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### Technical Report

# Ozone pollution: Sources of precursors, drivers of high ozone days and influence of wildfires

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#### **Executive Summary**

Photochemical reactions of nitrogen oxides (NO + NO<sub>2</sub> = NO<sub>x</sub>) and volatile organic compounds (VOCs) trigger the formation of ozone (O<sub>3</sub>), a secondary air pollutant that contributes to the deterioration of air quality in urban areas and affects human health. Formation of O<sub>3</sub> is most intense in summer because of increased incoming solar radiation that intensifies photochemistry. Urban communities with comparatively elevated emissions of NO<sub>x</sub> and VOCs also see increases in O<sub>3</sub>. This report summarizes the results of a study analyzing ambient concentrations of O<sub>3</sub> and its precursors to obtain a better understanding of conditions that lead to the occurrence of elevated O<sub>3</sub> concentrations in the El Paso/Ciudad Juárez/Doña Ana urban metroplex from 2008 to 2014.

Ozone and nitrogen oxides mixing ratios were continuously measured in multiple sites. Speciated, time-resolved VOC concentrations were measured at the AIRS 48-141-0044 site. Supplemental data were obtained to assist in the analysis effort. Those datasets included meteorological and air quality data from the TCEQ and NMED monitoring networks, air mass backward trajectories using the NOAA HYSPLIT model at several different elevations, the locations, durations, and associated burn areas of wildland events as well as model results for regional smoke aerosol concentrations.

The maximum hourly  $O_3$  levels ranged from 78 parts per billion by volume (ppbv) to 111 ppbv at the New Mexico sites, from 99 ppbv to 133 ppbv at the Texas sites, and from 113 ppbv to 145 ppbv at the Mexico sites. The average 1-hr  $O_3$  concentrations ranged from 28.7 in Mexico to 42.2 in New Mexico. In New Mexico, NO hourly levels varied from a few ppbv to 218 ppbv with an average of 2.6 and 1.2 ppbv for the two monitoring sites, while NO<sub>x</sub> concentrations ranged from 0 to 283 ppbv with a mean value of 6.1 and 10.8 ppbv, respectively. At Texas, the maximum 1-hour NO concentration was 608.2 ppbv and the mean varied from 8.6 to 15.2 18 ppbv at the two monitoring sites. The highest hourly NO<sub>2</sub> was 674 ppbv and the mean varied from 21.7 to 30.4 ppbv. Twelve organic compounds were identified. The highest hourly concentrations were measured for toluene (546.4 ppbv) and acetylene (69.8 ppmv).

Over the diurnal cycle,  $O_3$  mixing ratios increased rapidly in the early morning (~5:00) through the early afternoon, compared to few ppbv during the nighttime hours. The  $O_3$  concentrations peaked in the afternoon (~14:00) and then gradually declined in evening (starting at ~16:00). The precursors (NO, NO<sub>2</sub>, and VOCs) generally followed an opposite diurnal pattern with the lowest concentrations measured during the daytime, while ozone levels were at their highest. NO and VOC mixing ratios exhibited an early morning peak and an early evening gradual climb. This is consistent with the expectation that elevated concentrations of nitrogen oxides and VOCs are associated with traffic emissions during early morning and evening commute hours. For NO<sub>2</sub>, elevated nighttime concentrations were likely due to the NO<sub>x</sub> titration reaction. The progression of the mixing ratios of nitrogen compounds, VOCs, and ozone over the diurnal cycle was consistent with that observed in other urban areas.

There are two distinct regimes over the diurnal cycle that influence  $O_3$  and its precursors, well mixed daytime conditions and stagnant, stable nighttime conditions. At sunrise, the heating of the surface by incoming solar radiation warms the air near the surface resulting in enhanced vertical mixing, increase in the height of the boundary layer, and increase in surface and aloft wind speeds. Changes in surface wind direction that occur during the same morning period cause air to move from the south towards the north, accumulating pollutants in the north end of

the El Paso/Ciudad Juárez/Doña Ana urban metroplex. In the evening and nighttime, the cooling of earth surface results in lower wind speeds, a reduced mixing height, and a change in the wind direction. These conditions favor the accumulation of ozone precursors emitted in the evening and early morning within a shallow layer near their respective sources. These meteorological effects are corroborated by the fact that accumulation of O<sub>3</sub> for about 5-6 hours coincide at all sites with concurrent O<sub>3</sub> and NO<sub>x</sub> measurements. In addition, the high correlation coefficients, the low relative concentration difference ( $\Delta C/C_{ref}$ ) and COD values among O<sub>3</sub> mixing ratios at all sites where ozone was monitored indicate that O<sub>3</sub> levels increase or decrease simultaneously. This suggests that the daytime O<sub>3</sub> mixing ratios are controlled by the same meteorological regimes at all the sites.

In our study, the mean 24-hr toluene/benzene, *m/p*-xylene/toluene and *m/p*-xylene/benzene, ratios were comparable to those estimated for urban areas and the highway tunnels; however, high values of these ratios for individual days implied the enrichment of toluene and xylenes from fuel evaporation or industrial sources. The photochemical age (calculated based on VOCs) indicated the dominant influence of local sources (within 2 km) as compared to more distant sources.

The VOCs sources at the two monitoring sites were determined by principal components analysis (PCA). The two retained factors explained 90% of the dataset variability and the vast majority of VOC concentrations. The profiles and the relative contributions to the individual VOCs of the two factors were similar. In addition, the monthly, day-of-the-week and hourly variation of each factor contributions were comparable and indicative of traffic emissions. This was further corroborated by the toluene/benzene, m/p-xylene/toluene and m/p-xylene/benzene ratios for the two factors. The most noticeable difference between the two factors was associated with the decline contributions of factor 1 during the 2008-2014 period, while factor 2 contributions increased over the same time period. The absence of association between the two factors, in relation to the photochemical age of the air mass, suggested that the two retained factors represent two sources rather than different stages of photochemical processing of VOCs emitted from one source. Thus, the two retained factors may be tentatively and cautiously assigned to two different types of traffic emissions. The two sources added, on average, 2.7 ppbv, while the unexplained (i.e. intercept) O<sub>3</sub> was comparable to background O<sub>3</sub> levels in the absence of all anthropogenic emissions of VOC precursors in North America for the region.

Sources within southwest Texas, New Mexico and Northern Mexico, encompassing the El Paso/Ciudad Juárez/Doña Ana urban metroplex, contributed the most (approximately 25 ppbv) in O<sub>3</sub> concentrations, followed by the Baja California/Sonora Desert region. Sources in Utah, Colorado, Great Plains and Southwest Nevada added about 8.5 ppbv as compared to about 10.5 ppbv from sources in Central Mexico. Transport from southern California encompassing the urban areas of Los Angeles and San Diego added, on average, 1.5 ppbv.

Partly to assess the impact of wildfires, days with high  $O_3$  mixing ratios were further analyzed. The 80<sup>th</sup> percentile of the maximum 8-hr average concentration was used as the threshold for "high"  $O_3$  events for each site. While the classification was done using the distributions on a site-by-site basis, many of the high  $O_3$  days were coincided at several sites and often on consecutive days ( $O_3$  "events"). Fifteen high  $O_3$  events were identified spanning in length from five to fourteen days. For the three "high  $O_3$ " events, there was substantial evidence that smoke plumes from wildland fires were impacting air quality in the El Paso/Ciudad Juárez/Doña Ana urban metroplex. These events exhibited high 1-hr maximum  $O_3$  mixing ratios but low VOC and  $NO_x$  levels. A "high  $O_3$ " event in early July (July 2-6, 2013) may have been associated with the use of fireworks on July 4<sup>th</sup>, 2013. Four "high  $O_3$ " events showed moderate impact from wildfire smoke. These events were associated with higher  $NO_x$  and VOC levels. Hourly  $O_3$  levels were slightly lower than those measured for "high  $O_3$ " days when smoke was present. Seven of the "high"  $O_3$  events showed very little or no evidence of impact from wildfire smoke and were associated with higher  $NO_x$  and VOC levels as compared to events with strong evidence of smoke presence.

Limitations of this analysis include: (1) the limited number of measured VOCs which reduces the sensitivity of PCA analysis to identify and quantify the contributions of other sources and obtain clear profiles and (2) the inability of the TrMB model to accurately estimate source contributions on hourly or daily concentrations. Although, these two limitations may inhibit accurately identifying and locating unique sources or types of events that contribute to sporadic high ozone events; they exert minimal error in understanding and describing the underlying and predominant conditions and sources affecting O<sub>3</sub> concentrations in the El Paso/Ciudad Juárez/Doña Ana urban metroplex.

Overall, factors that affect  $O_3$  mixing ratios in the El Paso/Ciudad Juárez/Doña Ana urban metroplex include local emissions, regional fires, and local air circulation. The contribution of local emissions (mobile, point and area sources) is more dominant, constant and associated with regular activities such as motor vehicle traffic. Fires appeared to influence  $O_3$  levels on an episodic basis with minimal influence on NOx and VOCs levels suggesting either the penetration of aloft  $O_3$  or peroxyacetylnitrates (PANs) in the smoke plume. While emissions of  $O_3$  precursors are variable, both spatially and temporally,  $O_3$  mixing ratios across the valley are fairly uniform.

#### Introduction 1

Tropospheric ozone  $(O_3)$  is formed through the photo-oxidation of volatile organic compounds (VOCs) and nitrogen oxides (NO<sub>x</sub> = NO + NO<sub>2</sub>). The EI Paso MPO is seeking to identify the local and regional conditions that contribute to O<sub>3</sub> concentrations in the El Paso/Ciudad Juárez/Doña Ana urban metroplex. As part of this effort, the New Mexico State University (primary contractor to the El Paso MPO) partnered with the University of Alabama at Birmingham (UAB) to analyze air quality and meteorological data and investigate the patterns of ozone and its precursors. This report summarizes the results of  $O_3$ , VOCs and NO<sub>y</sub> measurements conjointly with meteorological conditions in multiple locations at the El Paso/Ciudad Juárez/Doña Ana metroplex. The study period was from January 1, 2008 to December 31, 2014. Since O<sub>3</sub> formation is intensified during summer, measurements collected between April and October were analyzed. The remainder of Chapter 1 of this report provides a brief background of the region and air monitoring sites. In Chapter 2, we provide detailed information of the development of the Central Database (CD). Chapter 3 analyses the patterns and relationships of  $O_3$  and its precursors.

The study area is composed of the El Paso/Ciudad Juárez/Doña Ana urban metroplex (Figure 1-1). The population exceeds 2,000,000 inhabitants, with 1.3 million living in Ciudad Juárez, about 800,000 in El Paso and over 200,000 in Doña Ana County including Las Cruces. The urban complex is a major industrial and transportation center, with more than 4.0 million passenger cars and 0.5 million commercial vehicles passing through the several crossings in the U.S.-Mexico border region in El Paso and Doña Ana County. El Paso and Doña Ana Counties have experienced air quality problems for most of the criteria pollutants with traffic exhausts and dust particles being the primary drivers. More recently, O<sub>3</sub> levels have been of concern in the metroplex. In May 2012, the El Paso County has been designated attainment/classifiable by the U.S. **Environmental Protection Agency** under then 2008 8-hr ozone National Ambient Air Quality Standard.



