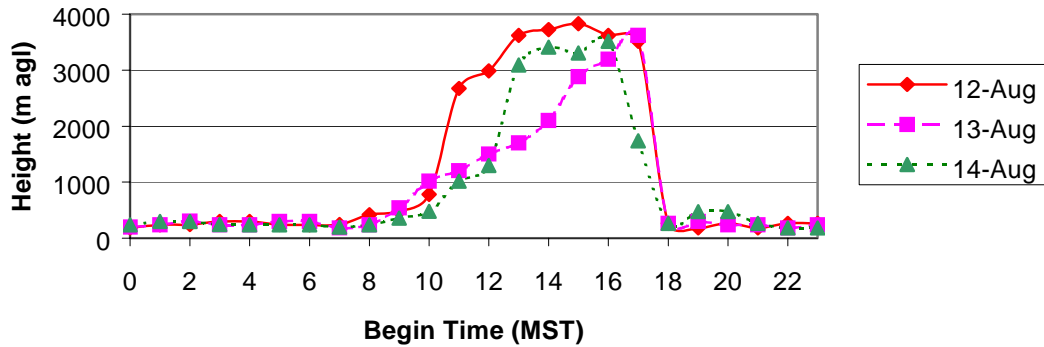


Figure 5. Ozone concentrations (ppb) on August 13 at 1100 MST.

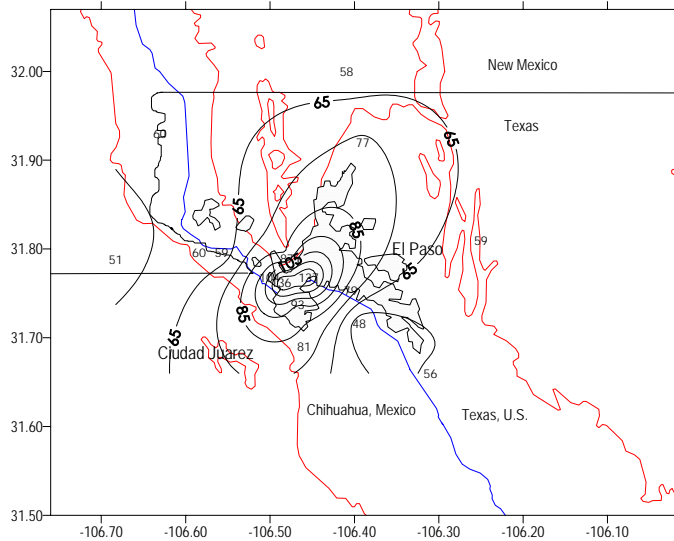


Figure 6. Ozone concentration (ppb) on August 14 at 1200 MST.

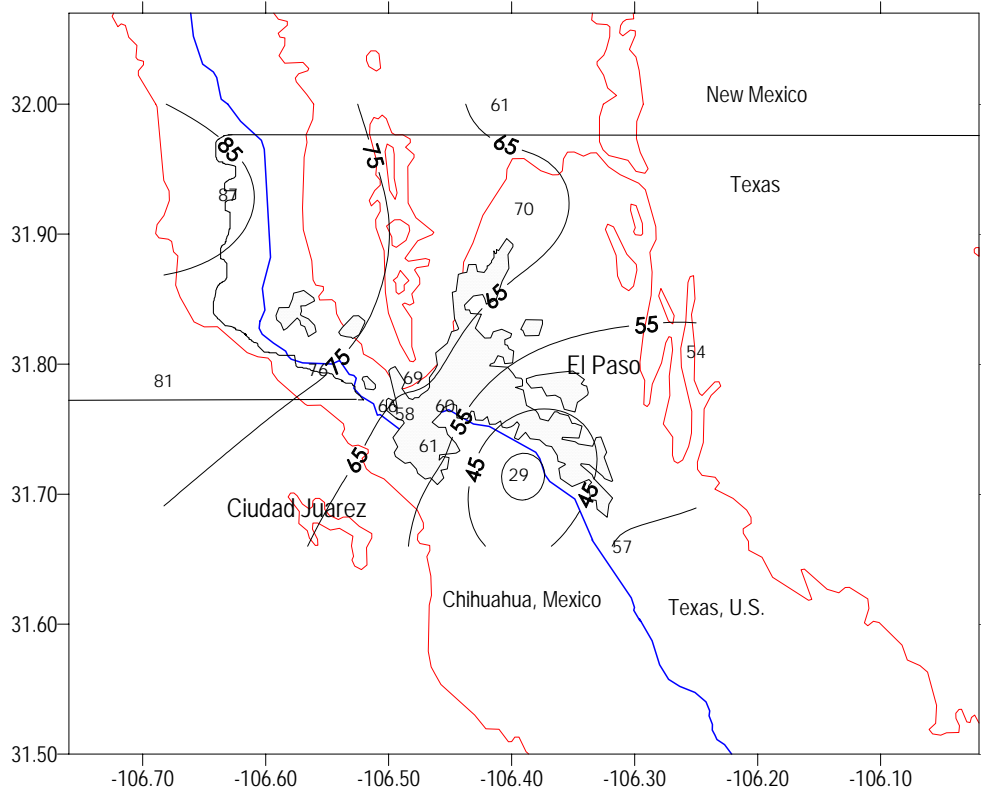


Figure 7. RASS virtual temperature at ELW on August 12 through 14, 1996 at 0600 MST.

