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WORK ORDER UNDER THE CONTRACT BETWEEN TCEQ AND CONTRACTOR: The University of Texas at Austin

GAD Number 582-17-72921

Ambient VOC Monitoring in El Paso, TX Project

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1. Background

This is the Draft and Final Report for Amendment No.3 to PGA/PCR Number: 582-20-11010-006.

The purpose of this project is to monitor ambient levels of volatile organic compounds (VOCs) that contribute to the formation of ozone. The University of Texas at Austin Center for Energy and Environmental Resources (UT) is collecting ambient VOC data using an Automated Gas

Chromatograph (auto-GC) and delivers the raw data electronically on an hourly basis to the Texas Commission on Environmental Quality (TCEQ) Leading Environmental Analysis System (LEADS) system and delivers validated auto-GC data within 90 days of collection. The monitoring site's location allows the instrument to sample ambient air from Ciudad Juarez, El Paso's mobile source fleet and other local sources of VOCs. These data can be used to better address the role of these emissions in ozone (O₃) formation. Research suggests that transported emissions affect air quality in El Paso, Texas. In addition, an oxides of nitrogen (NOx) instrument is deployed to track NOx concentrations and to conduct limitation ratio analysis and Age of Air-mass analysis.

El Paso is at risk of violating the 2015 O₃ National Ambient Air Quality Standard (NAAQS) which is based on the average of three years' annual fourth highest daily 8-hour maximum O₃ average not exceeding 70 parts per billion (ppb). This project will enable the TCEQ to better address the role played by local and international sources in El Paso's air quality.

The auto-GC monitoring station is in El Paso at 6700 Delta Drive. UT had previously operated an auto-GC at the Delta Drive site from August 2011 to August 2013. The station was reestablished in October 2017.

2. Summary of Recent Activities

Table 1 shows the approximate data return for Auto-GC validated data as reported by the TCEQ since January 2020 in LEADS as of June 30, 2022. Figure 1 shows the locations of the Delta Drive Continuous Ambient Monitoring Station (CAMS) station 1011, as well as the CAMS 123 Womble site and the CAMS 37 Ascarate Park site. Womble CAMS 123, is sited a short distance northwest of a refinery. Womble is 1.2 miles north-northwest of Delta, and Ascarate Park is 0.9 miles south-southeast of Delta. Despite the proximity of Womble and Ascarate Park (2.1 miles), the winds can differ owing to topography and channelization of winds along the river. Figure 2 shows the broader urbanized El Paso and Ciudad Juarez area including the Chamizal auto-GC station just under three miles to the west northwest.

Based on an extension of project, monitoring operations at the Delta Drive station are now expected to continue through the month of September 2022. A new purchase order is being processed for ORSAT LLC to continue operations.

A TEAMS meeting was held on June 9, 2022, between TCEQ and UT staff to discuss the interpretation of results to date for labeling the El Paso community as NOx-limited, VOC-limited, or mixed regarding O₃ control emphasis. The evidence is unconclusive and suggests a mixed label.

Months with validated data Approx. data return		Notes
January-2020	97%	
February-2020	96%	
March-2020	99%	
April-2020	83%	Some data loss 4/18-4/21
May-2020	86%	Some data loss 5/1-5/5
June-2020	96%	
July-2020	100%	
August-2020	98%	
September-2020	98%	
October-2020	100%	
November-2020	21%	Site temporarily shut down
	Monitoring susp	ended
April-2021	33%	Site restarted
May-2021	100%	
June-2021	87%	Preventive maintenance 6/21-6/23
July-2021	98%	
August-2021	99%	
September-2021	100%	
October-2021	99%	
November-2021	100%	
December-2021	100%	
January-2022	99%	
February-2022	98%	
March-2022	100%	
Average Jan. 2020-Mar. 2022	96.8%	(not including Nov. 2020 and Apr. 2021)

 Table 1 Delta auto-GC data return by month since Jan. 2020 (validated data only)

