Ozone Photolysis Rate Characterization for the PdN Region (Pilot Project)

Final Report on Pilot Project

Principal Investigator: Rosa M. Fitzgerald, Ph.D.
Physics Department
The University of Texas at El Paso

Co PI: William Stockwell, Ph.D.
Chemistry Department
Howard University

Co PI: Duanjun Lu, Ph.D.
Department of Physics, Atmospheric Sciences and Geosciences
Jackson State University

TCEQ Contract No. 582-15-52496
EPA Grant No. 900591
EPA Q-TRAK No.: 15-348
EPA technical lead: to be added
Cooperative Agreement No. BG-99662714-0

Table of Contents

Purpose of the project and specific project objectives

The main objective has been to measure hemi-spherically integrated spectrally resolved solar photon flux between the wavelengths of 300 and 700 nm (actinic flux), and use the measured actinic flux to improve air quality simulations. Photolysis is the main driver of ozone production and this factor defines the significance of this research work.

- Actinic flux has been measured during the summer of 2015 in the Paso del Norte Airshed, UTEP location.
- The actinic flux has been used to calculate photolysis rate coefficients for nitrogen dioxide (NO_2), ozone (O_3) and formaldehyde (HCHO).
- The improved photolysis rate coefficients have been integrated into a photochemical air quality model (CAMx), and simulations for a selected modeling summer 2015 ozone episode have been performed in an attempt to improve on air quality forecasting.

Scientific Background

The formation of photochemical air pollution, including ozone and particulate matter (PM), depends on the photolysis of NO_2, O_3, HONO, HCHO, aldehydes and ketones and other compounds. For example, the rate of ozone formation is controlled through the photolysis of NO_2.

$$NO_2 + h\nu\ (+O_2) \rightarrow O_3 + NO \qquad (1)$$

The magnitude of ozone concentrations is related to the NO_2 photolysis frequency, J, and NO_2 to NO concentration ratio.

$$[O_3] = J\,[NO_2] / k\,[NO] \qquad (2)$$

The photolysis of O_3 to make excited oxygen atoms, O^1D, produces ozone by making HO radicals that react with VOC to make HO_2 and organic peroxy radicals.

$$O_3 + h\nu \rightarrow O^1D + O_2 \qquad (3)$$
$$O^1D + H_2O \rightarrow 2\ HO \qquad (4)$$

A compound's photolysis frequency, J, is determined by the product of the spherically integrated photon flux (actinic flux), $I(\lambda)$, the compound's absorption cross sections, $\sigma(\lambda)$, and its quantum yields, $\phi(\lambda)$, all integrated over the range of available wavelengths.

$$J = \int I(\lambda) \times \sigma(\lambda) \times \phi(\lambda)\, d\lambda \qquad (5)$$

The quantity J should be considered a frequency because its dimension is $time^{-1}$. Photolysis rates are the product of the photolysis frequency and the photolysis species concentration.

Although photolysis frequencies are often a major cause of differences between modeling studies, they are usually not accurately measured in field studies. Photolysis frequencies are often

calculated for assumed sky conditions or they are estimated from Epply and UV radiometer measurements. These procedures may yield photolysis frequencies that are uncertain by as much as 30 to 40% (Madronich, 1987). The differences between modeled photolysis rate coefficients and those based on measured actinic flux may be very different. These differences have a strong effect on air quality simulations of ozone and these are discussed in Stockwell and Goliff (2004). An isopleth of the percent relative difference between maximum ozone calculated from photolysis rate coefficients based on measured actinic flux and the maximum ozone calculated from photolysis rate parameters based on modeled actinic flux are shown in Figure 1.

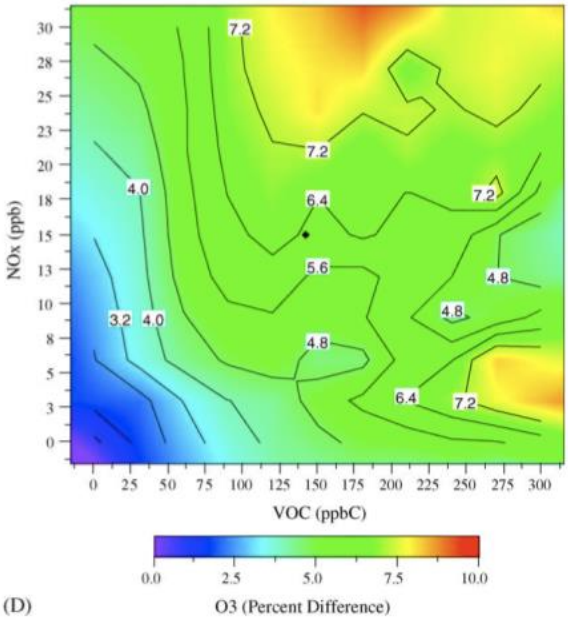

Figure 1. A comparison of the percent relative difference between maximum ozone calculated from photolysis rate coefficients based on measured actinic flux and the maximum ozone calculated from photolysis rate parameters based on modeled actinic flux for a range of conditions of nitrogen oxides (NOx) and volatile organic compounds (VOC).

Measurement Procedures

The UTEP project has used a spectrally resolved radiometer (spectrometer) (Figures 2, 3) to measure actinic flux that subsequently has been used to calculate the photolysis frequencies from Equation 5. Figure 4 shows a schematic of the operation of the spectrometer. An advantage of using spectrometer data is that any photolysis coefficients may be calculated from this data in the future, provided that the gas's absorption spectrum and its quantum yield probability of reacting after absorbing a photon are known.

Fig.2. Optical sensor installed on the roof of the Physical Sciences Building.

Figure 3. Actinic flux spectrometer collection head.

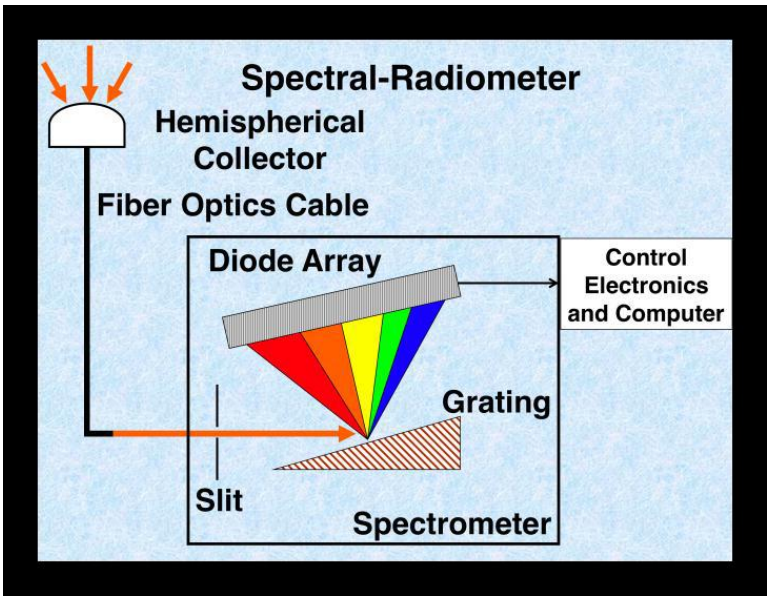

Figure 4. Actinic flux spectrometer schematic diagram.

The specifications for the spectrometer to be used are given in Table 1. It consists of a hemispherical radiation collection head and a monolithic monochromator with a 512 pixel diode array detector with a spatial resolution of 2.1 nm (FWHW). The spectrometers will have an extremely fast response time that is able to provide the actinic flux required to determine the photolysis rate coefficient for the photolysis of ozone to produce O_1D in 200 ms (or less).

Table 1

Spectrometer Type	Monolithic single monochromator with a fixed grating
Radiation Receptor Optics	Isotropic diffuser (quartz scattering dome with a nearly uniform response over 2-π steradian)
Optical Coupling Quartz Fiber	Round to slit converter
Detector Element	Cooled Charged Coupled Device (CCD)
Detector Configuration	512 pixel Hamamatsu pixel array
Spectral Range	280 nm – 650 nm
Spectral Resolution	2.1 nm Full-Width at Half Maximum (FWHM) at 300 nm
Temperature Sensitivity	< 0.05 nm/K
Spectral Reproducibility	0.01 nm or better
Stray Light Suppression	Electronic compensation using signal between 280 and 290 nm
Measurement time for JO3	< 200 ms
Resolution of JNO2	Better than 0.3 % for sun elevation at 25°C
Reproducibility of two successive scans	+/- 3 counts per pixel at 25°C
Instrument Housing	Air and water-tight, Isotropic diffuser is hermetically sealed (tested to 0.5 bar by manufacturer).

A pre-calibration test was done before the installation of the instrument and an initial preliminary analysis of the rate coefficients, the J-values, for a specific case (June 27, 28) was performed, as observed on Figures 5 and 6.

Spectrometer Location

The actinic flux spectrometer is located on the roof of the Physical Sciences Building at the University of Texas, El Paso, located in the city of El Paso. The collection head is at least two meters above the surface of the roof to reduce ground reflection effects.
This is a site that is representative of the El Paso region. Because El Paso is in a desert ecosystem with no major changes in the terrain during the study period, the albedo will be constant.

