Draft Final Report, August 15, 2023
Partially Satisfying Task 5

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

GAD Number 582-17-72921
TCEQ Project 582-23-43395-10
Tracking Number: 2023-14

Ambient VOC Monitoring in El Paso, TX Project

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Contents

1. Background 1
2. Summary of Recent Activities 2
3. Data Analysis 4
El Paso Ozone Trends 4
Hydrocarbon Data Analysis Results 11
Toluene at Delta Dr. and Chamizal Auto-GCs 11
Toluene in El Paso Canister Samples 16
VOC to NOx Ratios 26
4. Conclusions 27

1. Background

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 (O_3) 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 ozone formation limitation ratio analysis and Age of Air-mass analysis.

El Paso is at risk of violating the 2015 O_3 National Ambient Air Quality Standard (NAAQS) which is based on the average of three years' annual fourth highest daily 8-hour maximum O_3 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 United States Environmental Protection Agency (U.S. EPA) has recognized that El Paso is affected by precursor emissions and ozone formation originating from outside of the U.S. border.

The auto-GC monitoring station is sited in El Paso, TX 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. The station will be closed down and vacated before August 31, 2023.

2. Summary of Recent Activities

The Orsat contractor has been notified that monitoring should end in early August, and the equipment should be shipped to the Orsat office in Pasadena TX. UT is looking into the relocation or disposal of the monitoring station shelter, which is now close to 20 years old.

Under the Federal Clean Air Act, Section 179B allow some relaxation of NAAQS compliance deadlines if it can be shown that emissions from outside the U.S. border have prevented a region from meeting compliance deadlines. In the U.S. Federal Register on March 7, 2023, the U.S. EPA announced the following:

> The Environmental Protection Agency (EPA or "Agency") is proposing to determine that the El Paso-Las Cruces, Texas-New Mexico nonattainment area would have attained the 2015 ozone national ambient air quality standard (NAAQS) by the August 3, 2021 "Marginal" area attainment date, but for emissions emanating from outside the United States. If we finalize this action as proposed, the El Paso-Las Cruces, Texas-New Mexico ozone nonattainment area would no longer be subject to the Clean Air Act (CAA) requirements pertaining to reclassification upon failure to attain and therefore would remain classified as a Marginal nonattainment area for the 2015 ozone NAAQS. This action, if finalized as proposed, will discharge the EPA's statutory obligation to determine whether the El Paso-Las Cruces, Texas-New Mexico ozone nonattainment area attained the NAAQS by the attainment date.[1]

Figure 1 shows the locations of the Delta Dr. 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 of the Delta station.

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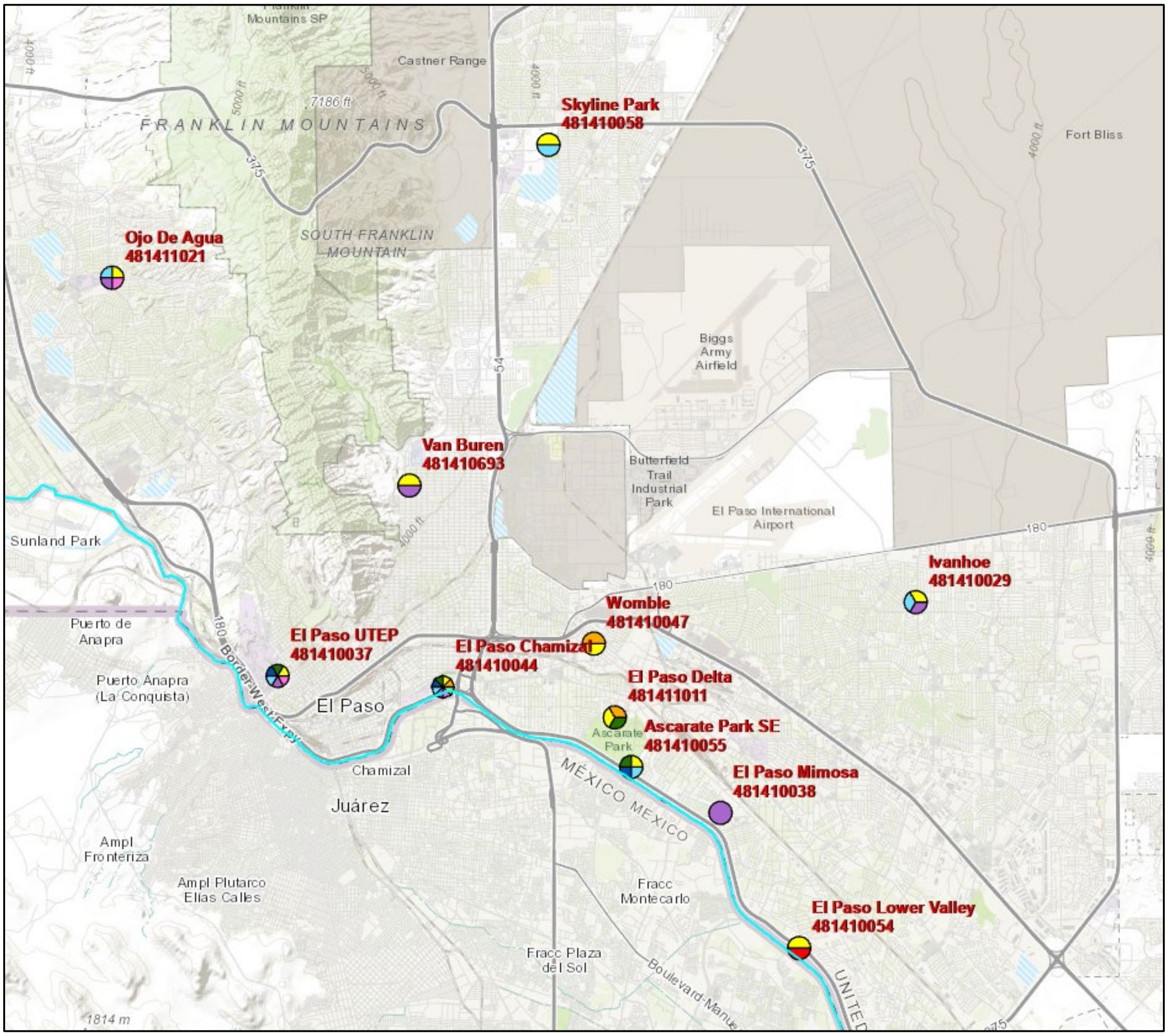
[1] See https://www.federalregister.gov/documents/2023/03/07/2023-04634/determination-of-attainment-by-the-attainment-date-but-for-international-emissions-for-the-2015 accessed July 2023.