Figure 1. Monitoring stations near the Delta Drive



Figure 2. Monitoring stations in urban El Paso



3. Data Analysis

3.1 Ozone (O₃) NAAQS Status

It is up to the Environmental Protection Agency (EPA) to make nonattainment designations. Currently, the El Paso-Las Cruses metropolitan area is designated marginal-nonattainment, with counties listed in the table below from <u>https://www3.epa.gov/airquality/greenbook</u> (accessed July 2022). After the most recent three-year period, the O₃ NAAQS design values for the monitoring stations with three years of data are shown in Table 3. These values are the truncated averages of the 4th highest 8-hour averages at each station from 2019, 2020, and 2021. Tests for data completeness were not conducted. The data suggest that the UTEP and Chamizal stations are <u>noncompliant</u> with the 70-ppb level of the NAAQS.

Table 2 Ozone Attainment for El Paso

El Paso-Las Cruces, TX-NM (Marginal - Nonattainment) NEW MEXICO (Region VI): Dona Ana County (P) TEXAS (Region VI): El Paso County

Station	O3 Design Value ppb
El Paso UTEP C12	75
Ascarate Park SE C37	63
Chamizal C41	71
Socorro Hueco C49	70
Skyline Park C72	70
Ivanhoe C414	67

Table 3 O₃ NAAQS Design Values at El Paso Stations, 2019 – 2021

3.2 Carbonyl Species in El Paso

The carbonyl data from El Paso County stations were downloaded from TCEQ's TAMIS database, and time series graphs were made for all the species. A total of 21 different or "overlapping" carbonyl species were found. The overlapping species are those for which two isomers are combined as one parameter. This was the case for in some instances for methyl ethyl ketone and methacrolein, and for m- and p- tolualdehyde. No data are available after 2018. Table 4 lists the species and the years for which 24-hour data were found in the TCEQ's TAMIS database. UT has examined these data in the context of coincident ozone, auto-GC hydrocarbons, NOx, and meteorology. There are also data from 2000 to 2006 at 1-hour time resolution from UTEP C12, Chamizal C41, and Ascarate C37, but the focus at this point is on the most recent data.

		C12	C41	C123	C40 Sun	C37
AQS	Species	UTEP	Chamizal	Womble	Metro	Ascarate
43502	Formaldehyde	х	2000-2010	х	х	2010-2018
43503	Acetaldehyde	х	2000-2010	х	х	2010-2018
43504	Propionaldehyde	х	2000-2010	х	х	2010-2018
43505	Acrolein - Unverified		2004-2010			2010-2018
12510	Butyraldabyda	2004-		2004-	2004-	2004, 2010-
43310	Butyraidenyde	2005		2005	2005	2018
43513	Isovaleraldehyde	х	2000-2010	х	х	2010-2018
43515	Methacrolein	х	x	х	х	2012-2018
43516	trans-Crotonaldehyde	х	2000-2010	х	х	2010-2011
43517	Hexanaldehyde	х	2000-2010	х	х	2010-2018
43518	Valeraldehyde	х	2000-2010	х	х	2010-2018
43528	Crotonaldehyde	х	х	х	х	2012-2018
			2000-2003,			
43549	MEK & Methacrolein	х	2004-2006,	х	х	2011
			2008-2010			
43551	Acetone	х	2000-2010	х	х	2010-2018
13552	Methyl Ethyl Ketone (MEK)	2004-	2004-2008	2004-	2004-	2004-2006,
40002		2007	2004-2008	2008	2008	2012-2018
43950	Heptanal	х	2000-2010	х	х	2010-2018
45501	Benzaldehyde	х	2000-2010	х	х	2010-2018
45503	2,5-Dimethylbenzaldehyde	х	2000-2010	х	х	2010-2018
45505	o-Tolualdehyde	х	2000-2010	х	х	2010-2018
45506	m & p-Tolualdehyde	х	х	х	х	2012-2018
45507	p-Tolualdehyde	х	2000-2010	х	х	2010-2011
45508	m-Tolualdehyde	х	2000-2010	х	х	2010-2011