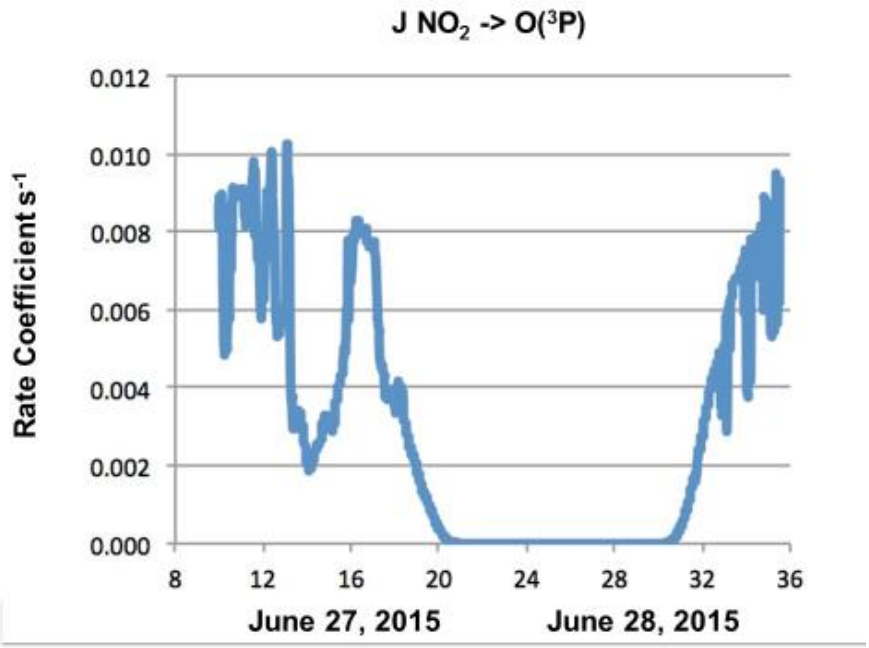

Figure 5. Photolysis Rate Coefficients for NO2

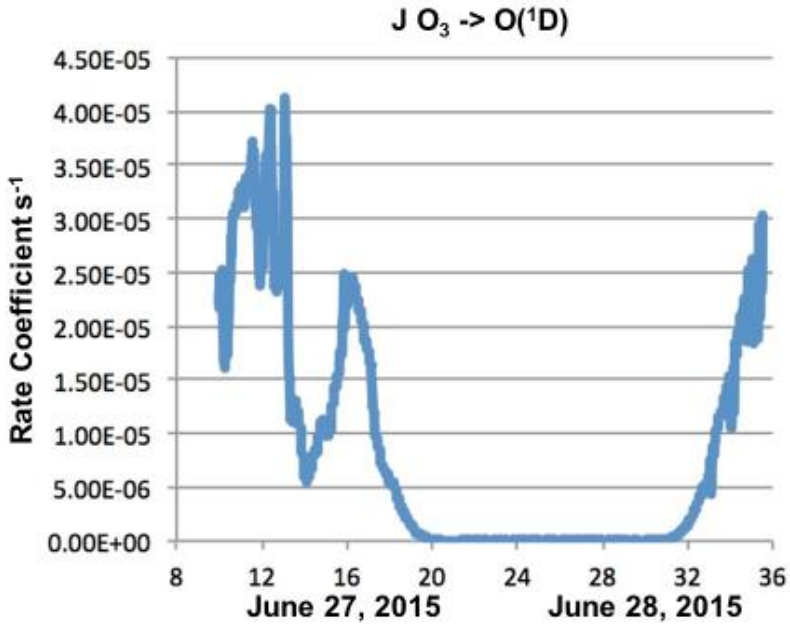

Figure 6. Photolysis Rate Coefficients for O3

Methodology

The first step was to establish a correlation between the photolysis rate coefficients, j-values, and the ozone concentrations. Figures 7-14 illustrate a minor correlation.