#### 2 **Database development**

One-hour (1-h)  $O_3$  measurements at thirteen (13 sites) in the El Paso/Ciudad Juárez/Doña Ana metroplex during the 2008-2014 period were retrieved from the US EPA's Air Data System (http://www3.epa.gov/airdata/). Table 1 shows the characteristics and monitoring periods for each site. Six (6) sites are operated by the New Mexico Environment Department, three of them within Las Cruces, four of them in the Sunland Park border region, one in Las Cruces and one in a rural community. There are six (6) sites within El Paso metropolitan area and 1 site at Ciudad Juárez in Mexico. These sites were operated by the Texas Commission on Environmental Quality. Nitrogen oxide (NO and total NO<sub>x</sub>) were measured in five (5) sites, three in El Paso and two in Doña Ana County. VOCs and reactive nitrogen oxides (NO<sub>y</sub>) were measured in one site (AIRS # 48-141-0044).

| Site name                     | AIRS code   | Latitude (°), longitude (°)<br>and elevation (m) |
|-------------------------------|-------------|--|
| St. Lukes                     | 35-013-0008 | 31.931; -106.631; 1204                           |
| Sunland Park                  | 35-013-0017 | 31.796; -106.558; n.a.                           |
| 6ZK                           | 35-013-0020 | 32.041; -106.409; 1250                           |
| 6ZM <sup>a</sup>              | 35-013-0021 | 31.796; -106.584; 1219                           |
| 6ZN <sup>a</sup>              | 35-013-0022 | 31.788; -106.683; 1280                           |
| 6ZQ                           | 35-013-0023 | 32.318; -106.768; 1219                           |
| Lee Trevino and Ivanhoe       | 48-141-0029 | 31.786; -106.324; 1239                           |
| El Paso UTEP <sup>a</sup>     | 48-141-0037 | 31.768; -106.501; 1158                           |
| El Paso Chamizal <sup>b</sup> | 48-141-0044 | 31.766; -106.455; 1158                           |
| Ascarate Park SE <sup>a</sup> | 48-141-0055 | 31.747; -106.403; 1122                           |
| Socorro                       | 48-141-0057 | 31.662; -106.303; 1109                           |
| Skyline Park                  | 48-141-0058 | 31.894; -106.426; 1201                           |
| Industria & Fernandez SE      | 80-006-0007 | 31.712; -106.395; n.a.                           |

Table 2-1. Site characteristics.

<sup>a</sup> Sites with concurrent NO<sub>x</sub> measurements

<sup>b</sup> Sites with concurrent NO<sub>x</sub>, NO<sub>y</sub> and VOCs measurements

#### **Data Validation and Database Development**

The Central Database (CD) was created from AIRS annual files to produce a dataset that meets the needs of this study. The original datasets included ozone, nitrogen oxides (NO, NO<sub>x</sub> and NO<sub>y</sub>), VOCs and meteorological (wind direction, wind speed, temperature, relative humidity, dew point and pressure). The IBM SPSS (v. 22) was used as the major tool for the development of the CD. The final CD is available at dbf and dat formats. The format is identical to that of the original datasets.

#### Supplementary datasets

#### Air Mass Trajectories

Backward trajectories with a resolution of one hour and going back five days were generated for the AIRS # 48-141-0044 site at 1 hour intervals using the NOAA HYSPLIT trajectory model (Draxler and Hess, 1997) and Eta Data Assimilation System (EDAS) meteorological fields as inputs. Starting heights was 500 m above ground level. Trajectories files are provided in their native format and merged as ArcMap shapefiles.

#### Wildland Fire Episodes

Wildland fire activity in the Northern America for the monitoring period was retrieved from the National Interagency Fire Center (<u>www.nifc.gov</u>). The locations of fire episodes were obtained using data collected by both TERRA MODIS and AQUA MODIS satellites and processed as a cooperative effort between the USDA Forest Service Remote Sensing Applications Center, NASA-Goddard Space Flight Center and the University of Maryland (Remote Sensing Applications Center; <u>www.fs.fed.us/eng/rsac/index.html</u>). The fires locations and characteristics are provided as ArcMap shapefiles.

#### 3 Advanced analysis

This section examines the spatiotemporal trends of  $O_3$ , the role of reactive nitrogen species and VOCs precursors and the influence of local and regional atmospheric conditions. The analysis focused on measurements obtained between April and October of the period 2008-2014 because of the dependence of  $O_3$  production on incoming solar radiation and temperature-dependent fugitive emissions of many VOCs. Figure 3-1 shows the monthly variation of mean and maximum 1-hr  $O_3$  concentrations for each site. For all sites the trends are comparable, with the highest average  $O_3$  concentration being measures in April and May, while the highest 1-hr  $O_3$  levels were measured in July, August and September. These differences may be indicative of the variability of factors controlling  $O_3$  production and transport. For example, high mean concentrations with moderate 1-hr max levels may indicate regionally transported contributions that also maintain considerable levels of  $O_3$  during night. On the other hand, high 1-hr  $O_3$  levels but moderate mean 1-hr concentrations may be associated with local sources that result in the accumulation of ozone during daytime but also in  $O_3$  destruction by titration during nighttime. Chalbot et al., (2013) previously showed spatial and temporal differences in the frequency of wildfires near and far away from the study area.

Figure 3-1. The monthly variation of the mean (up) and maximum (bottom) hourly  $O_3$  concentration (in ppm).



#### **Ozone and Its Precursors**

Table 3-1, Table 3-2 and Table 3-3 show the concentration of  $O_3$ ,  $NO_x$  and VOCs during the period 2008-2014 Apr-Oct. The highest mean  $O_3$  levels were measured on sites outside (north (AIRS # 48-141-0058 and AIRS # 35-013-0020 (in New Mexico)) and west (in New Mexico (AIRS # 35-0130021 and AIRS # 35-013-0022)) of the EI Paso/Ciudad Juárez complex, although the highest 1-hr measurements were obtained in sites in the urban complex. NO and NO<sub>x</sub> levels were higher in sites with the EI Paso urban area (AIRS # 48-141-0037, AIRS # 48-141-0044, AIRS # 48-141-0055) as compared to those measured in New Mexico sites (AIRS # 35-013-0022).

| AIRS site   | <b>O</b> <sub>3</sub> |
|-------------|-----------------------|
| 35-013-0008 | 98, 35.8 (15.7), 111  |
| 35-013-0017 | 97, 36.9 (15.2), 100  |
| 35-013-0020 | 94, 42.2 (12.9), 93   |
| 35-013-0021 | 96, 40.2 (14.7), 109  |
| 35-013-0022 | 96, 42.0 (14.0), 98   |
| 35-013-0023 | 97, 37.2 (15.1), 78   |
| 48-141-0029 | 93, 35.9 (14.1), 133  |
| 48-141-0037 | 95, 37.6 (16.0), 117  |
| 48-141-0044 | 98, 34.8 (16.7), 117  |
| 48-141-0055 | 96, 32.4 (16.3), 130  |
| 48-141-0057 | 83, 33.1 (16.4), 119  |
| 48-141-0058 | 97, 40.9 (14.4), 99   |
| 80-006-0004 | 61, 29.9 (15.0), 113  |
| 80-006-0006 | 64, 28.7 (16.1), 116  |
| 80-006-0007 | 88, 32.9 (16.4), 145  |

Table 3-1. Completeness (%), mean and standard deviation (in parentheses), and maximum hourly  $O_3$  concentrations (in ppbv) during the period Apr-Oct. 2008-2014.

Table 3-2. Completeness (%), mean and standard deviation (in parentheses), and maximum hourly NO, NO<sub>x</sub> and NO<sub>y</sub> concentrations (in ppbv) during the period Apr-Oct. 2008-2014.

| AIRS site    | NOy                    | ŇO                      | NO <sub>x</sub>        |
|--------------|------------------------|-------------------------|------------------------|
| 35-013-0021  | -                      | 94, 2.6 (7.6), 218      | 94, 10.8 (14.4), 283   |
| 35-013-0022  | -                      | 94, 1.2 (4.2), 182      | 94, 6.1 (9.2), 226     |
| 48-141-0037  | -                      | 92, 8.6 (20.2), 461     | 92, 21.7 (28.7), 544   |
| 48-141-0044  | 32, 26.9 (40.6), 484.7 | 100, 13.5 (35.6), 608.2 | 86, 27.4 (44.2), 674   |
| 48-141-0055  | -                      | 95, 15.2 (39.1), 544.1  | 95, 30.4 (47.4), 619.7 |
| 48-141-0057* | -                      | 0, 25.1 (49.2), 220     | 0, 39.6 (59.9), 268    |
| 48-141-0058* | -                      | 0, 0.8 (0.4), 1         | 0, 4.7 (4.7), 18       |

\* less than 90 measurements (special studies)

The most abundant VOCs at the 48-141-0044 site were toluene, *m/p*-xylenes, benzene, acetylene and propylene. Note that for acetylene, there were only 68% of valid hourly measurements. The maximum 1-hr concentrations were ten to hundred (for toluene) times higher than the average concentrations. Similar patterns were observed for VOCs during a limited scale study at the AIRS # 48-141-1011 site. The potential presence of some sources cannot be identified by differences in the concentrations, especially when the two sets are not identical.

The influence of fugitive emissions (most likely from the oil refinery) are indeed identified by the concentration diagnostic ratios

| VOC                    | Site                 | Site                |  |  |
|------------------------|----------------------|---------------------|--|--|
| 000                    | 48-141-0044          | 48-141-1011         |  |  |
| Propylene              | 81, 1.2 (1.4), 25.5  | 24, 0.7 (1.1), 22.2 |  |  |
| Acetylene              | 68, 1.1 (1.6), 69.8  | 24, 0.8 (1.1), 22   |  |  |
| 1,3-Butadiene          | 80, 0.2 (0.4), 7.8   | 24, 0.1 (0.3), 4.6  |  |  |
| <i>n</i> -Octane       | 81, 0.2 (0.4), 6.4   | 24, 0.2 (0.4), 8.5  |  |  |
| <i>m/p</i> -Xylenes    | 81, 2.0 (3.5), 65.3  | 24, 1.2 (2.1), 39.4 |  |  |
| Benzene                | 81, 1.4 (2.1), 47.1  | 24, 0.7 (0.9), 16.2 |  |  |
| Toluene                | 81, 4.9 (8.7), 546.4 | 24, 3.2 (5), 80.7   |  |  |
| Ethylbenzene           | 81, 0.7 (1.2), 21.6  | 24, 0.4 (0.8), 15.1 |  |  |
| o-Xylene               | 81, 0.7 (1.2), 24.2  | 24, 0.4 (0.8), 14.6 |  |  |
| 1,3,5-Trimethylbenzene | 78, 0.2 (0.4), 7.8   | 23, 0.1 (0.3), 5.2  |  |  |
| 1,2,4-Trimethylbenzene | 76, 0.5 (1.1), 23.7  | 23, 0.4 (0.8), 14.6 |  |  |
| Styrene                | 81, 0.1 (0.4), 12.5  | 24, 0.1 (0.3), 10.6 |  |  |

Table 3-3. Completeness (%), mean and standard deviation (in parentheses), and maximum hourly VOCs concentrations (in ppbv) during the period Apr-Oct. 2008-2014.

#### Atmospheric conditions and ozone formation

This section examines the influence of NO<sub>x</sub>, VOCs and meteorological conditions on ozone formation by analyzing their hourly variation during the period Apr-Oct. 2008-2014. Analysis of specific events is presented in later section of the study. The role of NO<sub>x</sub> is examined in sites with simultaneous O<sub>3</sub> and NO<sub>x</sub> measurements. The effect of VOCs and meteorological variables is determined only for the AIRS # 48-141-0044 site.

Figure 3-2 Mean 1-hr O3 concentrations at all sites



Figure 3-3. Diurnal variation of mean  $O_3$ ,  $NO_y$ , NO,  $NO_x$  (left y-axis) and individual VOCs (right y-axis) (in ppbv) at AIRS # 48-141-0044 site. The objective of the diagram is to demonstrate that VOCs follow the same diurnal distribution as nitrogen oxides, regardless of their concentrations.