Table 4 Carbonyl sampling data found in TAMIS for El Paso

The carbonyl data from Ascarate CAMS 37 were selected for study, as that site had the most recent data. Using 109 records of 24-hour concentrations from January 1, 2017, to October 29, 2018, for the 15 carbonyl species shown in Table 5, a principal component analysis (PCA) and rotated factor analysis (FA) procedures suggested 2 or 3 factors may be present in the carbonyl data set. These 15 species had the most non-zero values. Following these procedures, a positive matrix factorization (PMF) analysis was conducted. PMF suggested 4 or 5 factors, but a 4-factor model was deemed a better fit and was closer to the PCA and FA results. Because there was no total mass variable with the carbonyl data, a mass apportionment was not practical to run. One must also be cautioned as to the concern that carbonyl species are generally reaction products of the oxidation of hydrocarbon species as well as sometimes being the primary emission of a chemical or combustion process, and this can confound a source apportionment analysis. Figure 3 shows the time series for the four factors found from PMF, and Figure 4 shows the average factor contribution by month over the two years. Figure 4 appears to show that one factor – Factor 1 – is predominant in the summer months, and the other three factors are low in the summer and high in the winter. One hypothesis may be that Factor 1 plays a role in O₃

formation. Figure 5 through Figure 8 show the results of 200 bootstrapping runs that assess the stability in factor make-ups, and Figure 9 shows how each species is apportioned to each factor. Bar charts for the relative contribution of each species to the four factors appear in Figure 10 through Figure 13. These last four figures show the concentration of the species apportioned to each factor, and because Formaldehyde, Acetone and Acetaldehyde have the highest mean concentrations, they appear in all factors, whereas Crotonaldehyde only appears in Factor 2 but has a low concentration in all samples. However, Figure 9 shows that

- Acetone & Methyl Ethyl Ketone are tracers for Factor 3
- m/p-Tolualdehyde is a tracer for Factor 4
- Crotonaldehyde is a tracer for Factor 2
- 11 of 15 species contribute at least 25% of their concentration to Factor 1, and four species contribute at least 50% of their concentration to Factor 1.

Acetaldehyde
Acetone
Benzaldehyde
Butyraldehyde
Formaldehyde
Heptanal
Hexanaldehyde
lsovaleraldehyde
Propionaldehyde
Valeraldehyde
Methyl Ethyl Ketone
Acrolein Unverified
Methacrolein
m/p-Tolualdehyde
Crotonaldehyde

Table 5 Carbonyl species from Ascarate used in multivariate analyses (15 total)



Figure 3 Time series for every 6th day carbonyl factors at Ascarate 2017 - 2018





Figure 5 Ascarate carbonyl PMF rotated Factor 1 bootstrapped box plot of percent of species in this factor



Figure 6 Ascarate carbonyl PMF rotated Factor 2 bootstrapped box plot of percent of species in this factor



Figure 7 Ascarate carbonyl PMF rotated Factor 3 bootstrapped box plot of percent of species in this factor



Figure 8 Ascarate carbonyl PMF rotated Factor 4 bootstrapped box plot of percent of species in this factor

Figure 11 Rotated PMF Factor 2

Figure 12 Rotated PMF Factor 3

Figure 13 Rotated PMF Factor 4

3.3 The Effect of O₃ Precursors on O₃ Concentrations Using Graphs

A major effort has gone into looking at relationships among O₃ precursors and O₃ concentrations. Figure 14 shows an example of an "O₃ isopleth" showing the dependence of O₃ concentrations on mixed concentrations of volatile organic compounds (VOCs) and oxides of nitrogen (NOx) from earlier in the day. Data from El Paso monitoring stations were downloaded and precursors from all NOx stations and the two auto-GC stations were averaged over four morning hours of 6 MST through 9 MST and for all O₃ monitoring stations the daily O₃ four-hour maxima were calculated. Data were used from the months May through October from the

years 2019, 2020, and 2021 (552 days). Figure 15 shows scatter plots of the maximum 4-hour O₃ concentration at UTEP each day versus the morning NOx at UTEP and TNMHC at Chamizal. Below the scatterplots is a histogram of the O3 daily 4-hour maxima at UTEP, with the values at or above 70 ppb selected, the result of which is the bolder points in the scatter plots.