Figure 1. Monitoring stations near the Delta Drive

Figure 2. Monitoring stations in El Paso



3. Data Analysis

El Paso Ozone Trends

Ozone data from the TCEQ TAMIS database was extracted and 8-hour ozone daily maxima from the 1970s through recent years are shown in subsequent time series graphs. For a period in the 1980s, the ozone value was reported to the 10s of parts per million, causing some oddities in the hourly time series graphs. These oddities are muted in the 8-hour maximum graphs. All the graphs in Figure 3 through Figure 11 have the same x- and y-axes for comparison purposes. Overall concentrations have declined over time from a high frequency of 8-hour daily maxima above 100 ppm to that being a rare occurrence. This better illustrated in Figure 12 showing the long-term trend in the count of days each year that the daily 8-hour average maximum was 70 ppb or higher, and in Figure 13, which shows a more recent trend. Table 1 shows the fourth highest 8-hour daily maxima for 2020 to 2022 and the average for the three years, showing El Paso fails to meet the NAAQS requirements.

Figure 3. CAMS 6 Downtown 8-hr O3 daily maxima

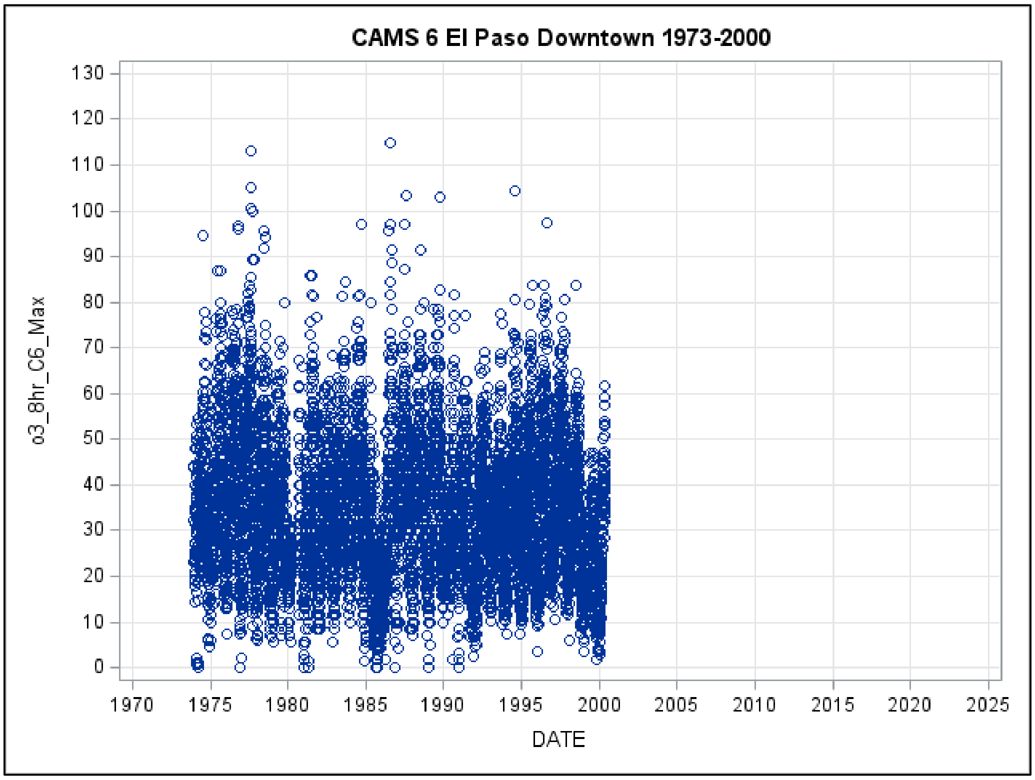


Figure 4. CAMS 30 East 8-hr O3 daily maxima

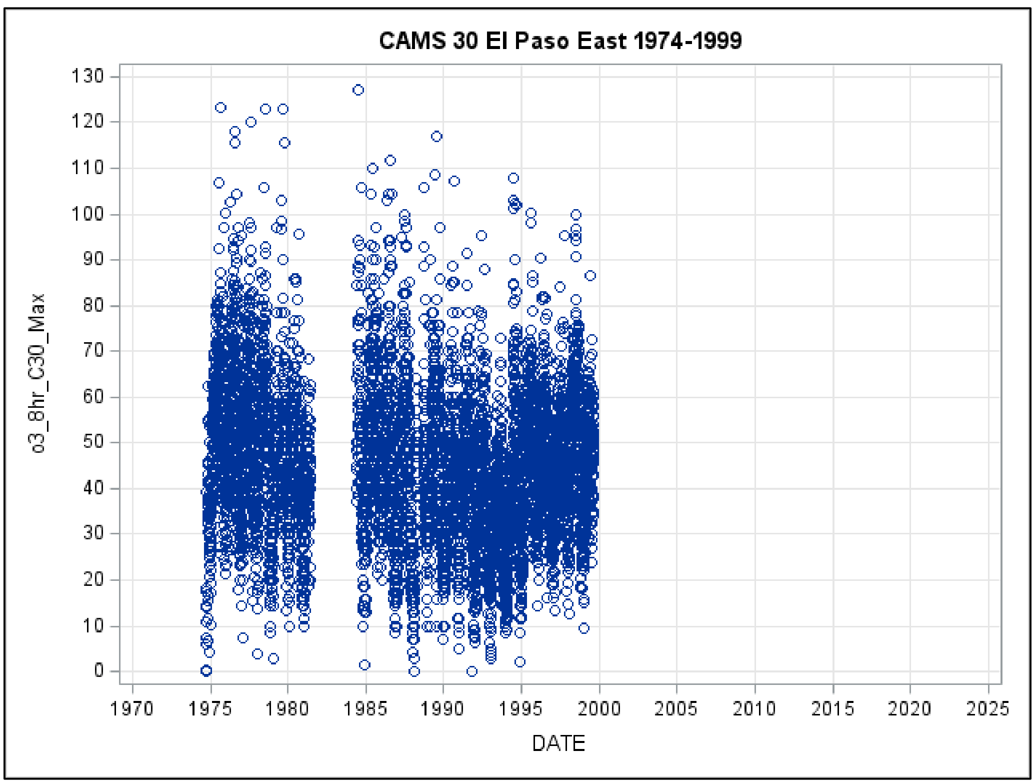


Figure 5. CAMS 12 UTEP 8-hr O3 daily maxima