Time of the day

The similar hourly  $O_3$  profiles at all sites (shown in Figure 3-2) were consistent with its photochemical formation mechanism during daytime. The amplitude, defined as the difference between maximum and minimum  $O_3$  concentrations, ranged from 25 ppbv for the AIRS # 35-013-0020 site to 34 ppbv for AIRS # 48-141-0057 site. In fact, the lowest amplitudes (less than 30 ppbv) were computed for the sites with the highest (> 40 ppbv) average 1-hr  $O_3$  concentration (see Table 3-1). This suggested that nighttime  $O_3$  (or carryover from previous day) accounted for a considerable fraction of  $O_3$  in a given day and underlined the need to consider lagged effects on previous days in addition to same-day conditions.

Figure 3-3 show the average diurnal variations of  $O_3$ , NO, NO<sub>2</sub> and VOCs at AIRS #48-141-0044 (Chamizal) site. Nighttime  $O_3$  mixing ratios were about 28-30 ppbv, followed by a moderate decrease to about 18 ppbv in early morning (5:00 – 6:00) due to  $O_3$  titration by NO<sub>x</sub>/NO<sub>y</sub> during the early morning commute.  $O_3$  mixing ratios grew rapidly during morning and early afternoon, reaching a maximum at around 12:00-14:00. Then,  $O_3$  declined till midnight and maintained low concentrations (about 25 ppbv) overnight. The decline in the evening is the combined outcome of increased NO emissions during the evening commute and the absence of solar radiation. The precursors (NO, NO<sub>x</sub>, NO<sub>y</sub> and VOCs) followed an opposite diurnal profile. For NO, concentrations increased rapidly in early morning, reaching their maximum levels at 6:00. Then, NO<sub>y</sub> levels decreased progressively until early afternoon. The minimum NO<sub>y</sub> concentration was measured at 13:00. Nighttime NO<sub>y</sub> increased to 30 ppbv. A similar pattern was also observed for NO and NO<sub>x</sub>. Elevated nighttime NO<sub>2</sub> concentrations are due to the NO<sub>x</sub> titration reaction.

For VOCs, the diurnal pattern followed a trend similar to NO, NO<sub>x</sub> and NO<sub>y</sub> with lower concentrations during daytime as compared to those measured at night. The pattern was identical for acetylene and propylene (with  $k_{OH-VOC}$  from 0.90 to 5.90 x 10<sup>-12</sup> cm<sup>3</sup>/(mol s)) and highly reactive aromatic VOCs with  $k_{OH-VOC}$  from 13.7 (for *o*-xylene) to 57.5 x 10<sup>-12</sup> cm<sup>3</sup>/(mol s) (for 1,3,5-trimethylbenzene).

Figure 3-4. Diurnal variation of wind speed (knots), temperature (in °F), dew point (in °F) and relative humidity (%) at AIRS # 48-141-0044 during the period Apr-Oct. 2008-2014.



Local meteorology and weather patterns are also important parameters in the chemistry of O<sub>3</sub>. Temperature is an indicator of the incoming solar radiation (the driving force for the initiation of photo-oxidation reactions) reaching as high as 90°F. Relative humidity (and dew point) decreased during daytime to 40% to 18%). Water vapor is an important factor in photochemical processes both directly as a source of OH radicals, and indirectly through the formation of secondary organic aerosol that influence the ultraviolet actinic flux. Wind speed increased from 5.5 knots in nighttime (4:00) to 6.5 knots in early morning (8:00 to 12:00) and up to 7.5 knots in late afternoon (16:00). Winds originated mostly from the west with wind speeds from 5 to 15 knots and from east-southeast with winds up to 10 knots.

Figure 3-5. Prevailing resultant wind conditions at the AIRS # 48-141-0044 during the period Apr-Oct. 2008-2014 (all hours). Wind speeds are in knots.



Table 3-4. 1-hr mean O<sub>3</sub> concentrations for selected ranges of wind direction, wind speed, temp<u>erature, relative humidity and dew point during the period Apr-Oct. 2008-2014 (all hours)</u>.

| •   |            |                 |             | <b>`</b>    |  |  |
|---|------------|-----------------|-------------|-------------|--|--|
| Wind direction (°)                                      |            |                 |             |             |  |  |
|   | 315-45 (N) | 45-135 (E)      | 135-225 (S) | 225-315 (W) |  |  |
| O <sub>3</sub>  | 35         | 29.7            | 37.2        | 38.6        |  |  |
|   |            | Wind speed (kno | its)        |             |  |  |
|   | 0          | 0-5             | 5-10        | 10          |  |  |
| O <sub>3</sub>  | 30.4       | 36.4            | 42.1        | 46.2        |  |  |
| Temperature (°F), Relative humidity (%), Dew point (°F) |            |                 |             |             |  |  |
|   | <40        | 40-60           | 60-80       | >80         |  |  |
| O <sub>3</sub>  | -          | 29.7            | 29          | 41.3        |  |  |
| O <sub>3</sub>  | 38.1       | 27.3            | 22.1        | 18.1        |  |  |
| O <sub>3</sub>  | 37.9       | 33.6            | 21.4        | -           |  |  |

Table 3-4 and Table 3-5 show the mean  $O_3$  concentrations for selected ranges of wind direction and speed, temperature, relative humidity and dew point. The mean  $O_3$  concentration increased for winds originating from the south and west sectors, the lowest  $O_3$  levels were measured for easterly winds. The  $O_3$  concentrations increased progressively with the wind speed. In fact the higher 1-hr mean  $O_3$  levels were measured during south and north winds blowing at 5 knots or higher. This pattern suggests that intrusion of aloft  $O_3$  from upwind sources may be present as the wind speed increases and reduces the stability of the boundary layer. This was based on work by Kavouras et al. (2013) that was performed in Boise, Idaho using vertical profiles of ozone. The radar wind profiler was not used in this analysis but could provide some useful information about vertical mixing.

Table 3-5. 1-hr mean  $O_3$  concentrations for combined ranges of wind direction and wind speed, temperature, relative humidity and dew point.

|           |   | Wind speed (knots) |      |      |      |
|-----------|---|--------------------|------|------|------|
|           |   | 0                  | 0-5  | 5-10 | 10   |
| n         | Ν | 29.5               | 36.6 | 41.9 | 41.1 |
| nd<br>tio | E | 26.4               | 34.4 | 36.4 | 34.0 |
| i Wi      | W | 36.9               | 38.2 | 39.6 | 39.8 |
| q         | S | 34.0               | 37.3 | 43.2 | 46.3 |

As anticipated, the highest 1-hr mean  $O_3$  concentrations were measured for temperatures higher than 80°F.  $O_3$  levels decreased drastically as temperatures decreased to 40°F.  $O_3$  showed a significant negative correlation with relative humidity with the highest 1-hr mean  $O_3$  concentrations recorded during dry conditions (less than 40%). For extremely humid conditions (higher than 80%), the mean  $O_3$  concentration was very low (18 ppbv).

#### **Ozone accumulation**

The accumulation of  $O_3$  driven by NO emissions may be estimated by calculating the  $O_3$  accumulation rate (in ppbv  $O_3/h$ ) as follows:

Equation 3-1 Acc.Rate = 
$$\frac{[O_3]_{tO3\_acc} - [O_3]_{tNO=O3}}{tO3\_acc - tNO = O3}$$

where tNO=O3 is the morning NO-O<sub>3</sub> crossover time (in h), tO3\_acc is the time of the day where the maximum O<sub>3</sub> concentration, and  $[O_3]_{tNO=O3}$  and  $[O_3]_{tO3_{acc}}$  are the O<sub>3</sub> concentrations at tNO=O3 and tO3\_acc times of the day, respectively.

Figure 3-6. Diurnal variation of average  $O_3$  and NO concentration at five sites



Figure 3-6 shows the hourly variations of  $O_3$  and NO at five monitoring sites (using the same yaxis). To calculate the  $O_3$  accumulation rate using Equation 3-1, NO maximum concentrations in early morning should sufficiently trigger the titration of overnight  $O_3$ , or, exceed  $O_3$  levels at the same time. For all sites, the minimum  $O_3$  concentrations at 5:00 or 6:00 were substantially higher than the NO concentrations. These findings provide initial evidence of the significant role of VOCs on  $O_3$  production. Note that these measurements refer to the specific sites and do not provide a metric of NO emissions in the study region. These very low NO/NO<sub>x</sub>/NO<sub>y</sub> levels may suggest NO<sub>x</sub>-limited conditions.

#### **Ozone spatiotemporal trends**

The Pearson correlation coefficient was applied to determine whether there is a uniform temporal profile (concentrations decrease or increase simultaneously). It was calculated on an hourly basis as follows:

$$r = \frac{1}{n} \cdot \sum \left( \frac{X_i - \overline{X}}{s_x} \right) \left( \frac{Y_i - \overline{Y}}{s_y} \right)$$

where  $\frac{X_i - \overline{X}}{s_x}$ ,  $X_i$ ,  $s_x$ ,  $\frac{Y_i - \overline{Y}}{s_y}$ ,  $\overline{Y}$  and  $s_y$  are the standard errors, and population mean and

standard deviation of X and Y populations. High (>0.70) correlation coefficients values indicate a positive linear relationship between variables, while negative values suggest a strong anticorrelation. Figure 3-7 shows the Pearson correlation coefficients of hourly O<sub>3</sub> concentrations for each site. With the exception of the AIRS # 35-013-0022 and AIRS # 80-006-0007 (located in Ciudad Juárez), the correlation coefficients values were higher than 0.75 suggesting similar hourly temporal profiles for O<sub>3</sub>.

Figure 3-7. The variation of Pearson correlation coefficient of hourly  $O_3$  concentration for each site.



The relative difference (% $\Delta$ C/Ref) of 24-hr paired concentration between two sites was computed as the percentage of the absolute concentration difference to the reference site concentration. Positive values indicate that ozone concentrations at the site are higher than those measured in reference site. Median relative differences provide an indication of systematic differences between the sites, whereas site-to-site variation is traced by the standard deviation. The coefficient of divergence (COD) is used to assess the spatial uniformity of measurements with respect to the concentration levels. The COD is estimated as follows (Pinto et el., 2004):

$$= \sqrt{\frac{1}{p} \cdot \sum_{i=1}^{p} \left(\frac{C_{ij} - C_{ik}}{C_{ij} - C_{ik}}\right)^2}$$

COD

where p is the total number of paired measurements, and  $C_{ij}$  and  $C_{ik}$  are the measured concentrations in fixed and home outdoor sites on the *i*-th day, respectively. COD values vary from 0 to 1, with COD values close to unit being indicative of strong spatial variation. In this analysis, the reference site was the AIRS # 48-141-0044 because O<sub>3</sub>, NO<sub>x</sub>, NO<sub>y</sub> and VOCs were measured at that site.

Table 3-6 shows the distribution (median and standard deviation) of the 24-hour relative differences at sites in El Paso in Texas, Ciudad Juárez in Mexico and Doña Ana county in New Mexico. The median relative difference values for sites within the El Paso/Ciudad Juárez urban complex were low, indicating a rather uniform spatial pattern in the valley on a day-to-day basis. High 24-hour O<sub>3</sub> relative difference values were estimated for the northern site in El Paso (AIRS # 48-141-0058) and the three O<sub>3</sub> sites located in Doña Ana County, with these sites registering 15 to 20% higher O<sub>3</sub> levels. The analysis of the site-to-site variation of O<sub>3</sub> concentrations, expressed by the standard deviation of  $\%\Delta C/Ref$  values, suggested common characteristics for all sites. The rather uniform spatial pattern of daily ozone concentrations was demonstrated by the low COD values (from 0.069 to 0.126) that were similar to those observed in previous years in the same area (Chalbot et al., 2013) and in other U.S. urban areas (Kavouras et al., 2013).