¹ <u>https://www.researchgate.net/figure/Ozone-isopleth-diagram-showing-constant-ozone-concentrations-as-isopleths-National_fig2_323342199</u>

Figure 15 Comparison of NOx at UTEP and TNMHC at Chamizal morning averages and UTEP O3 averages using May – October // 2019 – 2021 data

A second approach has been to look at all 46 individual hydrocarbon species from Chamizal and look for any significant correlations of morning 4-hour averages with daily O₃ 4-hour maxima. No significant correlations have been found.

As a next step, data used in regressions was expanded to 2010 to 2021 (12 years) from May through September each year (1,836 days). One approach taken has been to compare morning 6 MST though 9 MST (4 hours) averages of NOx and hydrocarbons and look at resultant afternoon O₃ concentrations as a function of the morning hydrocarbon to NOx ratio. Various approaches were used, including:

- Total nonmethane hydrocarbon to NOx ratio
- Total nonmethane hydrocarbon to NO₂ ratio
- Total nonmethane hydrocarbon minus ethane to NOx ratio, since ethane's reactivity is low enough to not be considered a VOC

The following four figures each show the results of combining 3 years each (2010-2012, 2013-2015, 2016-2018, 2019-2021) for NOx in ppb units and VOC (TNMHC minus ethane) in ppbC units, and the corresponding mean afternoon 4-hour average O₃ in ppb units from the UTEP

CAMS 12 station, by color shading. The x, y scales are held constant, and are driven by the observed maximum morning average UTEP NOx and Chamizal VOC values in the dataset. The data seem to show higher dependence on NOx (NOx-limited) O₃ in the earlier years, with a balance of NOx and VOC dependence in the most recent 3-years. Figure 20 shows the annual mean VOC to NOx ratio by year for days on which the afternoon average O₃ was 65 ppb or greater and for days on which it was less than 65 ppb. Taken together, Figure 19 and Figure 20 when related to the O₃ isopleth graph in Figure 14 suggest that the VOC to NOx ratio on high O₃ days in recent years tends to be in the 6 to 7 range, associated with a mixed condition calling for both reductions in NOx and VOC to reduce O₃.

Figure 16. Dependence of UTEP 2010 – 2012 May – Sept. p.m. O3 on a.m. NOx & Chamizal VOC

Figure 17. Dependence of UTEP 2013 – 2015 May – Sept. p.m. O3 on a.m. NOx & Chamizal VOC

Figure 18 Dependence of UTEP 2016 – 2018 May – Sept. p.m. O3 on a.m. NOx & Chamizal VOC

Figure 19 Dependence of UTEP 2019 – 2021 May – Sept. p.m. O₃ on a.m. NOx & Chamizal VOC

Figure 20. Average VOC to NOx ratios on higher O₃ days (orange) and lower O₃ days (blue)

3.4 The Effect of Meteorology on O₃ Concentrations

A review of ozone data in El Paso suggested the typical eight-hour maxima began at 9, 10, 11 MST. Thus, the eight-hour average O₃ from 10 through 17 MST (8 hours) was calculated for each day from May through September 2010 through 2021. In addition, traditional meteorological factors that influence O₃ concentrations were averaged over the same 8-hours: wind speed and direction, temperature, solar and ultraviolet radiation. Data were used only if 6 or more hours of data were present. Wind speed and direction were converted into Cartesian coordinates u (east-west) and v (north south). The eight-hour average data were analyzed in SAS using Proc Reg with the model:

 $C12_O3_8hr = b_{0} + b_{1}*C12_u_8hr + b_{2}*C12_v_8hr + b_{3}*C12_UV_Rad_8hr + b_{4}*C12_S1r_Rad_8hr b_{5}*C12_tempF_8hr$

This model was for CAMS 12 at UTEP, with the same model used for two other stations using data from CAMS 41 Chamizal and CAMS 37 Ascarate Park. Only CAMS 12 UTEP has ultraviolet radiation, so that variable we used in each of the three models.

Results are shown in the tables below. These are simple linear models, and in some cases the linearity may be too simple a model. Ultraviolet and solar radiation may be redundant, as may be temperature with the radiation variables. More advanced regression methods may be more important. Also, using Cartesian coordinates on wind direction alone with a separate wind speed value may be more productive.