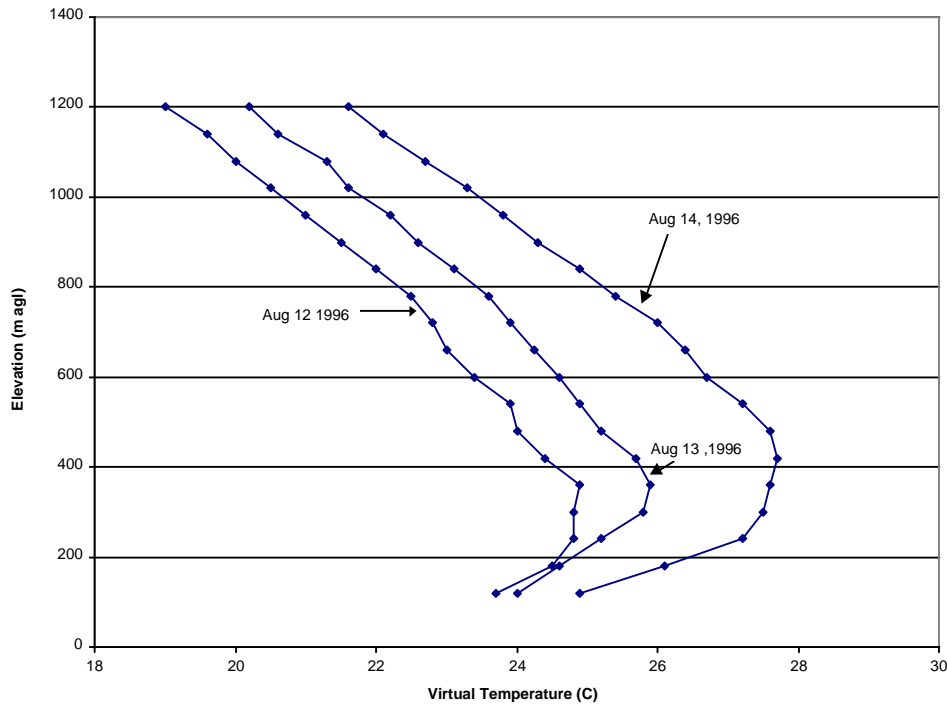


Figure 8. Distribution of NMHC/NO_x ratios at canister sites for the 0600-0800 MDT time period (top) and all data (bottom).

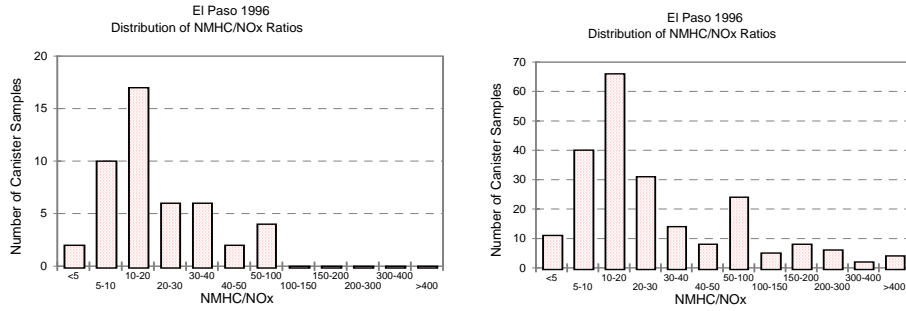


Figure 9. NMHC and NO_x concentrations for the 0600-0800 MDT sampling period at canister sites. Regression lines and coefficients are provided for Campbell (C), 20/30 Club (2), Winn Road (W), and Advanced Transformer (A). The data are labeled by site (T= Turf Road, SP = Sunland Park).

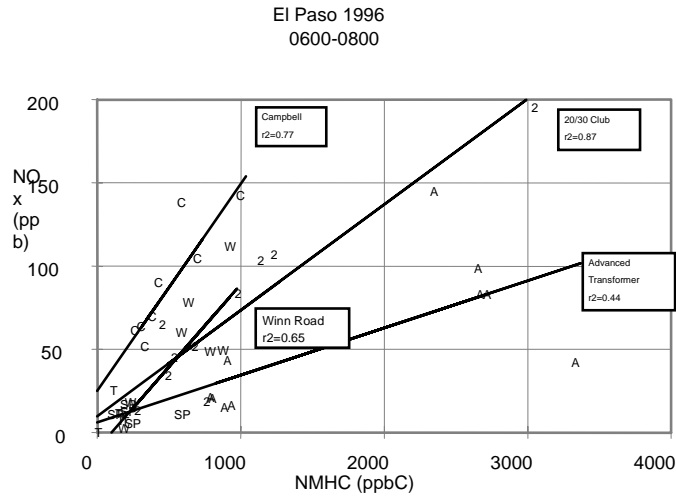


Figure 10. Distribution of median NMHC/NO_x ratios at canister sites by time of day (MDT).