Table 3-6. Median and standard deviation of the relative ( $\Delta C/C_{Ref}$ ) differences and the mean COD values of 24-hr mean concentration of O<sub>3</sub> at each site. Reference site: 48-141-0044. Keep in mind that a negative median simply says that ozone levels at the site in question is higher than the reference site 48-141-0044 in El Paso. Small COD values much smaller than 1.0 indicate that there is very little spatial variability.

| Sito        | ΔC/C   | COD  |       |
|-------------|--------|------|-------|
| One         | Median | σ    | COD   |
| 35-013-0008 | 2.9    | 16.4 | 0.078 |
| 35-013-0017 | 5.8    | 16.5 | 0.082 |
| 35-013-0020 | 20.7   | 19.7 | 0.126 |
| 35-013-0021 | 16.1   | 16.9 | 0.105 |
| 35-013-0022 | 21.1   | 20.2 | 0.126 |
| 35-013-0023 | 7.1    | 17.0 | 0.084 |
| 48-141-0029 | 4.0    | 14.7 | 0.073 |
| 48-141-0037 | 9.4    | 11.8 | 0.069 |
| 48-141-0055 | -6.7   | 12.9 | 0.076 |
| 48-141-0057 | -2.9   | 14.5 | 0.075 |
| 48-141-0058 | 17.9   | 14.9 | 0.105 |
| 80-006-0007 | -5.3   | 18.1 | 0.100 |

#### **VOCs source attribution**

Table 3-7 shows the average 1-hr toluene/benzene, m/p-xylene/benzene and m/p-xylene/toluene ratios at the AIRS # 48-141-0044 site and in urban/tunnel locations in the US. The mean 1-hr toluene/benzene ratio was 3.49. These values are somewhat higher than those estimated for most of the other urban areas and the highway tunnels. Higher toluene to benzene ratios may indicate the contribution of industrial and fugitive emissions of toluene. The mean values of m/p-xylene/benzene and m/p-xylene/toluene ratios were 1.27 and 0.35, respectively, and were also higher than those computed for the other urban areas. While the toluene to benzene ratio may identify the potential influence of fugitive emissions, which is likely given the presence of the oil refinery in the region; it may not be identified by an analysis such as Positive Matrix Factorization (PMF) because its overall contribution throughout the monitoring period is not high.

|                           | Toluene/ | <i>m/p</i> -Xylene | <i>m/p</i> -Xylene | Reference     |
|---------------------------|----------|--------------------|--------------------|---------------|
|                           | Benzene  | /Benzene           | /Toluene           |               |
| Mean                      | 3.49     | 1.27               | 0.35               | This study    |
| Standard<br>deviation     | 2.18     | 0.72               | 0.16               |               |
| Max<br><b>Urban areas</b> | 182.1    | 14.0               | 2.40               |               |
| 15 urban                  | 1.7      | 0.7                | 0.4                | Singh et al., |

Table 3-7 Concentrations ratios for benzene, toluene and m/p-xylenes in El Paso compared to other urban areas and in highway tunnels in the US

| locations in US                |            |            |            | Env. Sci.&<br>Technol., 1982,<br>16, 872   |
|--------------------------------|------------|------------|------------|--|
| Los Angeles, CA                | 1.9-3.5    | 0.8-1.2    | 0.2-1.6    | Baldasano et al.,<br>Env.<br>Sci.&Technol.,<br>1998, 32, 405;<br>Zielinska et al.,<br>Res.Chem.Inter<br>med. 1994,<br>20,321; Fraser<br>et al. Env.<br>Sci.&Technol.<br>1998, 32, 1760 |
| Chicago, IL                    | 0.8        | 0.3        | 0.4        | Baldasano et al.,  |
| Oakland, CA<br>Phoenix, AZ     | 2.0<br>2.7 | 0.9<br>1.4 | 0.5<br>0.5 | Env.<br>Sci.&Technol   |
| Denver, CO<br>Houston, TX      | 2.5<br>1.8 | 1.3<br>0.9 | 0.5<br>0.5 | 1998, 32, 405  |
| Philadelphia, PA               | 2.3        | 1.3        | 0.6        |  |
| Pittsburgh, PA<br>San Jose, CA | 1.7<br>1.8 | 0.3<br>1.3 | 0.3<br>0.7 |  |
| Boston, CA                     | 2.3        | 1.2        | 0.5        |  |
| 40 urban<br>location in US     | 2.1        | 1.1        | 1.0        |  |
| Highway Tunnels                | 1 2-1 4    | 0.8-1.1    | 0 52-0 60  | Zielinska et al  |
| Caluecoli                      | 1.2-1.4    | 0.0-1.1    | 0.32-0.00  | Sci. Total Envir.<br>1994, 146/147,<br>281; Kirchstetter<br>et al., Env.<br>Sci.&Technol.,<br>1996, 30, 661  |
| Fort McHenry                   | 1.2-1.6    | 1.2-2.5    | 0.7-2.1    | Sagebiel et al.,   |
| TUSCATUTA                      | 1.3-1.4    | 0.0-1.0    | 0.0-0.7    | Aurios. Eriv.<br>1996, 30, 2287;<br>Gertler et al.,<br>Atmos. Eriv.<br>1996, 30. 2297  |
| Van Nuys                       | 1.7        | 1.1        | 0.64       | Fraser et al.,   |
| Cassiar                        | 1.6        | 0.7        | 0.47       | Rogak et al.,<br>JAWMA, 1998,  |
|                                |            |            |            | 48, 004  |

The photochemical age (in hours) was computed using the measured toluene-to-benzene ratio, as follows:

Equation 3-4 
$$\Delta \tau = \frac{ln\left(\frac{X_{toluene}}{X_{benzene}}\right)_{t=0} - ln\left(\frac{X_{toluene}}{X_{benzene}}\right)}{[OH](k_{toluene} - k_{benzene})}$$

where  $k_{toluene}$  (5.63×10<sup>-12</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) and  $k_{benzene}$  (1.22×10<sup>-12</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) are the rate coefficients for the reaction with OH radicals and [OH] is the average concentration of the hydroxy radical (3.00×10<sup>6</sup> molecules cm<sup>-3</sup>). The  $\left(\frac{X_{toluene}}{X_{benzene}}\right)_{t=0}$  was set to 3.70.

The photochemical age varied tom approximately -2 hrs up to 1.25 hrs, indicating the dominant influence of local sources. Assuming an average wind speed of 3.0 m/sec (about 6 knots), VOCs sources are located within a 1-2 km away from the site. These include the Bridge of Americas Port of Entry (less than 0.5 km southeast of the site) and the Interstate Highway 10/110 intersection about 1.6 km northeast of the site.

The emissions ratio (ER) for each VOC in relation to acetylene ( $C_2H_2$ ) was mathematically calculated as follows:

Equation 3-5 
$$ln\left(\frac{[VOC]}{\{C_2H_2\}}\right) = lnER - (k_{VOC} - k_{C2H2}) \cdot \Delta\tau[OH]]$$

where [VOC] is the concentration of individual VOC,  $[C_2H_2]$  is the acetylene concentration, ER is the emission ratio of VOC relative to acetylene,  $k_{VOC}$  is the OH reaction constant of the VOC,  $k_{C2H2}$  is the OH reaction constant of acetylene (0.85  $10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> and  $\Delta T$ [OH]] is obtained from Equation 3-4. The variables ER (intercept) and  $k_{VOC}$  (slope) were determined by simple regression analysis and daily concentrations of individual VOCs. The ERs are presented in Table 3-8. For all VOCs, the emission ratios were higher than those computed for vehicle exhausts and in multiple US cities. For the aromatic VOCs, the computed ER ratio in El Paso was 2-5 times higher than those estimated elsewhere. These results indicated that the largest fraction of VOC was from vehicle exhausts, with secondary contributions of aromatic VOCs from fugitive area sources. These may include fugitive emissions of gasoline vapors from vehicles at the border crossing bridges.

To further resolve the sources of VOCs, a source apportionment approach was utilized. The US Environmental Protection Agency positive matrix factorization (version 3.0.2.2) model could not be used because uncertainties of measurements, a required dataset for PMF, were not available. Instead, we applied principal factor analysis (PCA), a well-known and validated source apportionment method (Kavouras et al., 2001).

Figure 3-8 Photochemical age of VOCs at the AIRS # 48-141-0044 site



| VOC                    | Emission ratio | Vehicle exhausts and<br>39 US cities<br>(Zielinska and Kavouras,<br>2012 and references<br>therein) |
|------------------------|----------------|---|
| Propylene              | 1.05           | 0.398-0.595   |
| 1,3-Butadiene          | 0.21           | -   |
| n-Octane               | 0.13           | 0.018-0.050   |
| m/p-Xylenes            | 1.60           | 0.330-0.351   |
| Benzene                | 1.18           | 0.326-0.474   |
| Toluene                | 4.37           | 0.749-0.937   |
| Ethylbenzene           | 0.57           | 0.114-0.123   |
| o-Xylene               | 0.57           | 0.123-0.140   |
| 1,3,5-Trimethylbenzene | 0.09           | 0.052-0.108   |
| 1,2,4-Trimethylbenzene | 0.36           | 0.158-0.183   |
| Styrene                | 0.07           | -   |

First, VOCs concentrations ( $X_i$ ) were transformed to ppbC-equivalent concentrations ( $X_i^c$ ) as follows:

Equation 3-6  $X_i^C = X_i \cdot (number \ of \ carbon \ atoms)$ 

The VOCs concentration matrix,  $X_i^c(nxm)$  with *n* rows (the number of analyzed species) and *m* columns (the number of samples analyzed) was standardized using the Z-score. The Z-score of

each VOCs for every sample was determined using the following formula:

Equation 3-7 
$$Z_{ik} = \frac{X_{ik} - \bar{X}_i}{\sigma_i}$$

where *i*=1,2,...n is the number of analyzed VOCs; *k*= ,2,....m is the number of samples;  $Z_{ik}$  is the standardized value of the *i-th* VOC for the *k-th* sample;  $X_{ik}$  is the concentration of the *i-th* VOC for the *k-th* sample;  $\overline{X}_i$  is the mean concentration of the *i-th* VOC; and  $\sigma_i$  is the standard deviation of the *i-th* VOC concentration distribution. PCA determined the eigenvector factor B(*nxn*) and the corresponding transpose B<sup>-1</sup>(*nxn*) matrices, which are used to calculate a diagonal table  $\Lambda(nxn)$  using the following equation:

Equation 3-8  $B(nxm) \times C(nxm) \times B^{-1}(nxm) = \Lambda(nxm)$ 

where C(nxn) is the correlation matrix. The matrix  $\Lambda(nxn)$  contains the eigenvalues of the corresponding eigenvectors-factors. Although n factors are initially extracted to explain the total variance of the system, a limited number of *p* factors accounted for more than 90% of the variance. Consequently, the dimensions of both the eigenvector [B(*nxn*)] and eigenvalues [ $\Lambda(nxn)$ ] matrices were reduced to (*pxn*).