Variable	Parameter Estimate	t Value	Pr > t
Intercept	16.53	6.72	<.0001
C12_u_8hr	0.046	1.11	0.2652
C12_v_8hr	-0.093	-0.78	0.4344
C12_UV_Rad_8hr	369	2.15	0.0318
C12_Slr_Rad_8hr	34.43	6.26	<.0001
C12_tempF_8hr	0.27	8.96	<.0001

Table 6 Regression results for UTEP, $R^2 = 34\%$, 1,623 valid observations, u, v not significant

Variable	Parameter Estimate	t Value	Pr > t
Intercept	11.35	4.28	<.0001
C41_u_8hr	-0.508	-15.11	<.0001
C41_v_8hr	0.250	2.42	0.0158
C12_UV_Rad_8hr	1,805	11.61	<.0001
C41_Slr_Rad_8hr	-8.39	-2.17	0.0301
C41_tempF_8hr	0.26	8.06	<.0001

Table 7 Regression results for Chamizal, R² = 43%, 1,535 valid obs., solar w neg. parameter

Table 8 Regression results for Ascarate Park, $R^2 = 34\%$, 1,593 valid observations

Variable	Parameter Estimate	t Value	Pr > t
Intercept	19.12	7.89	<.0001
C37_u_8hr	0.17	4.78	<.0001
C37_v_8hr	0.22	2.44	0.0146
C12_UV_Rad_8hr	939	5.30	<.0001
C37_Slr_Rad_8hr	18.4	3.72	0.0002
C37_tempF_8hr	0.16	5.56	<.0001

3.5 The Effect of O₃ Precursors on O₃ Concentrations

The next step in this investigation was to add morning NOx and VOC to these models. This may be done with linear regression, or with the graphing shown earlier in this report, in which the regression residuals from the above analyses could go into the color-coded figures replacing the actual afternoon O_3 concentrations.

In this section, NOx and VOC data have been added to the multivariate regressions. Data have been used from 2010 to 2021 (12 years) from May through September each year (1,836 days).

Model Construction

The eight-hour average O₃ from 10 through 17 MST (8 hours) was calculated for each day from months May through September and years from 2010 through 2021. Meteorological factors that influence O₃ concentrations were averaged over the same 8-hours: wind speed and direction (vector averaged), temperature, solar and ultraviolet radiation. Data were used only if 6 or more hours of data were present. Wind direction was converted into Cartesian coordinates u (east-west) and v (north south), and wind speed was handled as a separate variable. The eight-hour average data were analyzed in SAS using Proc Reg with the model for CAMS 12 at UTEP

shown below. The same model used for two other stations using data from CAMS 41 Chamizal and CAMS 37 Ascarate Park.

$$C12_O3_8hr = b_{o} + b_{1}*C12_u_8hr + b_{2}*C12_v_8hr + b_{3}*C12_WSR_8hr + b_{4}*C12_UV_Rad_8hr + b_{5}*solar_avg + b_{6}*tempF_avg + b_{7}*VOCh_4hr + b_{8}*C12_NOx_4hr$$

where

- the solar radiation and surface temperatures have been averaged among the three stations,
- the VOCh_4hr variable is the total nonmethane hydrocarbon minus ethane at Chamizal averaged from 6, 7, 8, and 9 a.m. CST,
- NOx_4hr variable is hourly NOx from the station averaged from 6, 7, 8, and 9 a.m. CST,
- only CAMS 12 UTEP has ultraviolet radiation, so the C12_UV_Rad_8hr variable was used in each of the three stations models, and
- only Chamizal VOCh was used, and each station's own NOx and wind data were used.

The 12 years of data were broken into 4 three-year periods, 2010 - 2012, 2013 - 2015, 2016 - 2018, and 2019 - 2021, in order to see what changes in models could be related to temporal changes in emission conditions in the area.

Results

Results on the scale described above are challenging to summarize. One oddity is that the R^2 values for the regressions, which ranged from 16.4% to 69.5% and averaged 47.6% over 12 regressions were perfectly correlated in ordinal ranking among the 3 stations, as shown in Figure 21.