Correlations between Ozone concentrations and J-values for June 27-July 4, 2015

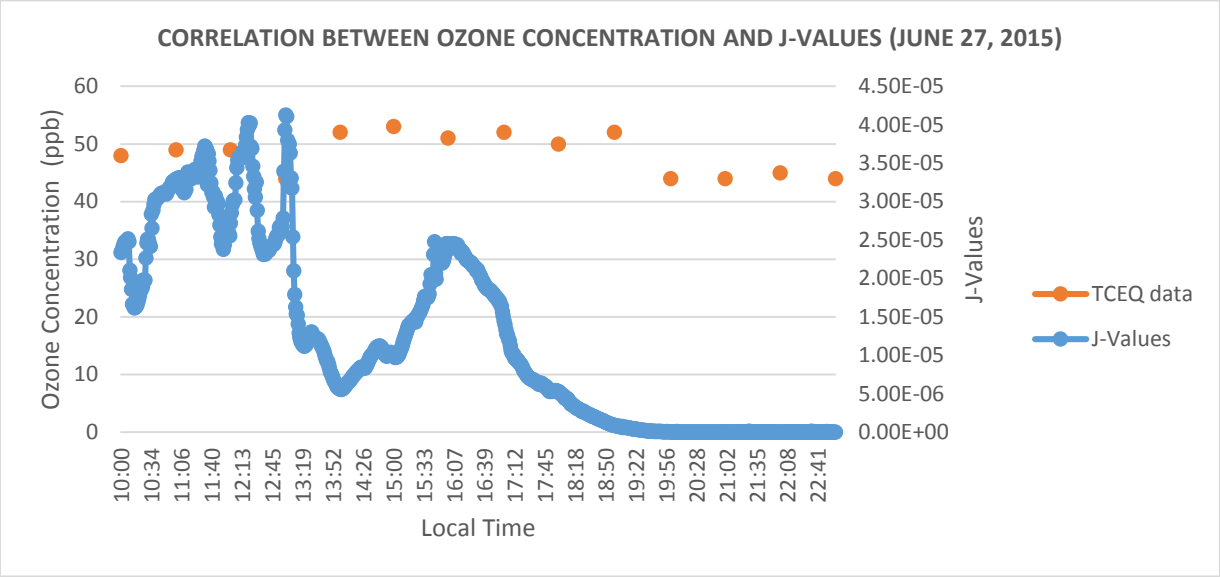

Figure 7

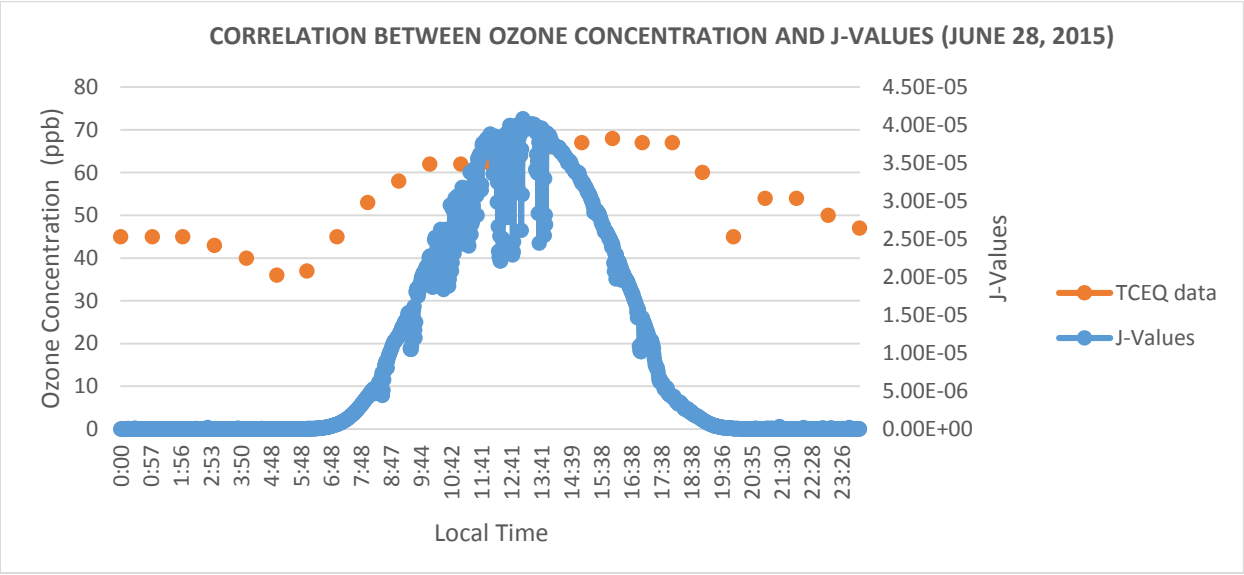

Figure 8

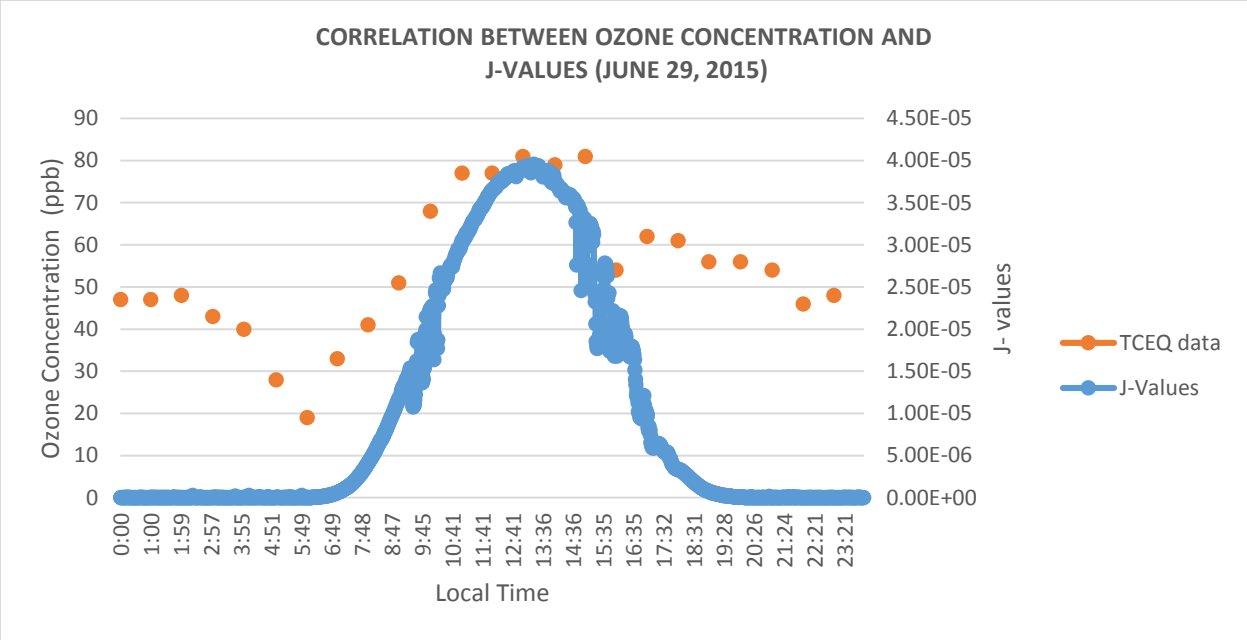

Figure 9

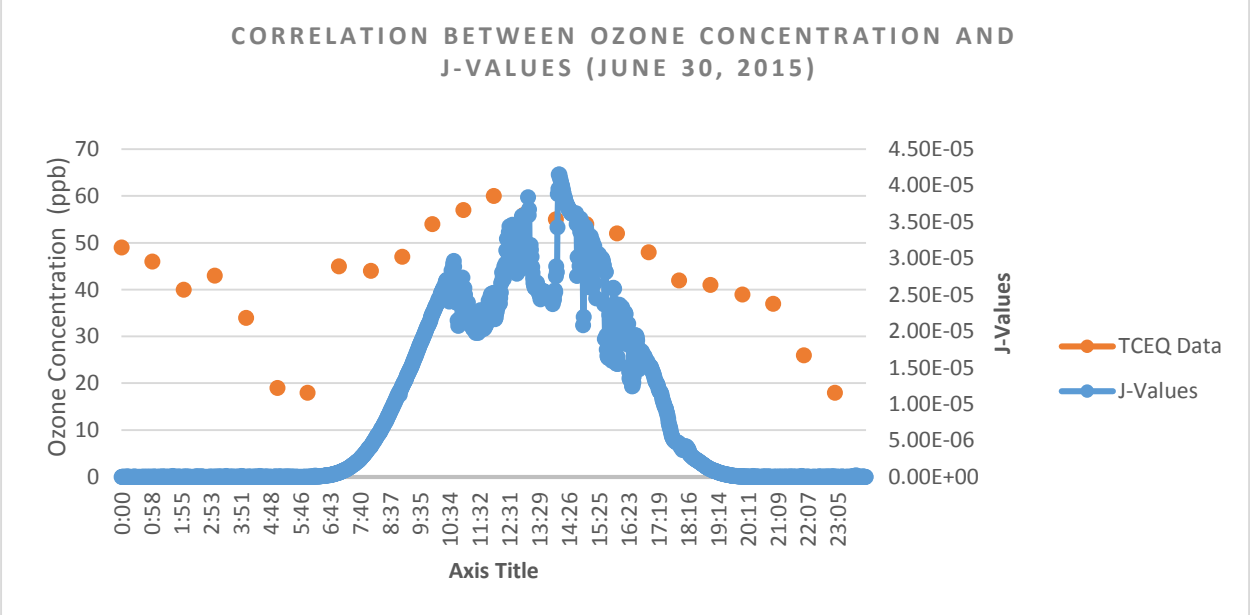

Figure 10

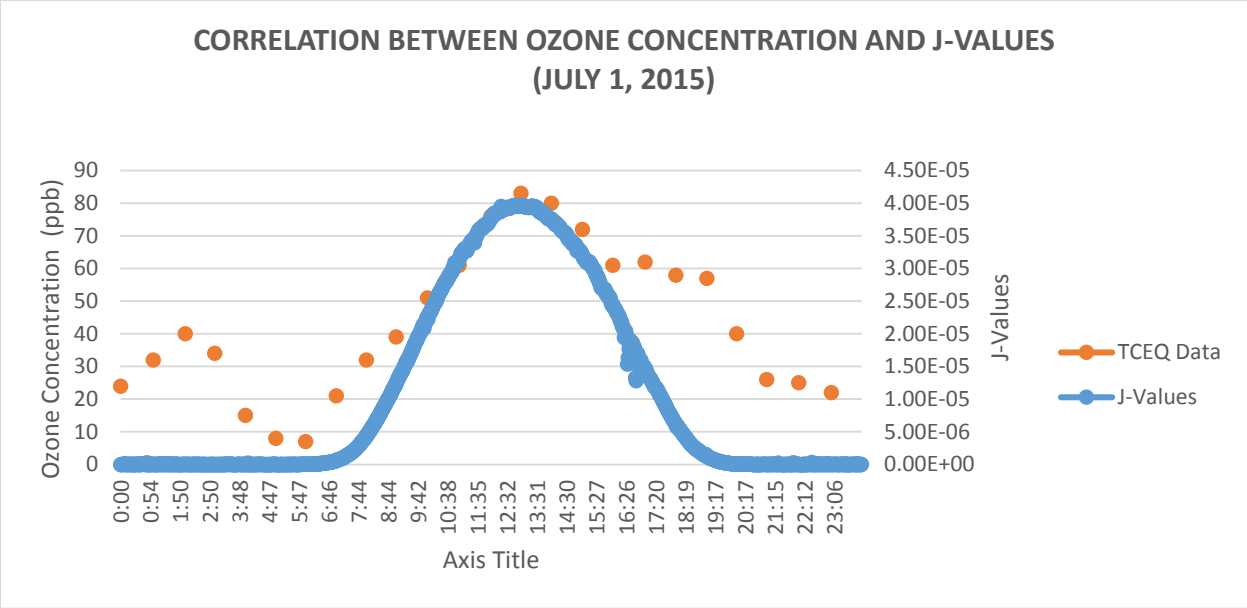

Figure 11

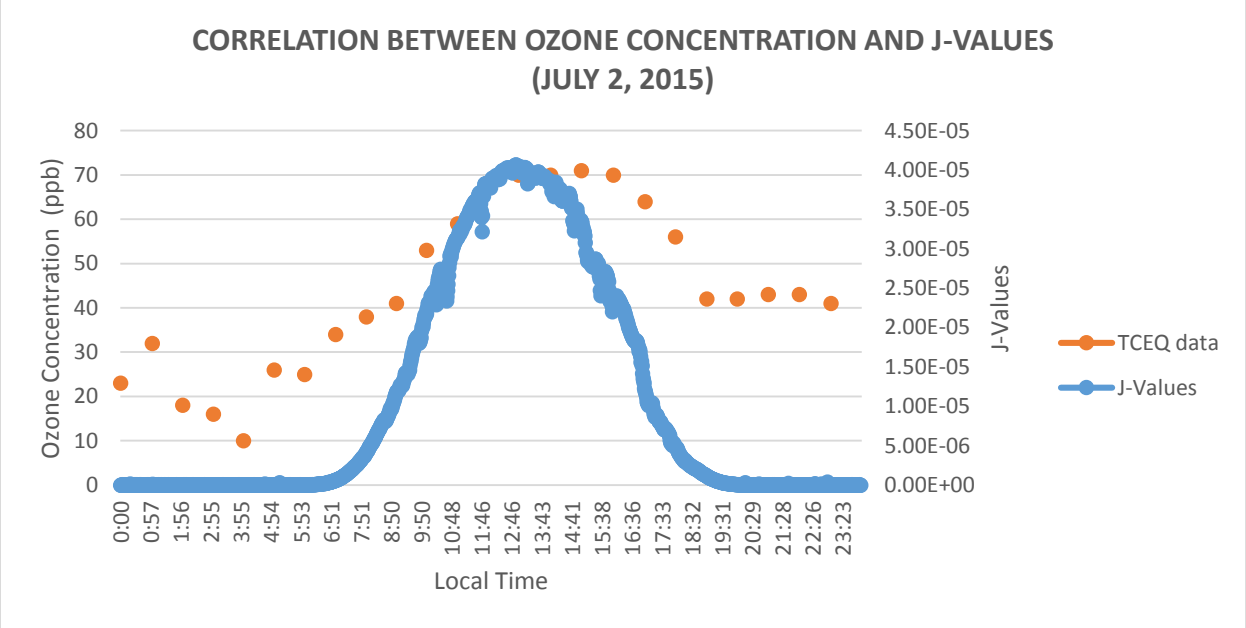

Figure 12

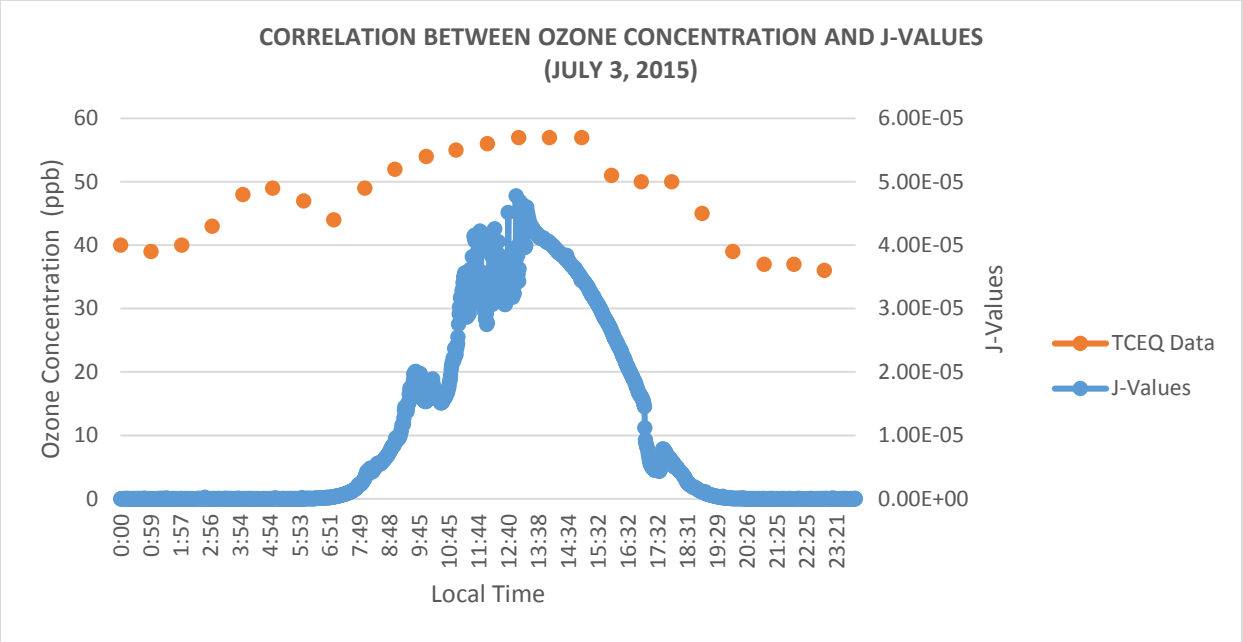

Figure 13

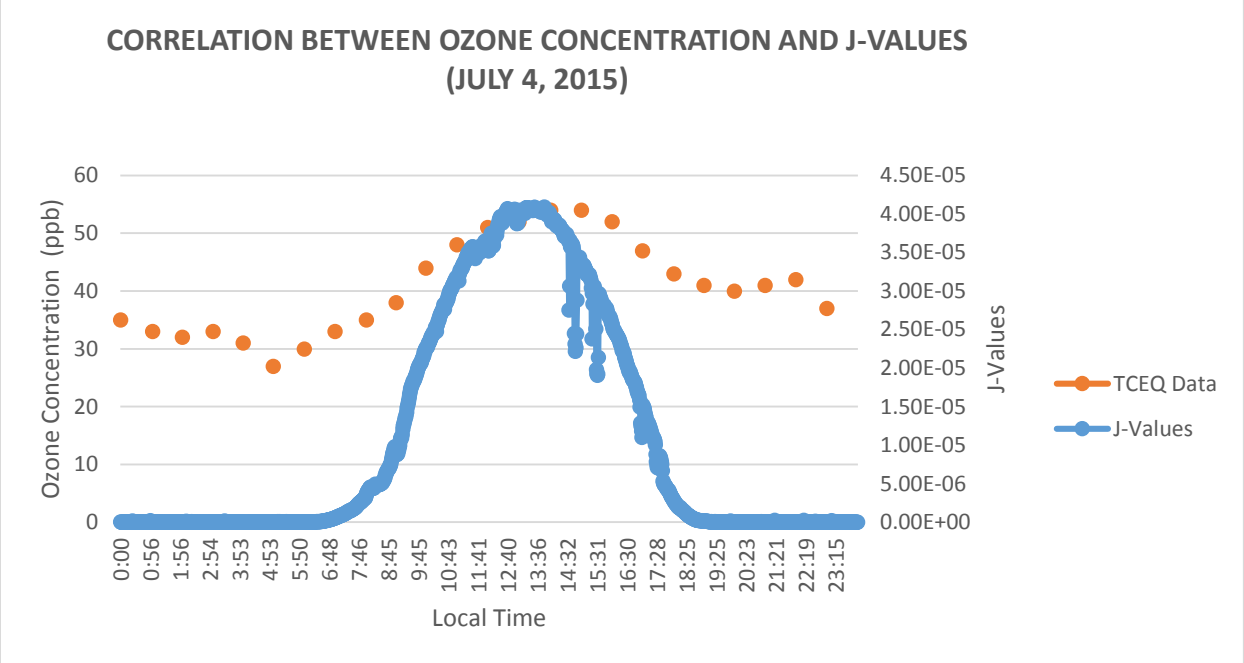

Figure 14

Methodology continues…

The photolysis rate frequencies at the surface, obtained using the spectrometer operating since June 27, 2015 up to the present day were examined, and due to the lack of the presence of clouds, two days were selected for simulations. The selected days were July 1 and July 2, 2015. A radiative transfer model, based on the 2-stream Delta Eddington Method, was used to try to simulate the ozone photolysis rate values at the surface that match the experimental ozone photolysis rate values at the surface which were obtained with the spectrometer. The ozone column, the albedo, etc were strategically chosen to achieve this. This guaranteed a continuous distribution of the ozone photolysis values throughout the entire vertical column in the atmosphere. The inter-comparison is observed on Figures 15 and 16. As observed the surface modeled j-values for ozone are in close agreement to the surface experimental j-values.

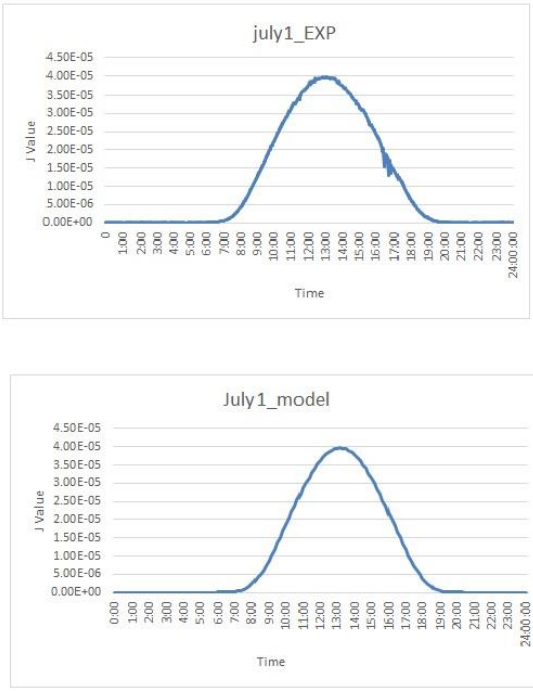

Figure 15. Experimental and modeled photolysis rate coefficients for July 1.

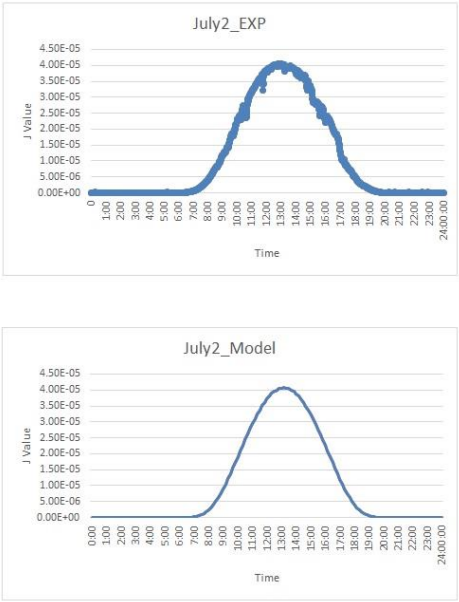

Figure 16. Experimental and modeled photolysis rate coefficients for July 2.

Simulations
Model configuration
The air quality simulations were performed using CAMx model.

In this project, the version of CAMx V6.1 was used (ENVIRON, 2015). The CAMx model requires a meteorological model to produce meteorological fields and an emissions processing system (Stockwell et al., 2013). In this project, the emissions are processed with the Sparse Matrix Operator Kernel Emissions (SMOKE, version 3.0; Houyoux et al. 2001). The SMOKE model is used to convert the source-level emissions (county total emissions) reported on a yearly basis to model-ready emissions which are spatially resolved, hourly and