To clarify the meaning of these factors, they were rotated. Although the factor loadings have been changed, the factor solutions (unrotated and rotated) are mathematically equivalent. We applied orthogonal rotation in which all retained factors rotated but maintained their orthogonal structure among each other (SPSS Version 22.0). The factor matrix, FS(pxm), is the product of the coefficient matrix of the variables [W(*pxn*)] and the Z-score matrix [Z(*nxm*)], as follows:

Equation 3-9  $FS(pxm) = W(pxn) \times Z(nxm)$ 

where

Equation 3-10  $B(pxm) = W(pxm) \times \lambda_i$ 

and  $\lambda_i$  is the eigenvalue of *p*-th factor (source). Because these factor scores (FS) are calculated from the Z-score normalized VOC concentrations, they have a mean value of 0 and a standard deviation of 1. To determine the real FS (source contributions), the "absolute zero FS" were calculated. This was achieved by separately scoring an extra day where ambient concentrations of VOCs were set at 0. The Z-score for this "extra day" is calculated as follows:

Equation 3-11 
$$Z_{ik} = \frac{-\bar{X}_i}{\sigma_i}$$

Using the following equation, the absolute zero factor scores (FS\*<sub>o</sub>) were calculated as follows:

Equation 3-12 
$$FS_o(px1) = W(pxn) \times Z(nx1)$$

The absolute FS (AFS) for each day can be calculated using

Equation 3-13 
$$AFS(pxm) = FS(pxm) - FS_o(pxm)$$

The contributions of the retained factors to the VOCs concentrations were computed using a

least-squares multivariate linear regression model

#### Equation 3-14 $X_{ik} = a + \sum_{k=1}^{p} (\beta_k \cdot AFS_k)$

where  $\beta_k$  is the regression coefficient to convert the contributions to ppbC/ppbC. The intercept,  $\alpha$ , was attributed to other sources. Negative regression coefficients indicated that there were too many factors. Table 3-9 and Table 3-10 show the loadings and contributions of retained factors to VOCs. Figure 3-9 presented a comparison between measured and reconstructed total VOCs concentration. The temporal patterns (annual, monthly, day of the week and hour of the day) of factor contributions are depicted in Figure 3-11.

|                        | Factor 1 | Factor 2 |
|------------------------|----------|----------|
| Eigenvalue             | 10.433   | 0.401    |
| % Variance explained   | 86.945   | 3.341    |
| Propylene              | 0.695    | 0.643    |
| Acetylene              | 0.892    | 0.294    |
| 1,3-Butadiene          | 0.728    | 0.596    |
| <i>n</i> -Octane       | 0.602    | 0.720    |
| <i>m/p</i> -Xylenes    | 0.706    | 0.689    |
| Benzene                | 0.766    | 0.571    |
| Toluene                | 0.668    | 0.623    |
| Ethylbenzene           | 0.712    | 0.684    |
| o-Xylene               | 0.711    | 0.687    |
| 1,3,5-Trimethylbenzene | 0.607    | 0.738    |
| 1,2,4-Trimethylbenzene | 0.589    | 0.711    |
| Styrene                | 0.293    | 0.876    |

Table 3-9 Table Factor Loadings/Eigenvalue

Figure 3-9. Comparison of measured and reconstructed concentrations of total VOCs in AIRS # 48-141-0049.



Factor 2 explained 3.3 of the remaining variability. This factor was stronger correlated with noctane, 1,3,5-trimethylbenzene, 1,2,4-trimethylbenzene and styrene. Toluene was also moderately associated with both factors. All these compounds are used as gasoline additives

and released in the air from automobiles. However, point sources (i.e. facilities that use them as solvents and materials in coating, pesticides, cleaning, rubber, printing and ink industries) constitute an equally large source of these chemicals. Fugitive emissions from the refinery may be particularly important during hot days. Since the potential contribution of fugitive emissions is sporadic, it cannot be identified by PMF. Given the diurnal and annual variations of the two identified sources (higher levels in morning and afternoon, when temperature is lower than noon), it is most likely that the two retained factors are associated with traffic emissions. The contribution of this factor increased progressively during the 2008-2014 period, with the highest contributions being measured in August and September. The weekday/weekend and hourly pattern were identical to those observed for factor 1. The majority of the variance (more than 90%) of this subset of data was explained by two eigenvectors-factors. The two retained factors the majority and the temporal variability of total VOCs concentration (expressed in ppbC) (intercept of approximately 5 ppbC). The two factors slightly over-predicted (negative intercept) VOCs concentrations except propylene with R<sup>2</sup> higher than 0.8. Despite the orthogonal rotation, the separation of the two retained factors was not very transparent. This may be due to the limited number of measured VOCs and their emissions from multiple sources.



Figure 3-10. Daily pattern of estimated contributions of the two retained factors.

Factor 1 accounted for 86.9% of the total variance and was stronger correlated with acetylene, 1,3-butadiene, benzene, xylenes and ethylbenzene. These VOCs are typically associated with vehicular exhausts. This factor accounted for the largest fraction of individual VOCs except styrene. The mean values of toluene, m/p-xylene/benzene and m/p-xylene/toluene for this factor (3.5, 1.44 and 0.30) were comparable to those calculated for traffic (see Table 3-7). The contribution of Factor 1 decreased from 2008 to 2014 with the highest contributions being computed for April and May followed by declining contribution in summer months. The highest contributions were also computed for urban areas dominated by anthropogenic sources. Factor 2 explained 3.3 of the remaining variability. This factor was stronger correlated with n-octane, 1,3,5-trimethylbenzene, 1,2,4-trimethylbenzene and styrene. Toluene was also moderately associated with both factors. All these compounds are used as gasoline additives and released in the air from automobiles. However, point sources (i.e. facilities that use them as solvents and materials in coating, pesticides, cleaning, rubber, printing and ink industries) constitute an equally large source of these chemicals. The contribution of this factor increased progressively

during the 2008-2014 period, with the highest contributions being measured in August and September. The weekday/weekend and hourly pattern were identical to those observed for factor 1.

Figure 3-11 Mean annual, monthly, day of the week and hourly contributions to total VOCs concentrations of the two retained factors.



Because of these similarities, we further investigated whether the two factors represented different stages of photochemical processing or distinct, albeit well-mixed sources by calculating the ratio of the VOC abundance in each factor and determine the association, if any, with the photochemical age ( $\Delta \tau$ ) using the following equation:

Equation 3-15 
$$\frac{VOC_{factor1}}{VOC_{factor2}} = A \cdot e^{-k_{OH/VOC} \cdot \Delta \tau[OH]}$$

where A is a scaling factor.

Figure 3-12 Dependence of  $ln(\frac{VOC_{factor1}}{VOC_{factor2}})$  to photochemical age ( $\Delta \tau$ )



No trends were observed for the two factors (Figure 3-12) while the mean  $\Delta \tau$ [OH] value, metric of the duration of the photochemical processing, was very low indicating that there were two uniquely identified VOCs sources.

| Table 3-10 Contributions of PC | A retained factors to | VOCs concentrations | (in ppbv) |
|--------------------------------|-----------------------|---------------------|-----------|
|                                |                       |                     |           |

| Compound               | R <sup>2</sup> | Factor 1 contribution | Factor 2 contribution | Intercept      | Reconstructed concentration | Measured concentration |
|------------------------|----------------|-----------------------|-----------------------|----------------|-----------------------------|------------------------|
| Propylene              | 0.945          | $0.632 \pm 0.006$     | 0.252 ± 0.005         | 0.282 ± 0.004  | 1.166 ± 0.009               | 1.166 ± 0.009          |
| Acetylene              | 0.948          | 0.922 ± 0.008         | 0.197 ± 0.004         | -0.120 ± 0.003 | 0.999 ± 0.010               | 1.070 ± 0.011          |
| 1,3-Butadiene          | 0.943          | 0.179 ± 0.002         | 0.059 ± 0.001         | -0.013 ± 0.001 | 0.226 ± 0.002               | 0.226 ± 0.002          |
| n-Octane               | 0.822          | 0.135 ± 0.001         | 0.071 ± 0.001         | -0.009 ± 0.001 | 0.197 ± 0.002               | 0.197 ± 0.002          |
| m/p-Xylenes            | 0.918          | 1.646 ± 0.015         | 0.649 ± 0.013         | -0.348 ± 0.008 | 1.948 ± 0.021               | 1.950 ± 0.022          |
| Benzene                | 0.886          | 1.139 ± 0.010         | 0.317 ± 0.007         | -0.095 ± 0.006 | 1.362 ± 0.013               | 1.363 ± 0.013          |
| Toluene                | 0.883          | 3.728 ± 0.034         | 1.448 ± 0.030         | -0.325 ± 0.022 | 4.851 ± 0.050               | 4.855 ± 0.051          |
| Ethylbenzene           | 0.923          | 0.574 ± 0.005         | $0.223 \pm 0.005$     | -0.098 ± 0.003 | $0.699 \pm 0.007$           | $0.699 \pm 0.008$      |
| o-Xylene               | 0.923          | $0.593 \pm 0.005$     | $0.232 \pm 0.005$     | -0.118 ± 0.003 | 0.706 ± 0.008               | 0.707 ± 0.008          |
| 1,3,5-Trimethylbenzene | 0.899          | 0.161 ± 0.001         | 0.078 ± 0.002         | -0.081 ± 0.001 | 0.157 ± 0.002               | 0.159 ± 0.002          |
| 1,2,4-Trimethylbenzene | 0.870          | 0.478 ± 0.005         | 0.212 ± 0.004         | -0.149 ± 0.003 | 0.541 ± 0.007               | 0.541 ± 0.007          |
| Styrene                | 0.877          | 0.057 ± 0.001         | $0.096 \pm 0.002$     | -0.044 ± 0.001 | 0.109 ± 0.002               | 0.109 ± 0.002          |

Table 1 show the contribution of the two VOCs retained factors to 1-hr maximum ozone concentrations. The intercept was  $52.9 \pm 4.0$  ppbv, comparable to those computed for the fourth highest policy relevant background (PRB) O<sub>3</sub> in the study region with wildfires (it refers to O<sub>3</sub> levels in the absence of all anthropogenic emissions of VOC precursors in North America). The two identified sources contributed, on average, 2.7 ppbv of O<sub>3</sub>. This very low contribution, which is also biased by the assumption of the linear association between ambient VOCs and O<sub>3</sub> levels, provided additional indications of dependence of O<sub>3</sub> formation on NO<sub>x</sub> emissions in the region.

Table 3-11 Contributions of VOCs sources to ozone concentrations in El Paso, Texas.

| Parameter                                  | Value     |
|--|-----------|
| Adjusted R <sup>2</sup>                    | 0.03      |
| Mean 1-hr max O <sub>3</sub> concentration |           |
| Measured                                   | 55.5 ppbv |
| Reconstructed by the two                   | 2.7 ppbv  |
| retained VOCs factors                      |           |
| Factor 1                                   | 2.7 ppbv  |
| Factor 2                                   | -0.0 ppbv |
| Unexplained by the two retained            | 52.9 ppbv |
| VOCs factors (intercept)                   |           |

#### **Trajectories analysis**

#### Local and regional contributions to ozone concentrations

The aim was to identify the regions that contribute to ozone concentration in the El Paso/Ciudad Juárez/Doña Ana urban metroplex. This is achieved by using the Tracer Mass Balance (TrMB) model and calculating the backward trajectories of air masses prior to their arrival at the study site. We feel that the TrMB method can be useful in this study with ozone since it has been developed and validated for sulfate aerosol which is also a secondary pollutant. The locations of the air masses every hour going backwards 72 hours were computed using the NOAA HYSPLIT trajectory model and Eta Data Assimilation System (EDAS) meteorological fields as inputs, with a starting height of 500 m above ground level (m.a.g.l.). It has been previously shown that 500 m.a.g.l. is within the planetary boundary layer during summer. Since backward trajectories were calculated every hour, each trajectory point represents the location of the trajectory for 1-hr. The residence time of a 0.25 degree latitude by 0.25 degree longitude cell was defined as the total number of trajectory points within the cell. The normalized residence time is the fraction of the residence time in each cell to the total time of backward trajectories for the study period (ca. 1280 days x 24 hrs/days x 72 traj.points/hr = 2,211,840 trajectory points).