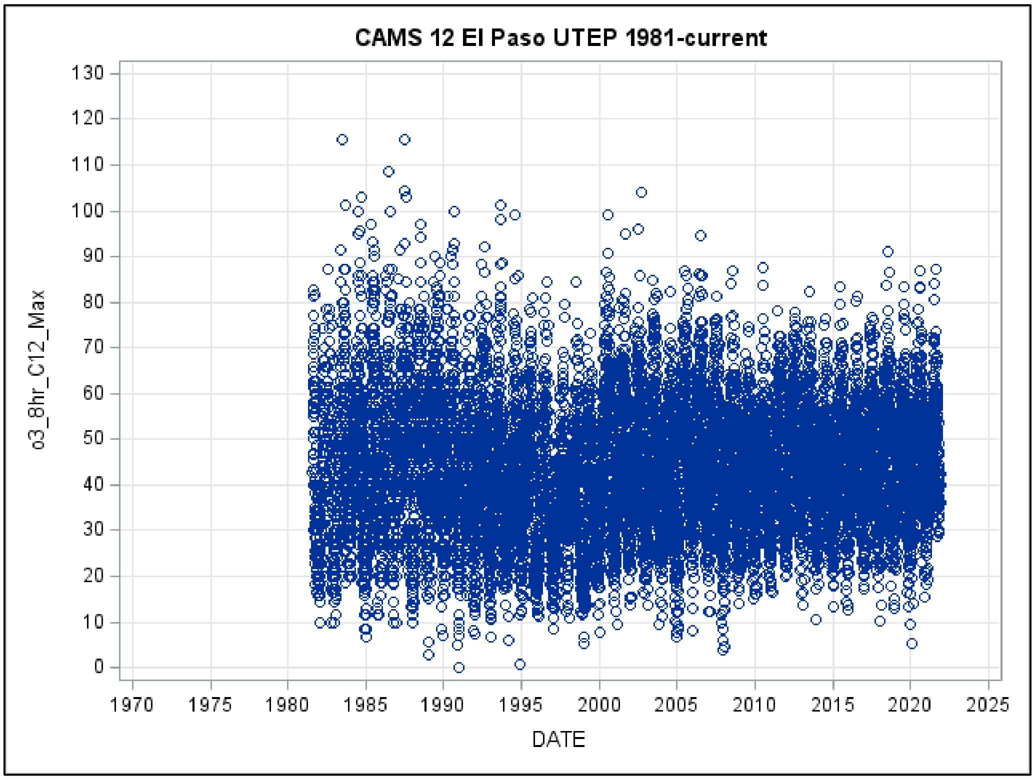


Figure 6. CAMS 41 Chamizal 8-hr O3 daily maxima

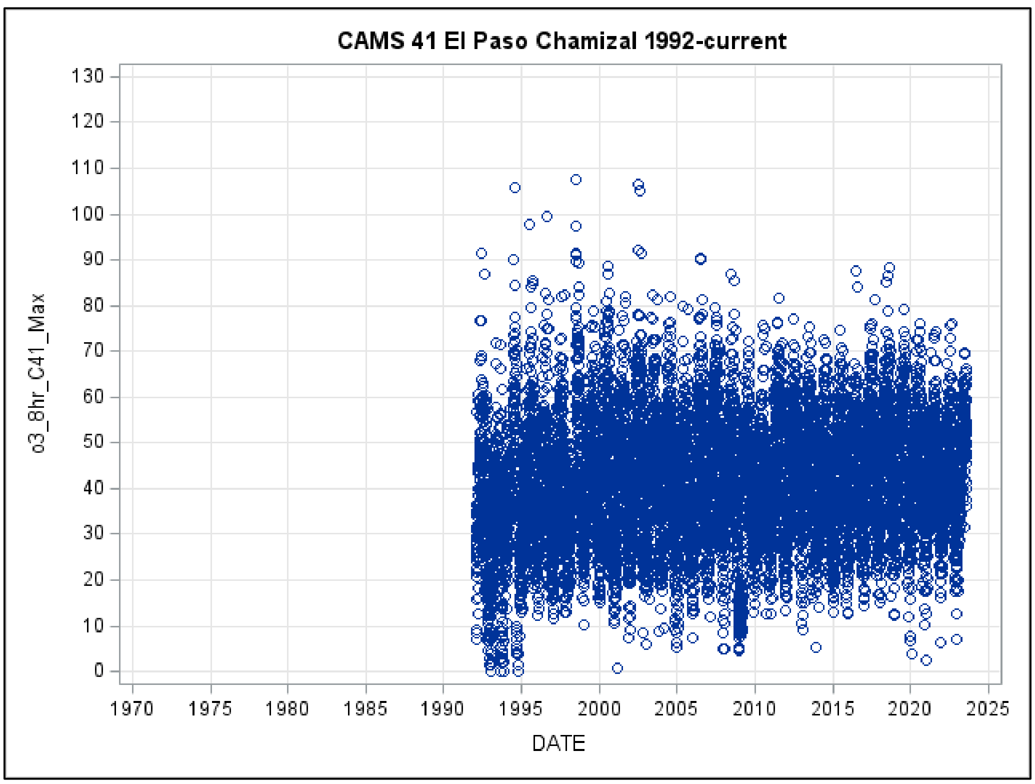


Figure 7. CAMS 414 Ivanhoe 8-hr O3 daily maxima

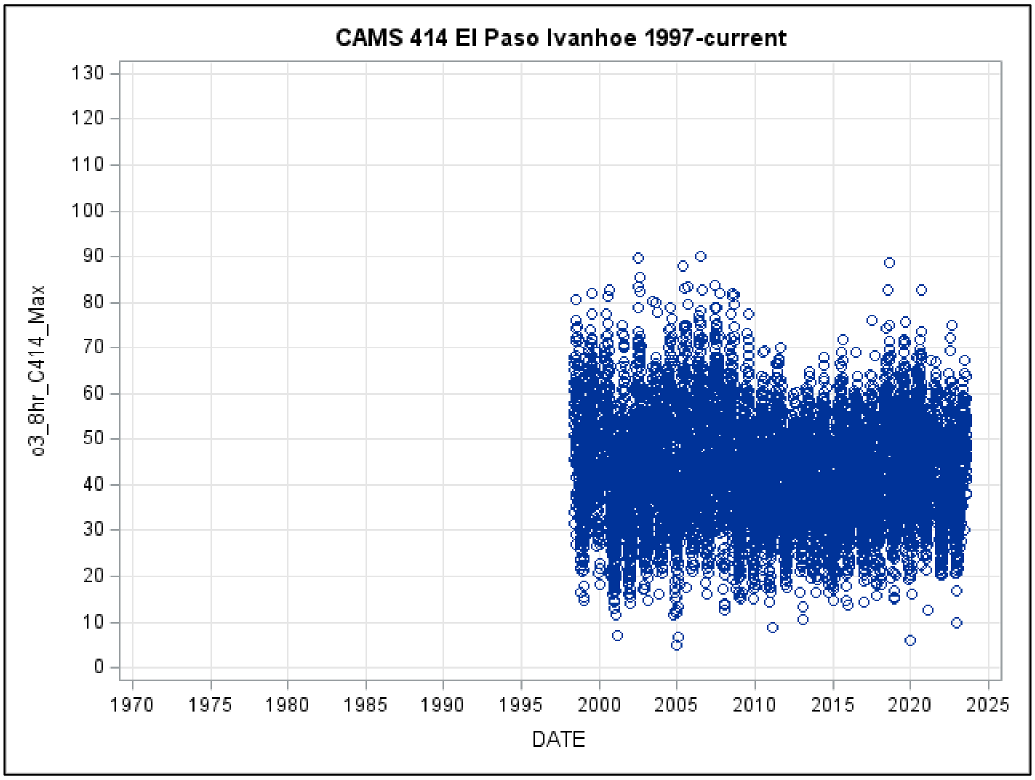


Figure 8. CAMS 37 Ascarate Park 8-hr O3 daily maxima

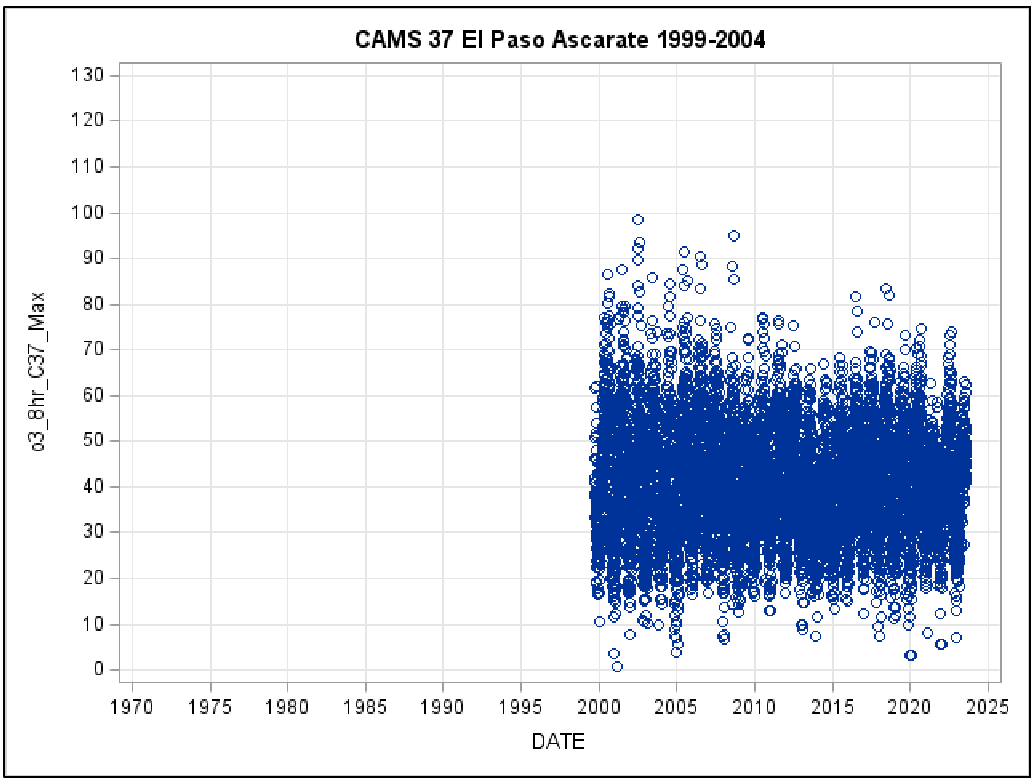


Figure 9. CAMS 72 Skyline 8-hr O3 daily maxima

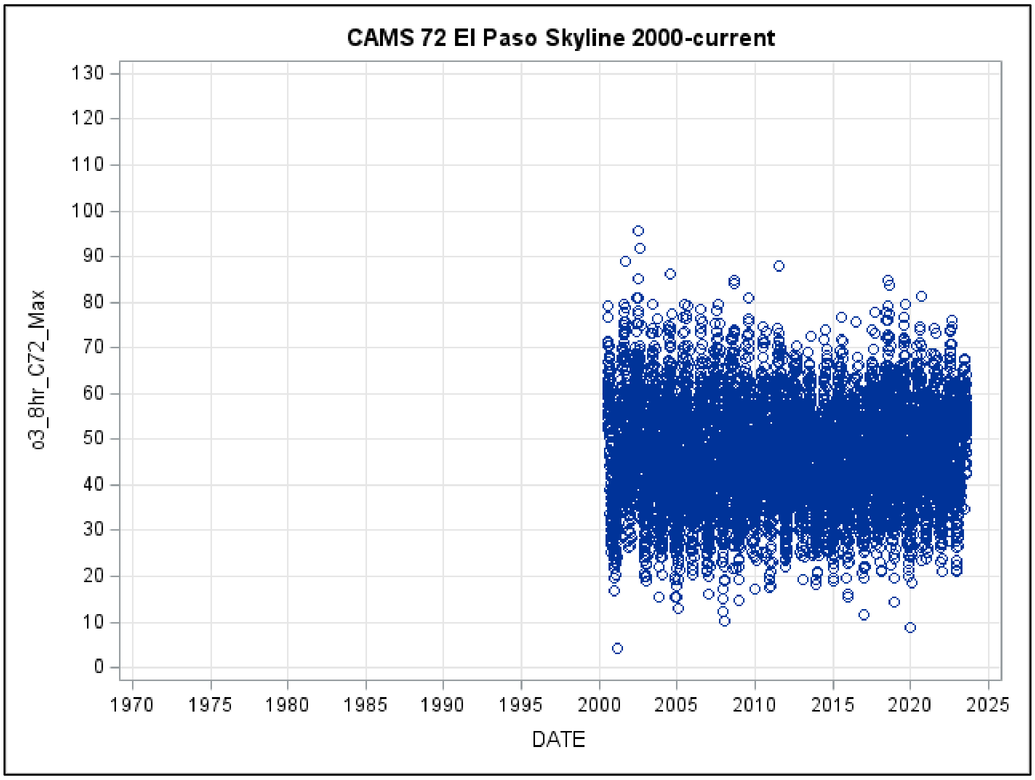