aggregated into model species. The meteorological model used is the Weather Research and Forecast model (WRF, version 3.4; Skamarock et al. 2001). In this project, the map projection is the Lambert Conformal, centered at the city of El Paso, TX. The WRF model meteorological results are output at hourly intervals. The data incorporated into the WRF model as initialization and lateral boundary conditions are obtained from NCEP Final Analysis (FNL) dataset with a 6-h interval. This is the global dataset in the format of the grid with the resolution of 1×1°. The four-dimensional data assimilation (FDDA) technique was applied to the WRF simulations. The emission inventory used in this study is the U.S. Environmental Protection Agency's (EPA) National Emission Inventory released originally in 2005 (NEI05) (US EPA, 2010), available from ftp://ftp.epa.gov/EmisInventory. Since the modeling domain includes both USA and Mexico, the latest released Mexico emission dataset (Mexico NEI99, http://www.epa.gov/ttn/chief/net/mexico.html), which includes six northern border-states of Mexico, has also been obtained as the supplementation for NEI05.
The CAMx model is run over a three-nested domain configuration with 36-, 12- and 4-km resolutions for coarse, middle and fine domains respectively, as observed below, Figure 17:

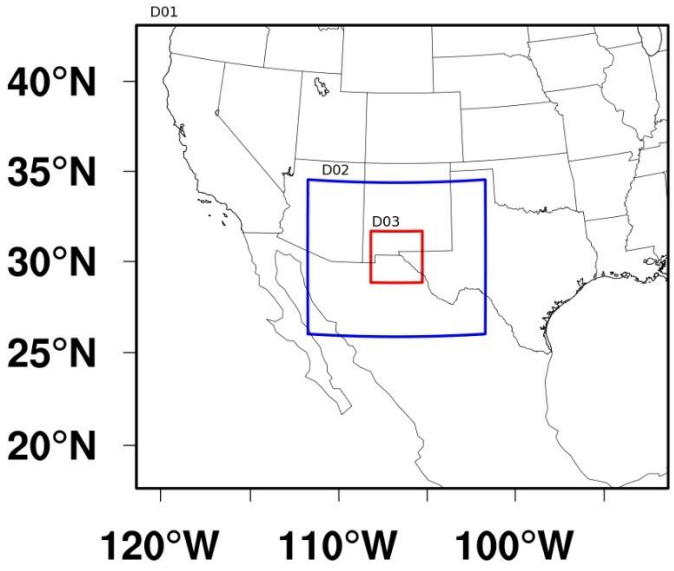

Figure 17

Three cases were selected for simulation for July1 and 2: Base case (with photolysis j-values used in models), P10 (increasing the photolysis j-values by 10% for all species) and ozone column (using the photolysis j-modeled values to match the instrument's ozone j-values at the surface, but for ozone only!)

Figures 18-35 are labeled by the date in the title, for example, 2015070120, corresponds to year 2015; month of July, 07; 01, for July1; and 20 for 20 hour in UTC.
The Base or Standard case shows NOx and O3, the P10 case shows the difference in NO2 and O3, defined as the difference of corresponding results for P10-the Base case.
Similarly, the ozone column case shows the difference in NO2 and O3, defined as the difference of corresponding results for ozone column case-the Base case.
Two hours are shown for July1, 20 and 22 UTC.

July 1 corresponds to an afternoon analysis and July 2 corresponds to a morning analysis.