Figure 3-13 shows the spatial variation of residence time arriving in the El Paso/Ciudad Juárez/Doña Ana urban metroplex. It shows two clear pathways of air masses movement near the ground from distinctively different regions. More specifically, air masses coming from the west originated often from southwest US including southern California and Arizona and Baja California. This region is mostly desert but also home to large urban areas (e.g. Los Angeles, San Diego and Phoenix) with known ozone pollution problems. On the other hand, air masses coming from the southeast sector extended along the Rio Grande River Valley (US-Mexico border) and Gulf of Mexico. This region is also a desert but it enables transport of pollutants released from port and oil/gas exploration activities in the Gulf of Mexico and includes emissions of ozone precursors (VOCs and NO<sub>x</sub>).

Figure 3-13 The normalized trajectories times of air masses arriving in the El Paso/Ciudad Juárez/Doña Ana urban metroplex during the period 2008-2014.



To further quantify the contribution of each region to ozone concentrations at the study area, the geographic region in which air masses spent at least 72 hours was divided in twenty-eight (28) source regions, including 16 source regions around the El Paso/Ciudad Juárez/Doña Ana urban metroplex (G1-8 and J1-8) as follows :

(A) Pacific Ocean off the US coast;

- (B) Pacific Northwest;
- (C) Northern Rockies and Plains;
- (D) Upper Midwest and NorthEast;
- (E) Central Pacific Ocean;
- (F) Southern California;
- (G) See below;
- (H) Baja California;
- (I) Midwest and Eastern Seaboard;
- (J) See below;
- (K) Off-Mexico Pacific Ocean;
- (L) Gulf of Mexico;
- (M) South Pacific Ocean;
- (N) Southern Mexico; and
- (O) Caribbean Sea.
- The 16 proximity sites were:
  - (G1) Northern Nevada and Utah;
  - (G2) Colorado Rockies;
  - (G3) Colorado;
  - (G4) Rural Nebraska;
  - (G5) Western Arizona including Phoenix;
  - (G6) Eastern Arizona and Western New Mexico;

(G7) Eastern New Mexico and Western Texas; and

- (G8) Northern Texas;
- (J1) Baja California and Sonora Desert;
- (J2) Chihuahua desert;
- (J3) El Paso/Ciudad Juárez;
- (J4) Southeastern Texas;
- (J5) Southern Baja California;
- (J6) Coastal Western Mexico;
- (J7) Central Mexico; and
- (J8) Eastern Mexico.

The relationship between ozone concentrations ( $y_i$ , in ppbv) and the time that air spends over each region ( $t_i$ , in hours) was determined as follows:

Equation 3-16 
$$y_i = \sum_{j=1}^{20} C_j \pm a = \sum_{j=1}^{20} t_j \beta_j \pm a$$

where  $C_j$  was the contribution of *j*-source region on *i*-sample,  $\beta_j$  (in (ppb/hr) were the impact factors of regions describing the combined outcome of emissions from the area, aging and pollutants removed due to gravitational settling, turbulent mix-out, and wet deposition during transport to the receptor site. The intercept,  $\alpha$ , accounts for contributions from source regions outside the study domain. In our study, we included all cells in which the air masses spent at least 72 hours over the study period; thus contributions from sources outside the regions described above may be negligible. We previously showed that the computed contributions using the TrMB approach with and without the intercept are statistically insignificant and they represent the upper and lower estimates of the contributions, respectively.

Figure 3-14 The pre-defined source regions for El Paso/Ciudad Juárez/Doña Ana urban metroplex (2008-2014).



Figure 3-15 shows the mean (± 3s) contributions of the twenty eight source regions to 8-h maximum ozone concentration concentrations in El Paso/Ciudad Juárez/Doña Ana urban metroplex. The four regions with the highest contributions were El Paso/Ciudad Juárez (J3, 10.4

ppbv); Chihuahua desert (J2, 8.1 ppbv), Eastern Arizona and Western New Mexico (G6, 7.6 ppbv) and Baja California and Sonora Desert (J1, 4.6 ppbv). The two local regions with the El Paso/Ciudad Juárez/Doña Ana urban located north of the US-Mexico border (G6 and G7) added 10.4 ppbv, while the two regions south of the border contributed 18.5 ppbv. The remaining region with the G and J boundaries in the US added 8.7 ppbv as compared to 10.8 ppbv added from the remaining source regions in Mexico, Central America and the Caribbean Sea. The source region with the highest contribution to ozone (except the 16 G and J) was the Southern California (1.4 ppbv). Long range transport from distant source regions (A, B, C, D, E, H, M and N) added 1.3 ppbv. Potential sources of ozone precursors across the Baja California and southern California corridor include wildfires and shipping emissions. The ports of Los Angeles and Long Beach in southern California are among the most busiest worldwide and the destination of the majority of vessels crossing the Panama Canal and traveling through the Baja California corridor.





Figure 3-16 Comparison of measured and predicted daily 8-hr maximum  $O_3$  concentrations in El Paso/Ciudad Juárez/Doña Ana urban metroplex (2008-2014)


The limitations of the TrMB model include: (i) errors in trajectories locations may not be random leading to large errors in the calculations of average source contributions and disproportionally influence days with high (or low) concentrations; (ii) source contributions for individual days may be highly unstable and; (iii) the contributions from sources near (i.e. within a few kilometers) the receptor cannot be estimated. However, the accuracy, sensitivity and reliability of the TrMB approach were validated for secondary sulfate aerosol by releasing perfluorocarbon tracers from source regions and monitoring their levels in receptor sites (Green et al., 2003) and has been applied to trace the origin of primary and secondary air contaminants (Xu et al., 2006; Huang et al., 2010; Chalbot et al., 2013). The impacts of the aforementioned limitations were substantially reduced to less than 10% for increasing averaging periods (Poirot and Wishinski, 1986; Gebhart et al., 2006, 2011). Previous studies showed that background ozone concentrations account in continental background locations in the region (Chihuahua refuge, Big Bend NP) excluding wildfires was 40 ppbv.

Figure 3-16 shows the correlation between measured and predicted 8-hr maximum ozone concentration using the daily values. The intercept was equal to 39.5 ppbv, very close for non-fire continental background  $O_3$  concentration.

# Characteristics of high ozone events

The characteristics of high ozone days were determined. The definition for high ozone days was: calendar days in which the 8-h maximum ozone concentration was equal or higher than the  $80^{th}$  percentile of the cumulative frequencies of 8-h maximum concentrations at this site. Note that the  $80^{th}$  percentile is determined on a site-by-site basis, thus it varies among the sites. This resulted on up to 216 calendar days per site (20% of days during the six-month "O<sub>3</sub>" season for the period 2008-2014.

Figure 3-17 Number of sites with high ozone concentration and mean 8-hr maximum ozone concentrations.



There was a total of 684 high  $O_3$  days during the period 2008-2012 in all sites. Most of them (40%) were observed in 1-2 sites indicating a localized event. There were 208 days with high  $O_3$ 

days in more than 7 sites indicating most of the area covered by the monitoring sites experienced elevated  $O_3$  concentrations. For approximately 100 of those days, a high ozone day was reported in more than 9 sites suggesting a widespread  $O_3$  event.

The conditions associated with each event are described in Appendix A. For each event, air mass backward trajectories and wildland fire activity in the Northern America (retrieved from the Terra and Aqua MODIS satellites were mapped. In addition, modeled smoke concentrations using Navy Aerosol Analysis and Prediction System (at 12:00Z time for each day) were retrieved. We agree that NAAPS may not quantitatively predict smoke concentrations alone. For this reason, we use it to qualitatively assess whether there may be smoke or not. In addition, the qualitative assessment of smoke presence does not rely on the NAAPS output, alone. Trajectory analysis and wildfire locations should also point towards the same. Increased PM<sub>2.5</sub> measurements do not necessarily indicate smoke presence. Extremely high PM<sub>2.5</sub> measurements (more than 100 µg/m<sup>3</sup>) may provide strong evidence of smoke presence (most likely very close to the region), regional smoke is typically not reflected significantly in PM<sub>2.5</sub>. Based on the analysis of prevailing weather conditions, air mass trajectories, occurrence of wildland fires in El Paso/Ciudad Juárez/Doña Ana urban metroplex, the impact of emissions from wildfires for each ozone event was characterized as strong, moderate, low or absent and as local or regional. Table 3-12 identifies the contributions of wildland fires for each high ozone event. Strong evidence of wildfires smoke was determined for three events (8, 9 and 13). Four events (3, 4, 5 and 12) exhibited moderate confidence of association with wildfires mostly transport from upwind fires, Six events (2, 6, 10, 11, 14 and 15 demonstrated low confidence of association with wildfires and two events (1 and 7) did not show any inputs from wildfires.

Figure 3-18 Number of days with high ozone concentration for multiple sites.



| Table 3-12 Contributior | s of wildland fires | on high O <sub>3</sub> events |
|-------------------------|---------------------|-------------------------------|
|-------------------------|---------------------|-------------------------------|

| ID | Episode                   | Wildland fires | Scale    |
|----|---------------------------|----------------|----------|
| 1  | June 13-17, 2008          | Absent         |          |
| 2  | July 31 - August 13, 2008 | Low            | Regional |
| 3  | July 24-31, 2009          | Moderate       | Regional |
| 4  | April 10-16, 2011         | Moderate       | Regional |
| 5  | July 11-17, 2011          | Moderate       | Regional |
| 6  | July 21-29, 2011          | Low            | Regional |
| 7  | August 18-23, 2011        | Absent         |          |

| 8  | May 11-17, 2012               | Strong   | Regional |
|----|-------------------------------|----------|----------|
| 9  | May 28 - June 4, 2012         | Strong   | Regional |
| 10 | July 4-17, 2012               | Low      | Regional |
| 11 | August 29 – September 2, 2012 | Low      | Regional |
| 12 | April 27 – May 1, 2013        | Moderate | Regional |
| 13 | July 2-6, 2013                | Strong   | Regional |
| 14 | August 15-21, 2013            | Low      | Regional |
| 15 | May 27-31, 2014               | Low      | Regional |

Table 3-12 shows the levels of  $O_3$ , NO, NO<sub>x</sub> and NO<sub>y</sub> during the fifteen high  $O_3$  events as well as the average for all high  $O_3$  events and remaining days. Because of the definition of high  $O_3$ days, mixing ratios of  $O_3$  in high  $O_3$  events were higher than those measured during the remaining days. There were significant differences between the average NO, NO<sub>x</sub> and NO<sub>y</sub> concentrations during the high  $O_3$  events and the remaining days. The higher NO and NO<sub>x</sub> levels were measured for the events 1 and 4, previously identifies as absent smoke and moderate/regional smoke contribution. During the events 8 and 9, NO and NO<sub>x</sub> concentrations were comparable to those measured during the remaining days.