Figure 21. Values for R² for the 3 stations in 4 periods, well correlated

At Chamizal C41, UV radiation, low wind speed, and westerly wind consistently had p-values < 0.02, and neither VOC nor NOx appeared to play a role.

At Ascarate C37, no one parameter had a low p-value (<0.05) for all four periods. Only in the 2010-2012 period did there appear to be a NOx disbenefit, in which a low p-value (0.037) was associated with a coefficient of -0.051 suggesting an increase in NOx would lower the resulting O₃ concentration. Low wind speed was a factor in three of the four periods.

At UTEP C12, low wind speed was a factor in all four period. Wind directionality was inconsistent. Solar or UV was important in each of the four years.

Three MS Excel files were provided to the TCEQ containing the SAS model results. The tables were color coded for p-values less than 0.05. In most cases, the y-intercept was also significant and sometimes quite large.

A principal component analysis could potentially be used to shrink the number of parameters, and steps could be taken to address potential nonlinearities or add cross product terms.

3.6 NOx Species in El Paso

After a long absence of data flow dating from February 2019, the NOy monitor at Chamizal was restored on February 1, 2022. Figure 22 shows the comparison of the hourly NOx monitor nitric oxide (NO) (x-axis) to the NOy monitor NO (y-axis) for February 1 to May 10, 2022. The agreement is very good and within the standard 15 percent confidence interval on NOx species in the TCEQ's Quality Assurance Project Plan.

Figure 23 and Figure 24 show time series graphs for NOx species at Delta Dr. and Chamizal, respectively. Concentrations appear to be generally higher at Chamizal, which is not unexpected given its location near a cluster of highways including the International Bridge. However, NO₂ concentrations at both stations average close to 11.5 ppb over the past one year.

Figure 22. Chamizal NO POC2 from NOy analyzer vs POC1 from NOx analyzer, Feb. – May 2022

Figure 24. Time series graph of Chamizal NOx, NO, and NO₂ from April 2021 to May 2022

3.7 New Mexico Air Monitoring

Data from the U.S. Environmental Protection Agency's Air Quality System (AQS) database have been downloaded and data from southern New Mexico are being examined for clues as to upwind source areas that may be coincidental with those associated with El Paso. This work is just getting underway. Data from 2000 through 2021 are in hand. Figure 25 show a map of the New Mexico air monitoring network in 2022, showing several stations near El Paso and two other stations in the southern parts of the state. For one of those stations, the Carlsbad, NM station (AQS number 350151005), the hourly data have been analyzed, and Figure 26 shows the trends by year for the various central tendency and upper percentile values one-hour O₃ values using data from May through September each year, from 2000 through 2021. The year 2003 was incomplete, and 2020 is missing 22 days in July and 8 days in August but other years were nearly all complete. The graph shows the time series and trend lines for the median, 75th, 90th, 95th, and 99th percentile hourly values. For this analysis, all hours of the day were used, as the Carlsbad station was hypothesized to be subject to long range pollutant transport, in which case elevated concentrations could exist at night. All the regression slopes are positive, and the R^2 values range from 21% to 42%. The p-values on the regressions range from 0.035 to 0.0015. A preliminary conclusion is that O₃ concentrations at Carlsbad have risen since 2000.

Figure 25 New Mexico Air Monitoring Network in 2022

Figure 26 Trends in various percentile values for Carlsbad NM summer hourly O₃

4. Conclusion

Evidence suggests that El Paso is "mixed" in terms of being VOC or NOx limited regarding O3 formation. Some evidence exists to suggest that transport of O3 and/or O3 precursors happens from active oil and gas extraction regions hundreds of kilometers away². Monitoring continues at the Delta Dr. station through the summer of 2022 and another Final Report will follow conclusion of that work.

² •Karle, N. N, R. M. Fitzgerald, R. K. Sakai, D. W. Sullivan, W. R. Stockwell, "Multi-scale Atmospheric Emissions, Circulation and Meteorological Drivers of Ozone Episodes in El Paso-Juárez Airshed," Atmosphere 2021, 12(12), 1575; <u>https://doi.org/10.3390/atmos12121575</u>