Figure 36 shows the time series inter-comparison of all 3 cases against TCEQ data for July 1, 2 for the TCEQ monitoring station, CAMS12, located in the UTEP campus. The Base case and the ozone column case are superimposed on each other and appear as a single line in the scale shown.

July 1 (afternoon analysis):

Base case:

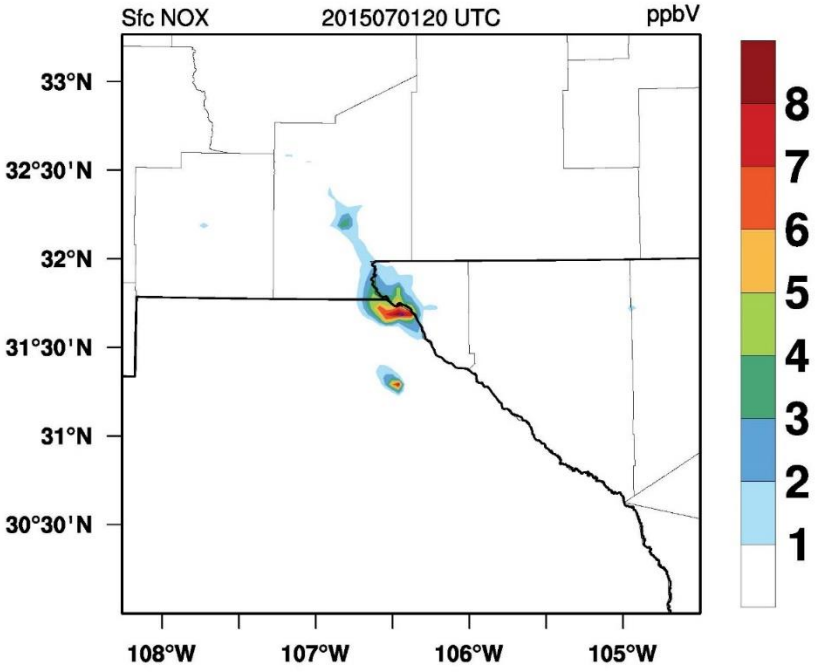

Figure 18

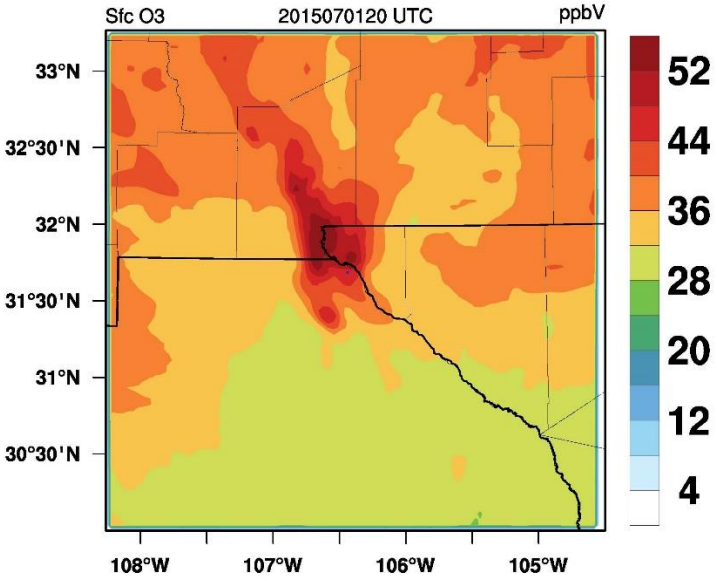

Figure 19

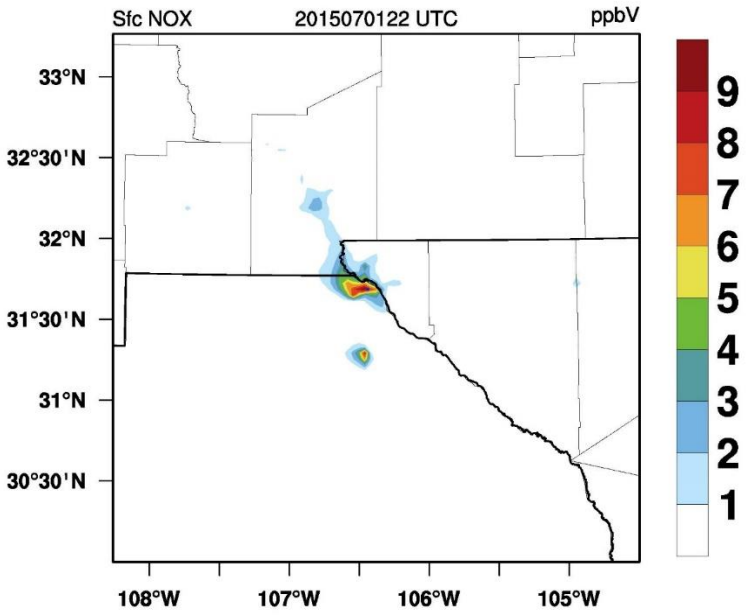

Figure 20

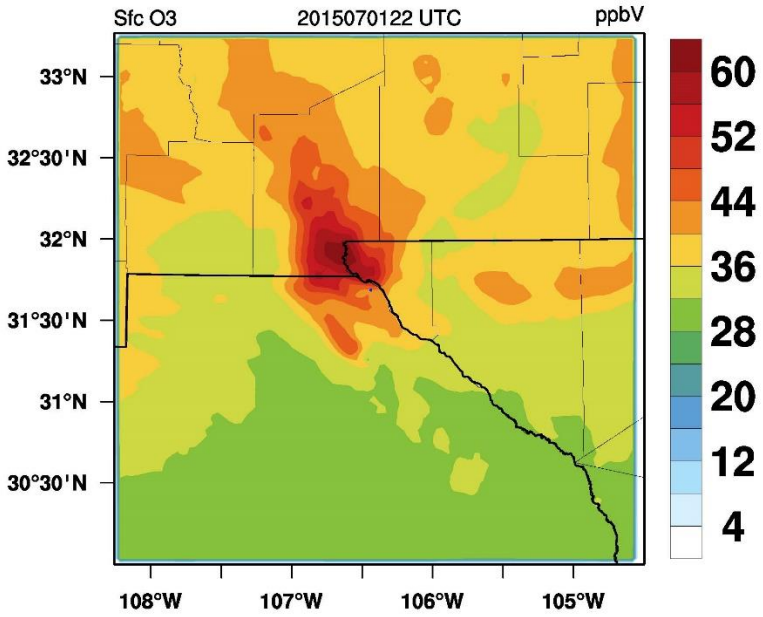

Figure 21

P10 Case:

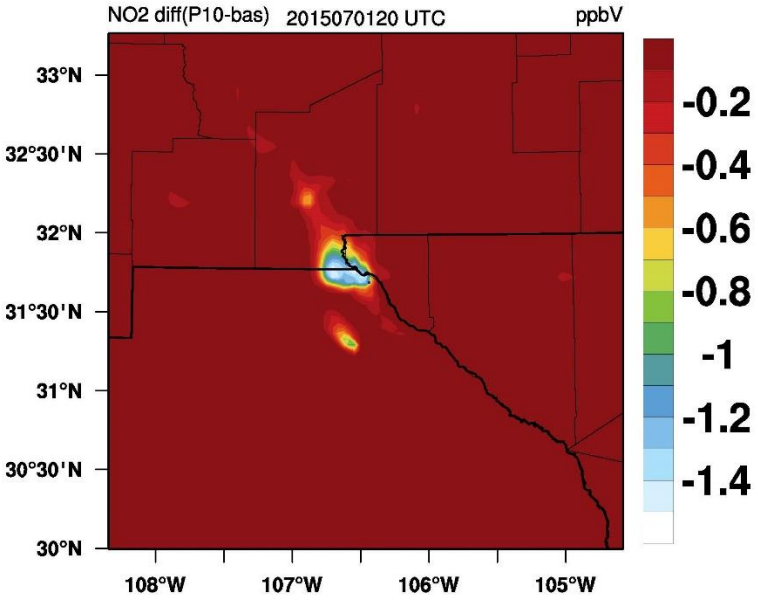

Figure 22

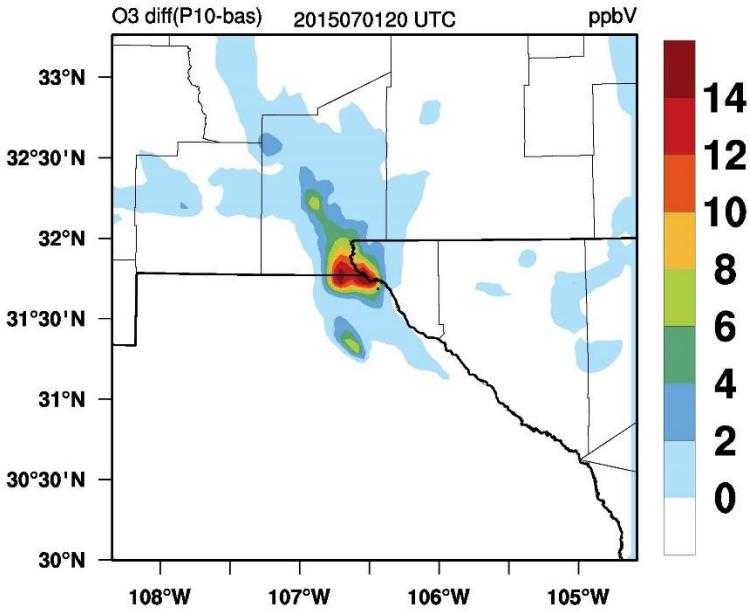

Figure 23

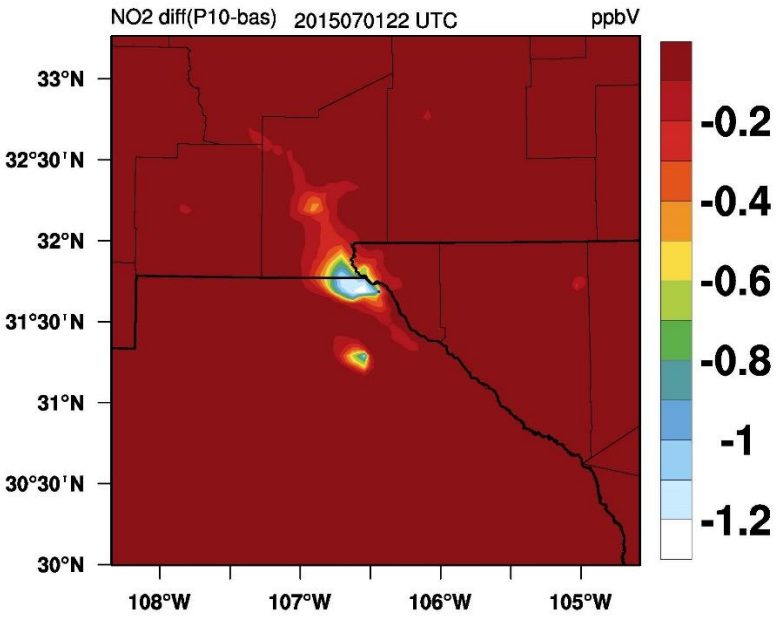

Figure 24

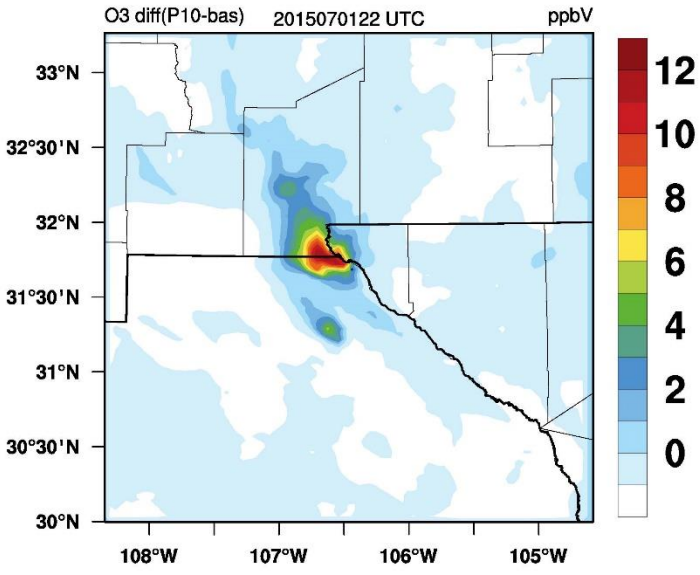

Figure 25

Changing the ozone column to match the instrument's j-values:

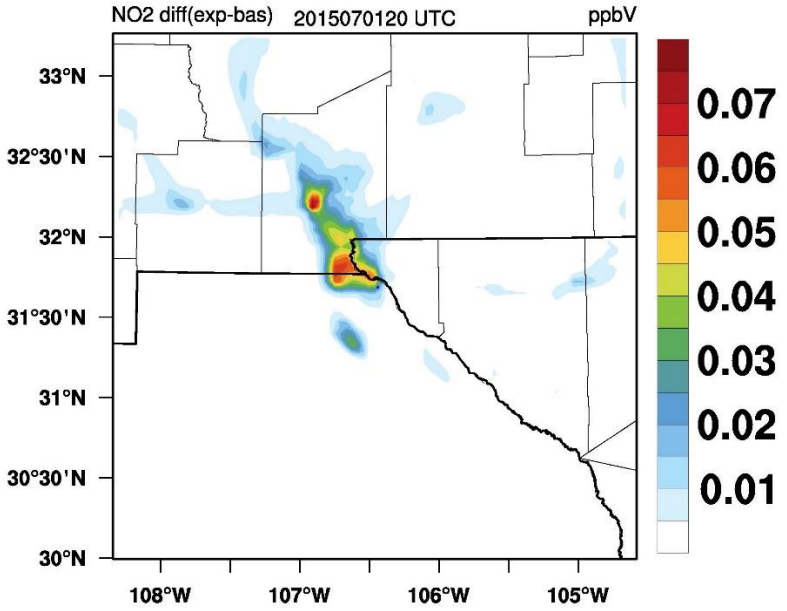

Figure 26

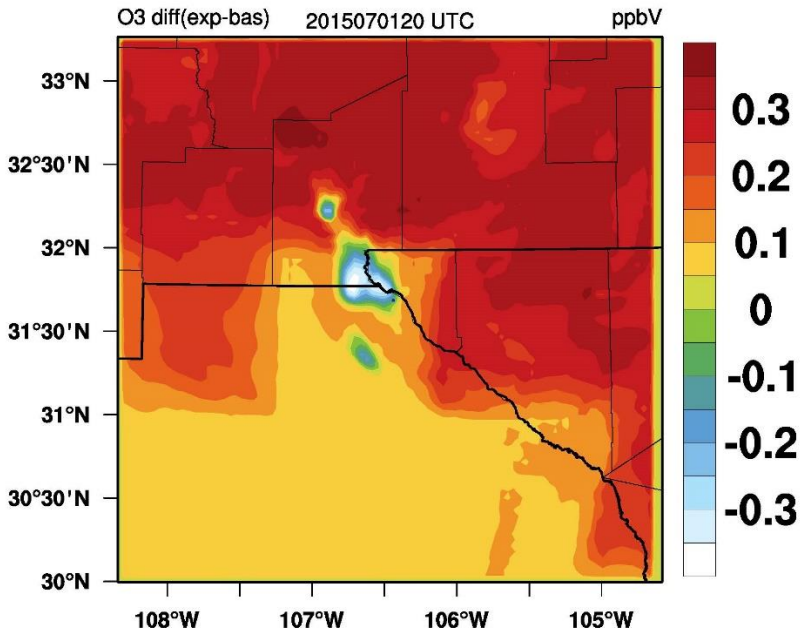

Figure 27

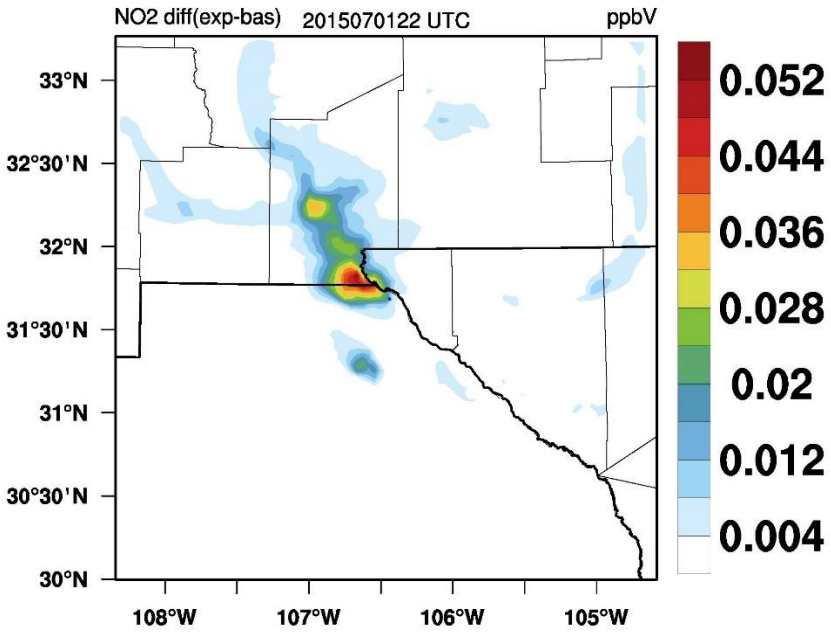

Figure 28

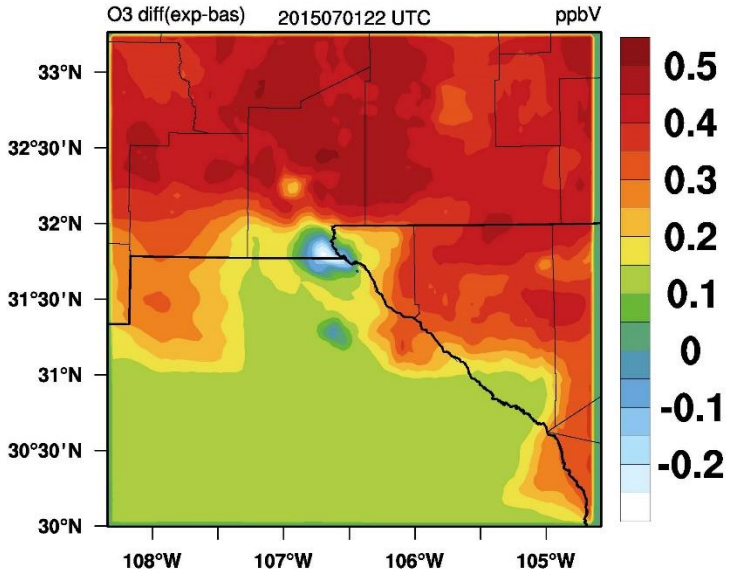

Figure 29

July 2 (morning analysis):

Base case:

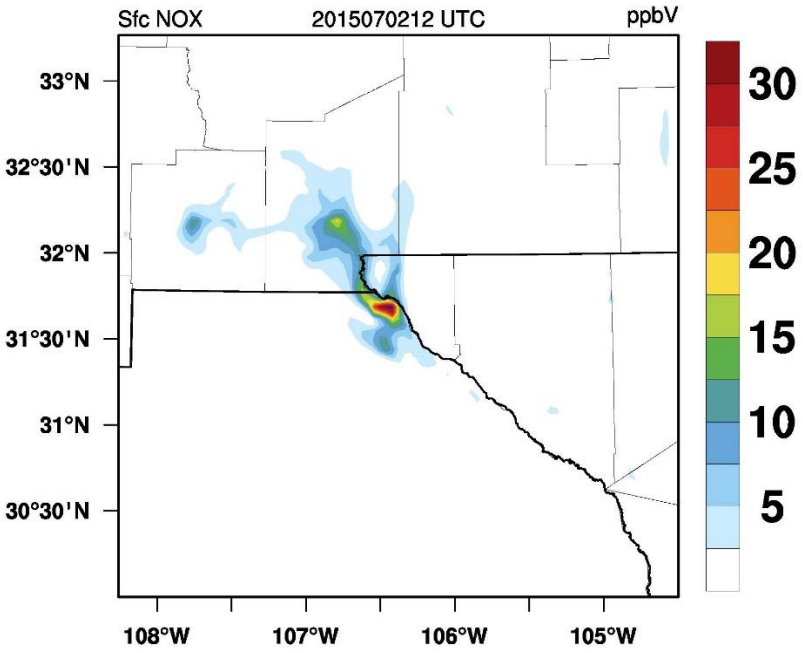

Figure 30

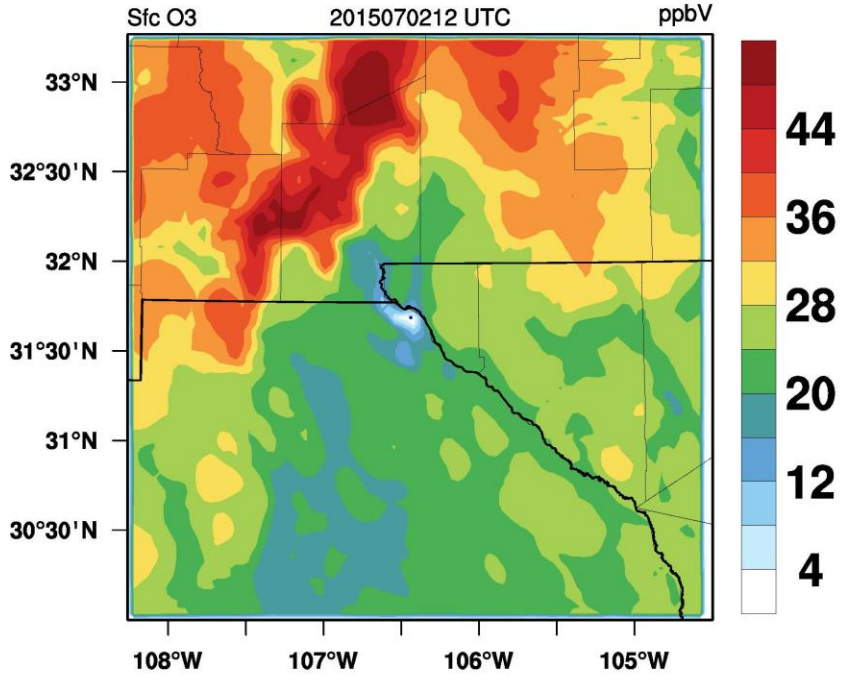

Figure 31

P10 Case:

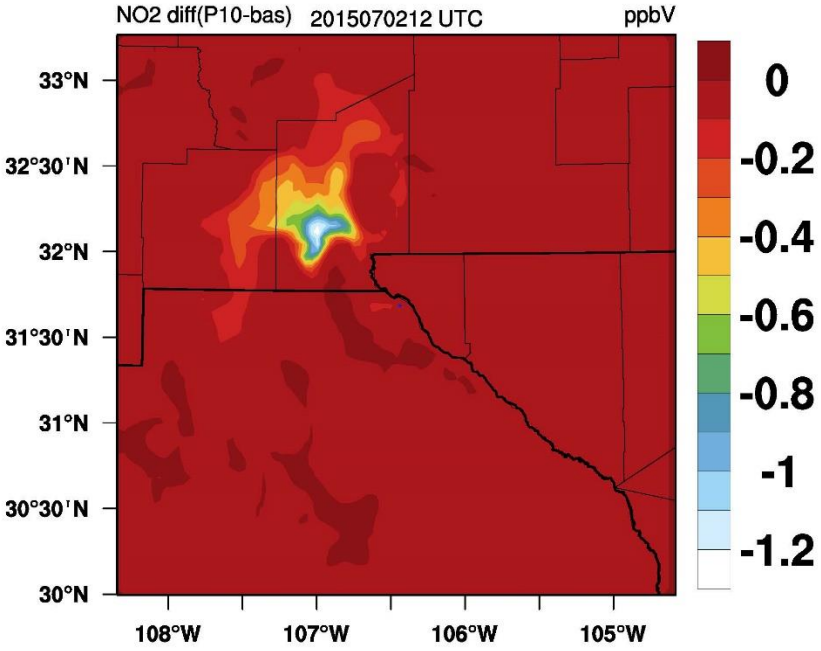

Figure 32

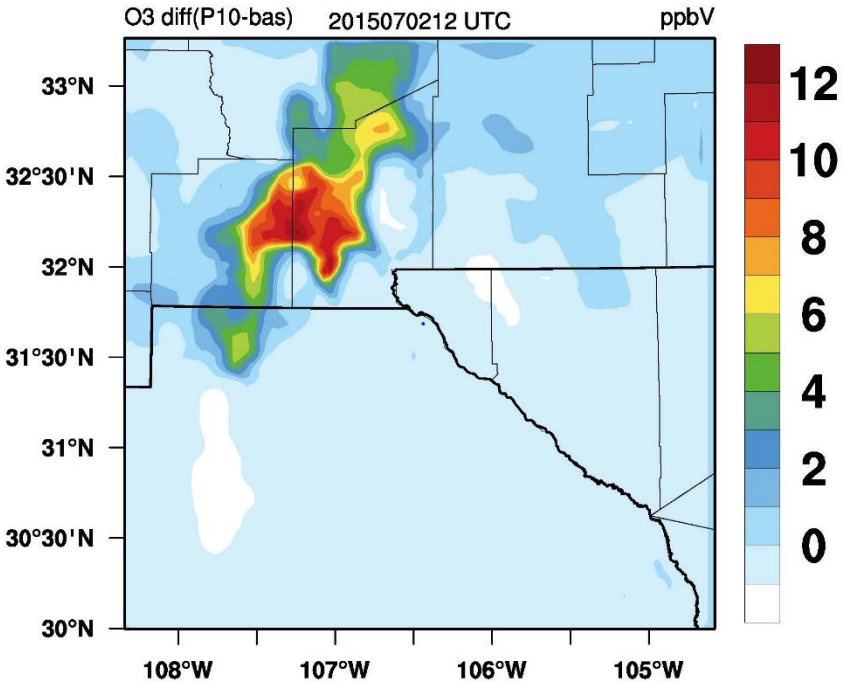

Figure 33

Changing the Ozone column:

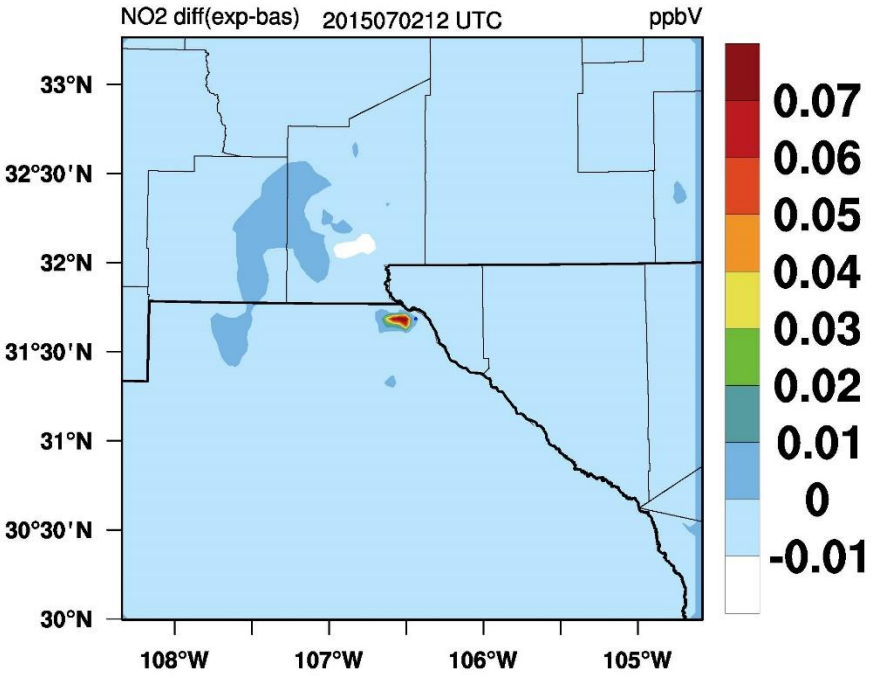

Figure 34

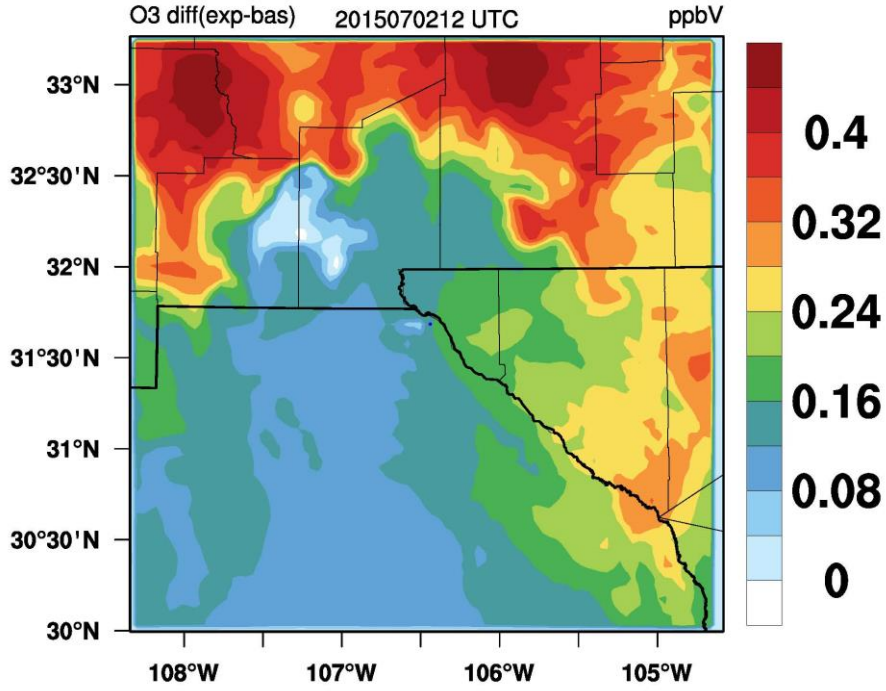

Figure 35

Time Series for CAMS 12/TCEQ Station
Inter-comparison of all 3 cases against TCEQ data for July 1, 2