| ID | Episode                        | O₃ (ppbv) | NO (ppbv) | NO <sub>x</sub> (ppbv) | NO <sub>y</sub> (ppbv) |
|----|--------------------------------|-----------|-----------|------------------------|------------------------|
| 1  | June 13-17, 2008               | 39 ± 1    | 7 ± 2     | 21 ± 5                 | n.m.                   |
| 2  | July 31 - August 13, 2008      | 40 ± 2    | 3 ± 1     | 15 ± 2                 | n.m.                   |
| 3  | July 24-31, 2009               | 44 ± 1    | 1 ± 1     | 11 ± 2                 | n.m.                   |
| 4  | April 10-16, 2011              | 42 ± 4    | 12 ± 6    | 26 ± 9                 | 16 ± 6                 |
| 5  | July 11-17, 2011               | 44 ± 3    | 3 ± 1     | 14 ± 2                 | n.m.                   |
| 6  | July 21-29, 2011               | 47 ± 1    | 2 ± 1     | 8 ± 1                  | n.m.                   |
| 7  | August 18-23, 2011             | 44 ± 3    | n.m.      | n.m.                   | n.m.                   |
| 8  | May 11-17, 2012                | 46 ± 3    | 2 ± 1     | 16 ± 3                 | n.m.                   |
| 9  | May 28 - June 4, 2012          | 44 ± 2    | 4 ± 1     | 17 ± 3                 | n.m.                   |
| 10 | July 4-17, 2012                | 46 ± 1    | 2 ± 1     | 12 ± 1                 | 14 ± 1                 |
| 11 | August 29 – September 2, 2012  | 37 ± 1    | 4 ± 1     | 23 ± 2                 | 27 ± 3                 |
| 12 | April 27 – May 1, 2013         | 41 ± 2    | 4 ± 1     | 21 ± 3                 | 19 ± 3                 |
| 13 | July 2-6, 2013                 | 47 ± 2    | 1 ± 1     | 12 ± 1                 | 11 ± 1                 |
| 14 | August 15-21, 2013             | 40 ± 2    | 3 ± 1     | 17 ± 2                 | 17 ± 2                 |
| 15 | May 27-31, 2014                | 44 ± 3    | 4 ± 2     | 21 ± 3                 | 22 ± 4                 |
|    | All high O <sub>3</sub> events | 42 ± 1    | 4 ± 1     | 17 ± 1                 | 18 ± 1                 |
|    | Remaining days                 | 34 ± 1    | 4 ± 1     | 15 ± 1                 | 16 ± 1                 |

Table 3-13 Mean 1-hr ozone, NO, NO<sub>x</sub> and NO<sub>y</sub> concentrations for the high O<sub>3</sub> events

Table 3-14 shows the levels of VOCs during the fifteen high  $O_3$  events as well as the average for all high  $O_3$  events and remaining days. Similarly, the average levels of individual VOCs during the high ozone episodes were comparable to those measured during the remaining days. For most of the VOCs, the highest levels were measured during the events 1, 2 and 11; events previously identified as no and low smoke influence. The VOCs levels for the two high ozone events with strong confidence of smoke contribution were lower than those measured during the remaining days.

# Table 3-14 Mean 1-hr VOC concentrations for the high $O_3$ events

| ID | Episode                        | Acetylene | Propylene | 1,3-<br>Butadiene | <i>n</i> -Octane | Benzene | Toluene | <i>m/p</i> -<br>xylnene | o-xylene | Styrene | Ethyl-<br>benzene | 1,2,4-<br>Trimethyl-<br>benzene | 1,3,5-<br>Trimethyl-<br>benzene |
|----|--------------------------------|-----------|-----------|-------------------|------------------|---------|---------|-------------------------|----------|---------|-------------------|---------------------------------|---------------------------------|
| 1  | June 13-17, 2008               | 1.7±0.4   | 1.4±0.3   | 0.3±0.1           | 0.3±0.1          | 3.1±0.8 | 8.4±2.5 | 3.3±1.1                 | 1.2±0.4  | 0.2±0.1 | 1.2±0.4           | 0.8±0.3                         | 0.3±0.1                         |
| 2  | July 31 - August 13,<br>2008   | 1.7±0.1   | 1.9±0.1   | 0.3±0.1           | 0.4±0.1          | 3.1±0.4 | 8.2±0.1 | 3.1±0.1                 | 1.2±0.1  | 0.1±0.1 | 1.3±0.1           | 0.8±0.1                         | 0.3±0.1                         |
| 3  | July 24-31, 2009               | 1.0±0.2   | 0.8±0.1   | 0.2±0.1           | 0.1±0.1          | 1.6±0.3 | 4.3±0.9 | 1.5±0.3                 | 0.6±0.1  | 0.1±0.1 | 0.6±0.1           | 0.4±0.1                         | 0.1±0.1                         |
| 4  | April 10-16, 2011              | 1.6±0.5   | 1.7±0.5   | 0.4±0.2           | 0.2±0.1          | 1.8±0.6 | 6.5±2.3 | 2.4±1.0                 | 0.8±0.3  | 0.2±0.1 | 0.9±0.4           | n.m                             | 0.4±0.1                         |
| 5  | July 11-17, 2011               | 0.8±0.3   | 0.9±0.3   | 0.2±0.1           | 0.1±0.1          | 0.7±0.3 | 3.6±1.3 | 1.7±0.4                 | 0.6±0.1  | 0.1±0.1 | 0.6±0.1           | 0.4±0.2                         | 0.1±0.1                         |
| 6  | July 21-29, 2011               | 0.7±0.2   | 0.8±0.1   | 0.2±0.1           | 0.1±0.1          | 0.6±0.1 | 3.4±0.6 | 1.3±0.3                 | 0.5±0.1  | 0.1±0.1 | 0.4±0.1           | 0.3±0.1                         | 0.1±0.1                         |
| 7  | August 18-23, 2011             | 0.6±0.1   | 0.8±0.1   | 0.2±0.1           | 0.1±0.1          | 0.7±0.1 | 3.5±0.6 | 1.4±0.3                 | 0.5±0.1  | 0.1±0.1 | 0.5±0.1           | 0.4±0.1                         | 0.1±0.1                         |
| 8  | May 11-17, 2012                | 0.8±0.1   | 1.0±0.1   | 0.2±0.1           | 0.2±0.1          | 0.9±0.1 | 3.4±0.4 | 1.3±0.1                 | 0.5±0.1  | 0.1±0.1 | 0.5±0.1           | 0.3±0.1                         | 0.1±0.1                         |
| 9  | May 28 - June 4, 2012          | 0.8±0.2   | 0.9±0.2   | 0.1±0.1           | 0.2±0.1          | 0.9±0.2 | 4.2±1.1 | 1.5±0.5                 | 0.6±0.2  | 0.1±0.1 | 0.6±0.2           | 0.4±0.1                         | 0.1±0.1                         |
| 10 | July 4-17, 2012                | 0.7±0.1   | 0.9±0.1   | 0.2±0.1           | 0.2±0.1          | 0.9±0.1 | 4.6±0.6 | 1.6±0.2                 | 0.6±0.1  | 0.1±0.1 | 0.6±0.1           | 0.5±0.1                         | 0.1±0.1                         |
| 11 | August 29 -                    |           |           |                   |                  |         |         |                         |          |         |                   |                                 |                                 |
|    | September 2, 2012              | 1.4±0.2   | 1.7±0.2   | 0.3±0.1           | 0.5±0.1          | 1.7±0.2 | 8.2±0.8 | 3.2±0.3                 | 1.2±0.1  | 0.2±0.1 | 1.2±0.1           | 0.9±0.1                         | 0.3±0.1                         |
| 12 | April 27 – May 1, 2013         | 1.1±0.2   | 1.2±0.2   | 0.2±0.1           | 0.2±0.1          | 1.1±0.3 | 5.3±1.3 | 2.0±0.6                 | 0.7±0.2  | 0.1±0.1 | 0.7±0.2           | 0.5±0.1                         | 0.1±0.1                         |
| 13 | July 2-6, 2013                 | 0.7±0.1   | 0.7±0.1   | 0.2±0.1           | 0.1±0.1          | 1.1±0.2 | 3.7±0.8 | 1.5±0.3                 | 0.5±0.1  | 0.1±0.1 | 0.6±0.1           | 0.3±0.1                         | 0.1±0.1                         |
| 14 | August 15-21, 2013             | 1.2±0.1   | 1.1±0.2   | 0.3±0.1           | 0.2±0.1          | 1.5±0.2 | 5.9±1.0 | 2.4±0.5                 | 1.0±0.2  | 0.6±0.1 | 1.0±0.2           | 0.7±0.2                         | 0.2±0.1                         |
| 15 | May 27-31, 2014                | n.m.      | 2.3±0.1   | 0.2±0.1           | 0.3±0.1          | 1.5±0.3 | 5.9±1.4 | 2.2±0.5                 | 0.8±0.2  | 0.2±0.1 | 0.8±0.2           | 0.7±0.2                         | 0.2±0.1                         |
|    | All high O <sub>3</sub> events | 1.0±0.1   | 1.2±0.1   | 0.2±0.1           | 0.2±0.1          | 1.4±0.1 | 4.9±0.1 | 2.0±0.1                 | 0.7±0.1  | 0.1±0.1 | 0.7±0.2           | 0.6±0.1                         | 0.2±0.1                         |
|    | Remaining days                 | 1.0±0.1   | 1.2±0.1   | 0.2±0.1           | 0.2±0.1          | 1.3±0.1 | 5.2±0.4 | 2.0±0.1                 | 0.7±0.1  | 0.1±0.1 | 0.7±0.1           | 0.5±0.1                         | 0.2±0.1                         |

# 4 Appendix

# June 13- June 17, 2008

The trajectories of air masses arriving in El Paso/Ciudad Juárez/Doña Ana urban metroplex at 500m and the locations of wildland fires are presented in Figure 4-1. Smoke concentrations are shown in Figure 4-2. The origin of air mass at 500m was variable. There were a few small fires in central Texas and western Mexico. There were no particulate smoke concentrations in the region.

Figure 4-1 Backward trajectories at 500m and locations of wildland fire events (red indicators) during June 13 - June 17, 2008.















-90 



-125

-120

-115

-110

-105

-100

-95

# July 31 - August 13, 2008

The trajectories of air masses arriving in El Paso/Ciudad Juárez/Doña Ana urban metroplex at 500m and the locations of wildland fires are presented in Figure 4-3. Smoke concentrations are shown in Figure 4-2. The origin of air mass at 500m was variable but mostly from the central Texas, Arkansas and Louisiana. The trajectories intersected fires burning in these regions. This was further corroborated by the predicted particulate smoke concentrations in Arkansas and Louisiana.

Figure 4-3 Backward trajectories at 500m and locations of wildland fire events (red indicators) during July 31 – August 13, 2008.









NAAPS Surface Concentration (ug-m\*\*3) for 00:00Z 06 Aug 2008 Smoke



NAAPS Surface Concentration (ug-m\*\*3) for 00:00Z 04 Aug 2008 Smoke

NAAPS Surface Concentration (ug-m\*\*3)

for 00:00Z 02 Aug 2008 Smoke

125



-95



NAAPS Surface Concentration (ug-m\*\*3) for 00:00Z 07 Aug 2008 Smoke



NAAPS Surface Concentration (ug-m\*\*3)



NAAPS Surface Concentration (ug-m\*\*3) for 00:00Z 03 Aug 2008 Smoke

-90

50

45

40

35

30

25







16

8

2

4

NAAPS Surface Concentration (ug-m\*\*3) for 00:00Z 11 Aug 2008 Smoke -120 -115 -110 125 -105 -100

NAAPS Surface Concentration (ug-m\*\*3)



NAAPS Surface Concentration (ug-m\*\*3)



for 00:00Z 09 Aug 2008 Smoke for 00:00Z 08 Aug 2008 Smoke -105 -100 -95 -90

-95

90

50

45

40

### July 24 - July 31, 2009

The trajectories of air masses arriving in El Paso/Ciudad Juárez/Doña Ana urban metroplex at 500m and the locations of wildland fires are presented in Figure 4-5. Smoke concentrations are shown in Figure 4-6. Air masses spent most of their time locally with contributions from Mexico and southwest Arizona. The trajectories intersected fires burning in these regions. This was further corroborated by the predicted particulate smoke concentrations.



Figure 4-5 Backward trajectories at 500m and locations of wildland fire events (red indicators) during July 24 – July 31, 2009.