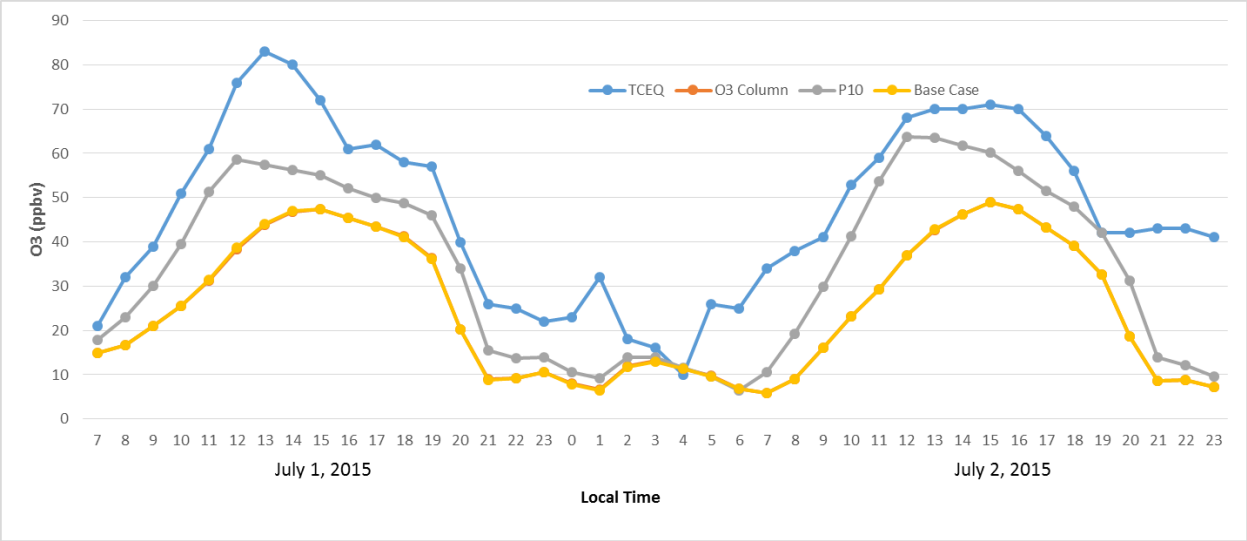

Figure 36. Inter-comparison of all 3 cases against TCEQ data for July 1, 2

July 1

R^2 TCEQ between O3 Column	0.87555
R^2 TCEQ between P10	0.95147
R^2 TCEQ between Base Case	0.87944

July 2

R^2 TCEQ between O3 Column	0.83559057
R^2 TCEQ between P10	0.83705724
R^2TCEQ between Base Case	0.83598086

Performance Metrics	Unpaired Peak Ratio	PMNG (paired mean normalized gross error)
P10 case	0.8985915	0.30223178
Ozone Column case	0.6890141	0.52356947

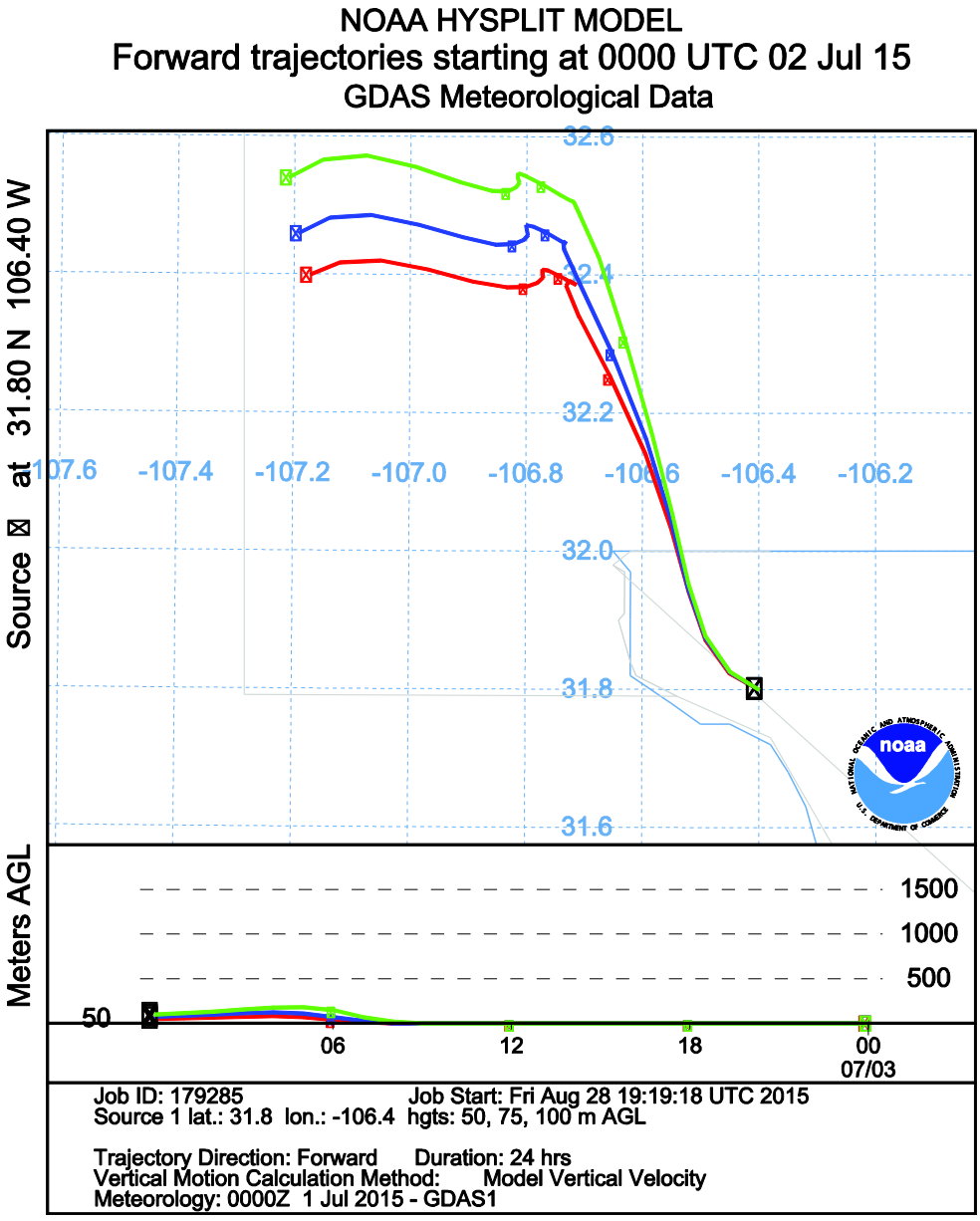

Figure 37. Hysplit Trajectory Plot showing the transport of air masses from west Texas towards western states on July 2.

Conclusions

- The model simulation for the Base case under-predicts ozone but all cases follow faithfully the overall trend of the experimental ozone results.
- The case that performed best was the P10 case, as observed in Figure 36. It is observed that as the photolysis rate coefficients for all the species are raised by 10% the NO_2 concentration decreases, and it appears that the NO decreases even faster, causing the Ozone to increase its concentration, in closer agreement to the experimental values.
- The 'ozone column case' shows a slight increase in surface ozone, which is not visible in the scale chosen for the graph, which was selected to exhibit all cases. It is evident that it would be necessary to perform further studies and to develop a multi-variate methodology that optimizes the photolysis rate coefficients not only for ozone, but also for NO_2 and formaldehyde. This will result in an improved methodology.
- For the July 2 analysis, the morning case study, the Hysplit analysis shows the transport of air masses from west Texas towards western states, causing the July 1 ozone episode disturbance based in the El Paso-Juarez region, to move towards the west, as observed in the July 2 graphs.

This was a pilot study, and further studies are needed. P10 case shows promising results and demonstrates that optimizing the photolysis rate coefficients will improve the accuracy of air quality simulations and forecasting capability.

References

- Houyoux, M.R., Vukovich, J.M., Coats, C.J. 2001. Emission inventory development and processing for the seasonal model for regional air quality (SMRAQ) project. J. Geophys. Res. 105, 9079–9090.
- ENVIRON: User's Guide to the Comprehensive AirQuality Model with Extensions (CAMx). Access in 2015. Version 6.1, http://www.camx.com.
- Madronich, S., Intercomparison of NO_2 Photodissociation and UV Radiometer Measurements, *Atmos. Environ., 21(3): 569-578, 1987*.
- Skamarock, W.C., Klemp, J.B., Dudhia, J. 2001. Prototypes for the WRF (Weather Research and Forecasting) model. Reprints, Ninth Conf. on Meso-scale Processes, Fort Lauderdale, FL, Amer. Meteor. Soc., J11-J15.
- Stockwell, W.R. and W.S. Goliff, Measurement of Actinic Flux and the Calculation of Photolysis Rate Parameters for the Central California Ozone Study, *Atmos. Environ., 38, 5169-5177, 2004.*
- Stockwell, W.R., R.M. Fitzgerald, Duanjun Lu and Roberto Perea, Differences in the variability of measured and simulated tropospheric ozone mixing ratios over the Paso del Norte Region, *Journal of Atmospheric Chemistry, 70, 91-104, 2013*
- TCEQ website. Database of Texas Commission for Environmental Quality (TCEQ) monitoring stations. Access in 2015. http://www.tceq.texas.gov/cgi-bin/compliance/monops/daily_average.pl?44201.
- U.S. EPA (United States Environmental Protection Agency), 2005 National Emissions Inventory Data & Documentation web site, 2010. Available at: http://www.epa.gov/ttnchie1/net/2005inventory.html (last access: 21 October 2014).