25



NAAPS Surface Concentration (ug/m\*\*3) for 00:00Z 30 Jul 2009 Smoke





NAAPS Surface Concentration (ug/m\*\*3)







-105

-100

-95

-90

1

1

2

4

8

16

32

64

2

NAAPS Surface Concentration (ug/m\*\*3) for 00:00Z 26 Jul 2009 Smoke

-110

-115

-125

-120



8

4

32

16

64

NAAPS Surface Concentration (ug/m\*\*3) for 00:00Z 27 Jul 2009 Smoke

### April 10- April 16, 2011

The trajectories of air masses arriving in El Paso/Ciudad Juárez/Doña Ana urban metroplex at 500m and the locations of wildland fires are presented in Figure 4-7. Smoke concentrations are shown in Figure 4-8. Air masses originated from the western/southwest US and the Pacific Ocean. There were a few fires in the central western NM and Arizona. Fire in western Mexico did not appear to be intersected by air mass trajectories. The predicted particulate smoke concentrations from these fires in Mexico were up to 2  $\mu$ g/m<sup>3</sup>.

Figure 4-7 Backward trajectories at 500m and locations of wildland fire events (red indicators) during April 10 – April 16, 2011.









Smoke Surface Concentration (ug/m\*\*3)

Smoke Surface Concentration (ug/m\*\*3) for 00:00Z 14 Apr 2011



Smoke Surface Concentration (ug/m\*\*3) for 00:00Z 16 Apr 2011





### July 11- July 15, 2011

The trajectories of air masses arriving in El Paso/Ciudad Juárez/Doña Ana urban metroplex at 500m and the locations of wildland fires are presented in Figure 4-9. Smoke concentrations are shown in Figure 4-10. Air masses spent most of their time locally with contributions from Mexico and southwest Arizona. The trajectories intersected fires burning in these regions. This was further corroborated by the predicted particulate smoke concentrations.

Figure 4-9 Backward trajectories at 500m and locations of wildland fire events (red indicators) during July 11 – July 15, 2011.







Smoke Surface Concentration (ug/m\*\*3) for 00:00Z 13 Jul 2011



Smoke Surface Concentration (ug/m\*\*3) for 00:00Z 14 Jul 2011



Smoke Surface Concentration (ug/m\*\*3) for 00:00Z 15 Jul 2011



### July 21- July 29, 2011

The trajectories of air masses arriving in El Paso/Ciudad Juárez/Doña Ana urban metroplex at 500m and the locations of wildland fires are presented in Figure 4-11. Smoke concentrations are shown in Figure 4-12. Air masses spent most of their time locally with contributions from Mexico and Arizona. There were no fires in the region as corroborated by predicted particulate smoke concentrations.

Figure 4-11 Backward trajectories at 500m and locations of wildland fire events (red indicators) during July 21 – July 29, 2011.













Smoke Surface Concentration (ug/m\*\*3) for 00:00Z 27 Jul 2011



Smoke Surface Concentration (ug/m\*\*3) for 00:00Z 24 Jul 2011



Smoke Surface Concentration (ug/m\*\*3) for 00:00Z 26 Jul 2011



Smoke Surface Concentration (ug/m\*\*3) for 00:00Z 28 Jul 2011



Smoke Surface Concentration (ug/m\*\*3) for 00:00Z 29 Jul 2011



### August 18- August 23, 2011

The trajectories of air masses arriving in El Paso/Ciudad Juárez/Doña Ana urban metroplex at 500m and the locations of wildland fires are presented in Figure 4-13. Smoke concentrations are shown in Figure 4-14. Air masses originated from southern New Mexico and Arizona and also travelled along the Rio Grande River stating from the Gulf of Mexico. There were fires burning in these regions as it was corroborated by the predicted particulate smoke concentrations.

Figure 4-13 Backward trajectories at 500m and locations of wildland fire events (red indicators) during August 18 – August 23, 2011.







Smoke Surface Concentration (ug/m\*\*3) for 00:00Z 20 Aug 2011



Smoke Surface Concentration (ug/m\*\*3) for 00:00Z 22 Aug 2011



#### Smoke Surface Concentration (ug/m\*\*3) for 00:00Z 21 Aug 2011



Smoke Surface Concentration (ug/m\*\*3) for 00:00Z 23 Aug 2011



### May 11 – May 17, 2012

The trajectories of air masses arriving in El Paso/Ciudad Juárez/Doña Ana urban metroplex at 500m and the locations of wildland fires are presented in Figure 4-15. Smoke concentrations are shown in Figure 4-16. Air masses spent most of their time in the western Tecas, southern New Mexico and northern Mexico. They intersected several fires in Texas and may be influence by fires in western Mexico. The predicted particulate smoke concentrations were as high as 8  $\mu$ g/m<sup>3</sup>.

Figure 4-15 Backward trajectories at 500m and locations of wildland fire events (red indicators) during May 11 – May 17, 2012.







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Smoke Surface Concentration (ug/m\*\*3)



Smoke Surface Concentration (ug/m\*\*3)

Smoke Surface Concentration (ug/m\*\*3)



#### Smoke Surface Concentration (ug/m\*\*3) for 00:00Z 14 May 2012



Smoke Surface Concentration (ug/m\*\*3) for 00:00Z 16 May 2012



### May 28 – June 4, 2012

The trajectories of air masses arriving in El Paso/Ciudad Juárez/Doña Ana urban metroplex at 500m and the locations of wildland fires are presented in Figure 4-17. Smoke concentrations are shown in Figure 4-18. Air masses spent most of their time in the southern New Mexico, Arizona and Baja California. They intersected several fires in western Mexico. The predicted particulate smoke concentrations were as high as 16  $\mu$ g/m<sup>3</sup>.











Smoke Surface Concentration (ug/m\*\*3)



Smoke Surface Concentration (ug/m\*\*3) for 00:00Z 31 May 2012 -115 -105 -120





8

-110

Smoke Surface Concentration (ug/m\*\*3)

Ċ,

16

-105

4

-115

4

2

1

8

16

32

64

for 00:00Z 04 Jun 2012

32

-100

64

-95

-90

50

45

50

25

Smoke Surface Concentration (ug/m\*\*3) for 00:00Z 02 Jun 2012

45 ŧ۵ 35

32



8

Smoke Surface Concentration (ug/m\*\*3)

4

16

for 00:00Z 30 May 2012 -125 -120 -115 -110 -105 -100

2

1

-95

64

90

50

1

-125

2

-120

### July 9 - July 17, 2012

The trajectories of air masses arriving in El Paso/Ciudad Juárez/Doña Ana urban metroplex at 500m and the locations of wildland fires are presented in Figure 4-19. Smoke concentrations are shown in Figure 4-20. Air masses travelled mostly from Texas and Great Plains. They intersected several fires these regions. Trajectories on June 16 and 17 indicated transport from Arizona, and intersected fires in this region. The predicted particulate smoke concentration was 2  $\mu$ g/m<sup>3</sup>.

Figure 4-19 Backward trajectories at 500m and locations of wildland fire events (red indicators) during July 9 – July 17, 2012.







Smoke Surface Concentration (ug/m\*\*3) for 00:00Z 11 Jul 2012







Smoke Surface Concentration (ug/m\*\*3) for 00:00Z 15 Jul 2012



Smoke Surface Concentration (ug/m\*\*3) for 00:00Z 12 Jul 2012



Smoke Surface Concentration (ug/m\*\*3) for 00:00Z 14 Jul 2012



Smoke Surface Concentration (ug/m\*\*3) for 00:00Z 16 Jul 2012



Smoke Surface Concentration (ug/m\*\*3) for 00:00Z 17 Jul 2012



### August 29 – September 2, 2012

The trajectories of air masses arriving in El Paso/Ciudad Juárez/Doña Ana urban metroplex at 500m and the locations of wildland fires are presented in Figure 4-21. Smoke concentrations are shown in Figure 4-22. Air masses travelled mostly from Texas, Great Plains and Northern Mexico. They intersected several fires these regions. Trajectories on June 16 and 17 indicated transport from Arizona, and intersected fires in this region. The predicted particulate smoke concentrations was up to 8  $\mu$ g/m<sup>3</sup>.

Figure 4-21 Backward trajectories at 500m and locations of wildland fire events (red indicators) during August 29 – September 2, 2012.







Smoke Surface Concentration (ug/m\*\*3) for 00:00Z 31 Aug 2012



Smoke Surface Concentration (ug/m\*\*3) for 00:00Z 01 Sep 2012



Smoke Surface Concentration (ug/m\*\*3) for 00:00Z 02 Sep 2012



## April 27 – May 1, 2013

The trajectories of air masses arriving in El Paso/Ciudad Juárez/Doña Ana urban metroplex at 500m and the locations of wildland fires are presented in Figure 4-23. Smoke concentrations are shown in Figure 4-24. Air masses travelled mostly from Texas, New Mexico and Northern Mexico. They intersected several fires these regions. The predicted particulate smoke concentrations was no more than 2  $\mu$ g/m<sup>3</sup>.

Figure 4-23 Backward trajectories at 500m and locations of wildland fire events (red indicators) during April 27 – May 1, 2013.











Smoke Surface Concentration (ug/m\*\*3) for 00:00Z 30 Apr 2013



Smoke Surface Concentration (ug/m\*\*3) for 00:00Z 01 May 2013



### July 2 - July 6, 2013

The trajectories of air masses arriving in El Paso/Ciudad Juárez/Doña Ana urban metroplex at 500m and the locations of wildland fires are presented in Figure 4-25. Smoke concentrations are shown in Figure 4-26. Air masses travelled mostly from Texas, New Mexico and Northern Mexico. They intersected several fires these regions. The predicted particulate smoke concentrations was up to 8  $\mu$ g/m<sup>3</sup>.

Figure 4-25 Backward trajectories at 500m and locations of wildland fire events (red indicators) during July 2 – July 6, 2013.











Smoke Surface Concentration (ug/m\*\*3) for 00:00Z 05 Jul 2013



Smoke Surface Concentration (ug/m\*\*3) for 00:00Z 06 Jul 2013



# August 15 – August 21, 2013

The trajectories of air masses arriving in El Paso/Ciudad Juárez/Doña Ana urban metroplex at 500m and the locations of wildland fires are presented in Figure 4-27. Smoke concentrations are shown in Figure 4-28. Air masses travelled mostly from Texasalong the Rio Grande river valley. They may intersected several fires these regions. The predicted particulate smoke concentrations were up to 4  $\mu$ g/m<sup>3</sup> during the last two days of the event.

Figure 4-27 Backward trajectories at 500m and locations of wildland fire events (red indicators) during August 15 – August 21, 2013.



100°0'0"W





Smoke Surface Concentration (ug/m\*\*3) for 00:00Z 17 Aug 2013



Smoke Surface Concentration (ug/m\*\*3) for 00:00Z 19 Aug 2013



Smoke Surface Concentration (ug/m\*\*3) for 00:00Z 21 Aug 2013



Smoke Surface Concentration (ug/m\*\*3) for 00:00Z 18 Aug 2013



Smoke Surface Concentration (ug/m\*\*3) for 00:00Z 20 Aug 2013



# May 27 – May 31, 2014

The trajectories of air masses arriving in El Paso/Ciudad Juárez/Doña Ana urban metroplex at 500m and the locations of wildland fires are presented in Figure 4-29. Smoke concentrations are shown in Figure 4-30. Air masses travelled mostly from Central Texas where they may intersected several fires these regions. The predicted particulate smoke concentrations were up to 4  $\mu$ g/m<sup>3</sup>.

Figure 4-29 Backward trajectories at 500m and locations of wildland fire events (red indicators) during May 27 – May 31, 2014.



Figure 4-30 Smoke concentration ( $\mu g m^{-3}$ ) for May 27 – May 31, 2014.


Smoke Surface Concentratian (ug/m\*\*3) for 2014052900 .





Smoke Surface Concentration (ug/m\*\*3) for 2014053000





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