Figure 10. CAMS 49 Socorro Hueco 8-hr O3 daily maxima

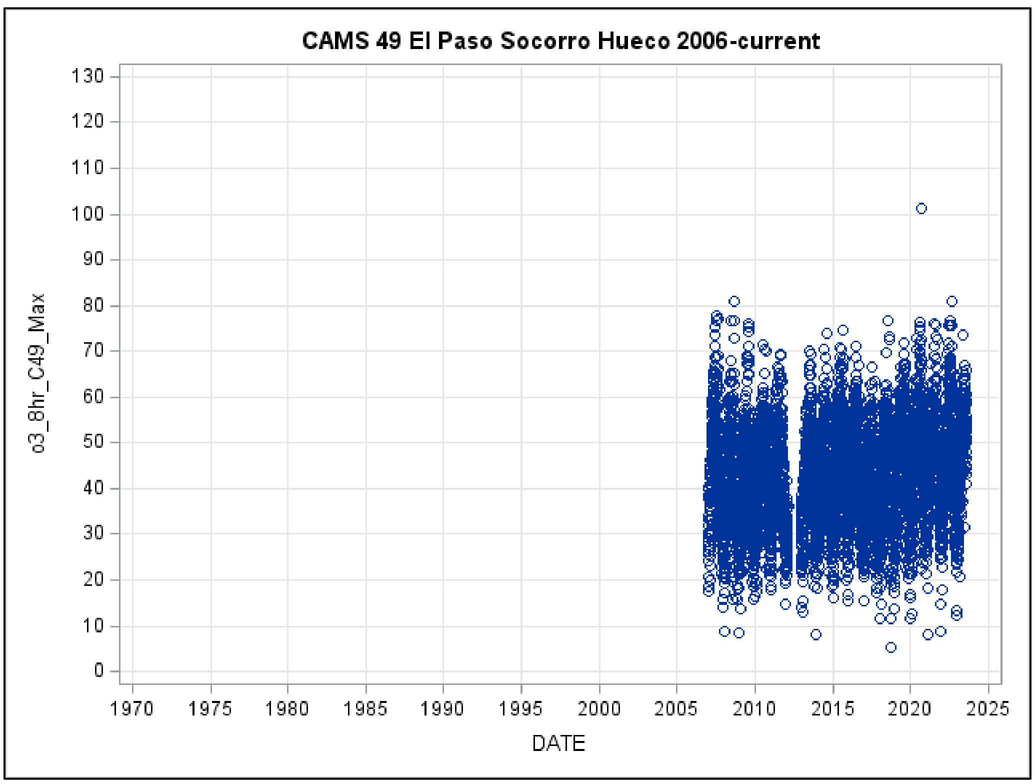


Figure 11. CAMS1021 Ojo de Agua 8-hr O3 daily maxima

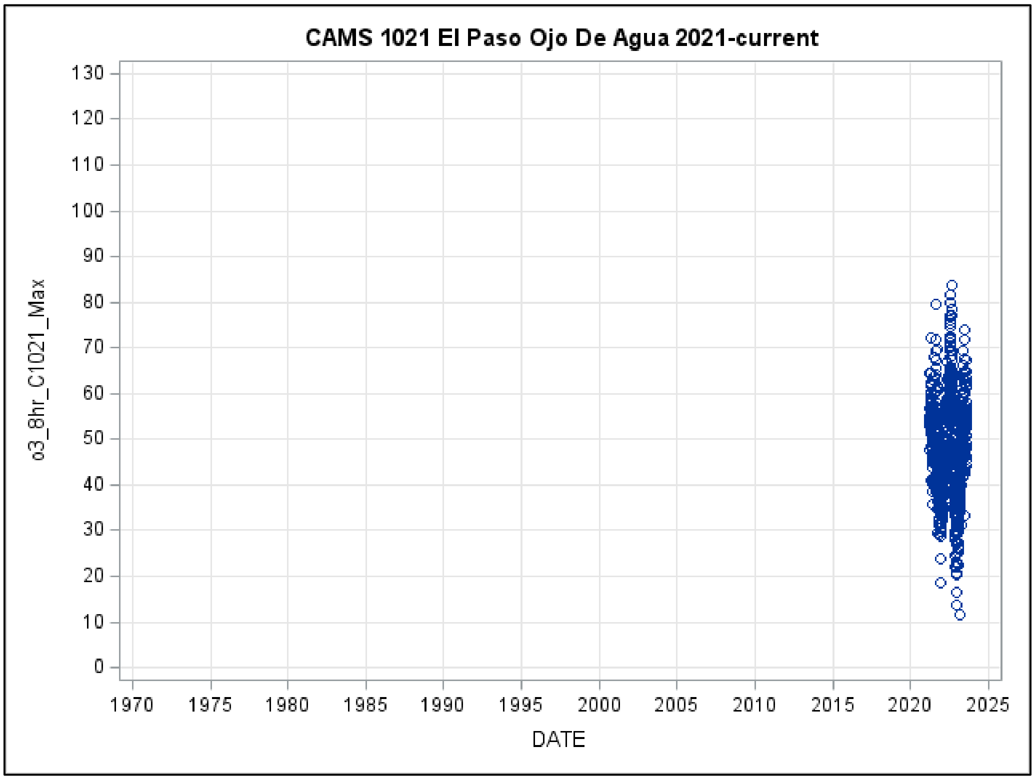


Figure 12. Long term trend in elevated 8-hour O_3 days in El Paso

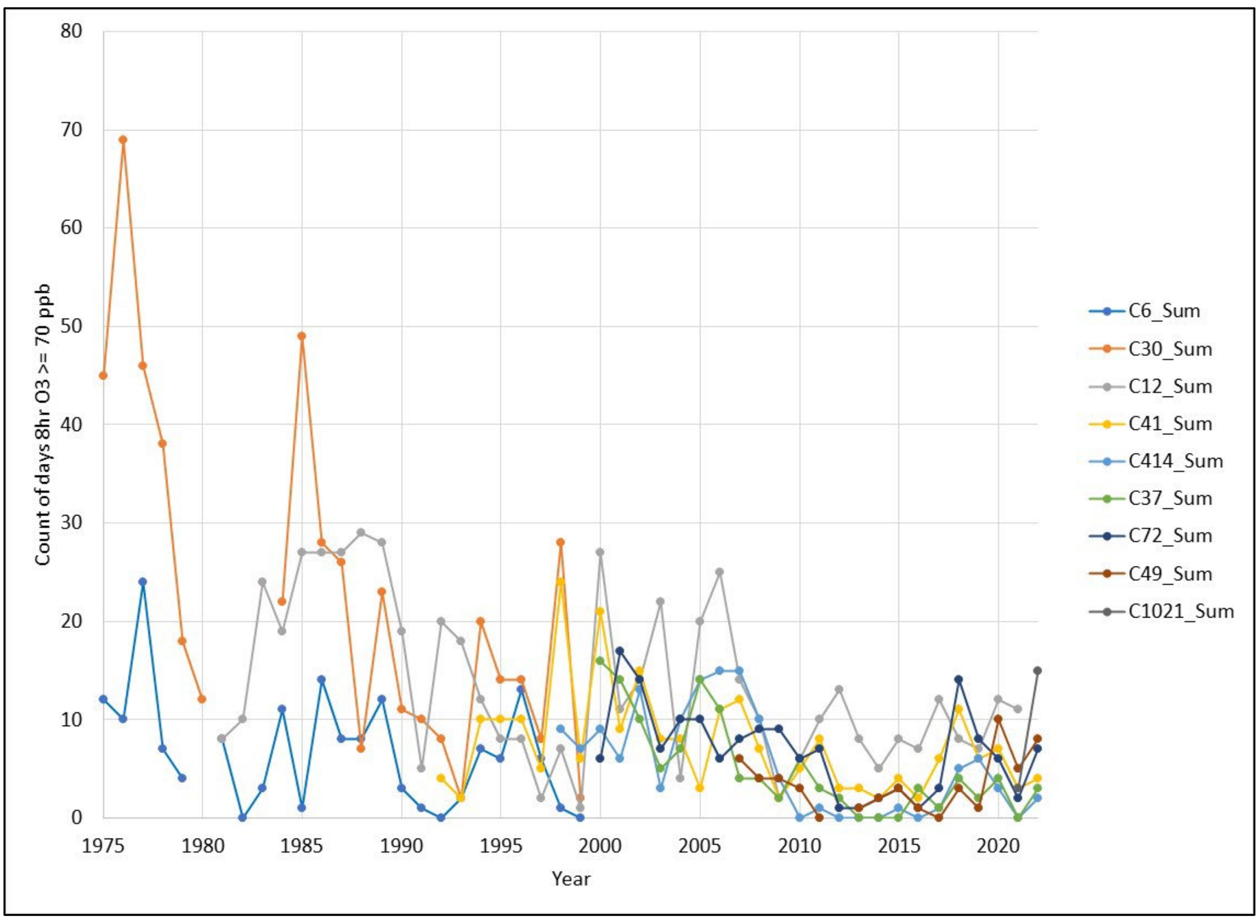


Figure 13. More recent trend in elevated 8-hour O_3 days in El Paso

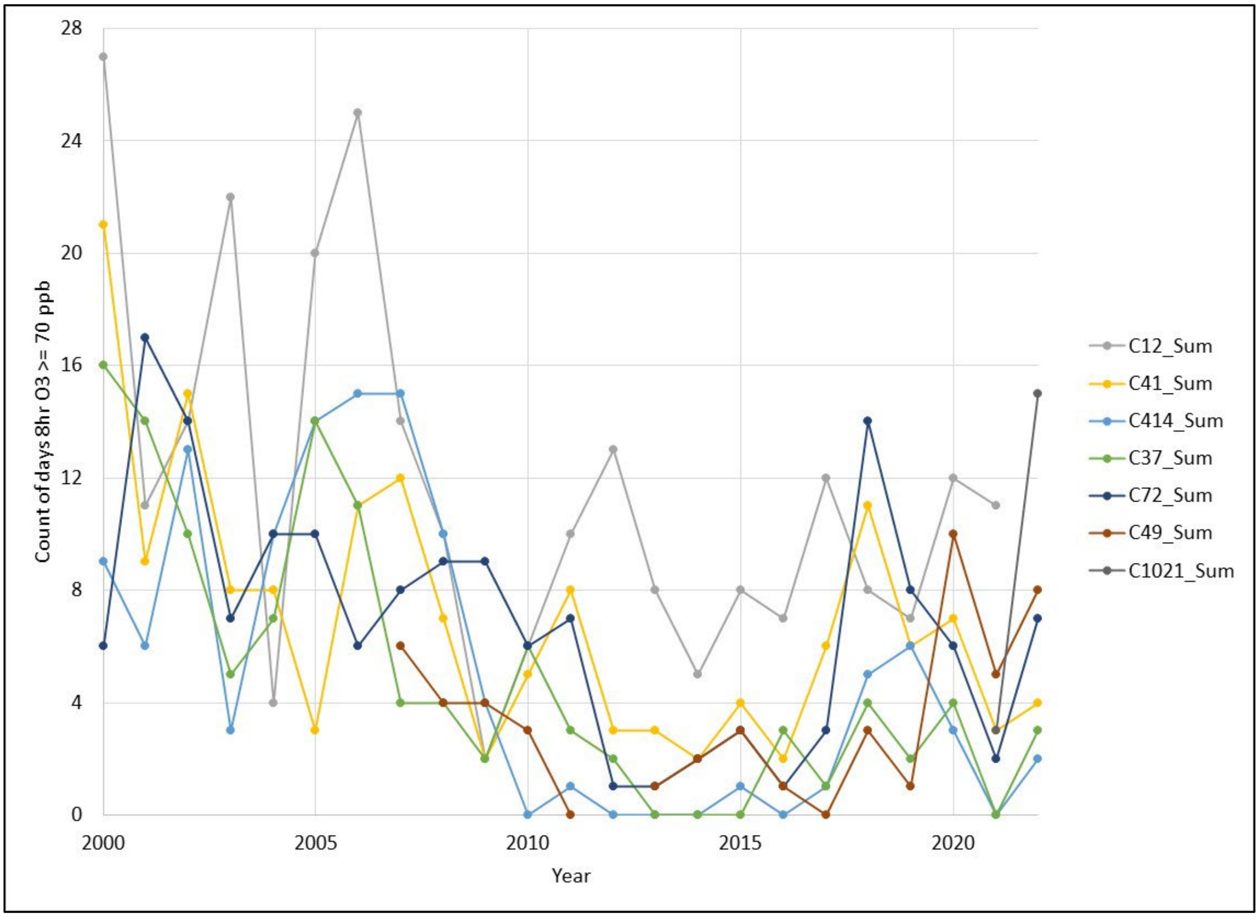


Table 1. El Paso fourth highest 8-hour daily max and 3-year average

Station	2020	2021	2022	3-year mean
Ivanhoe C414	68	64	64	65
El Paso UTEP C12	79	73		
Socorro Hueco C49	74	71	75	73
Ojo De Agua C1021		71	79	
Skyline Park C72	71	68	72	70
Chamizal C41	72	69	68	69
Ascarate Park SE C37	69	56	68	64

Hydrocarbon Data Analysis Results

The auto-GC data from the Delta Dr. station have been examined using a range of multivariate data analysis methods. Caution must always be used in this type of analysis, as several hydrocarbon species are highly chemically reactive and so the measured concentrations may not be very representative of the upwind emissions, while other species are relatively inert and thus have more utility in source apportionment studies. One approach to using more species is to select a period of low photochemical activity such as nighttime, but this may also affect the mix of emission sources present, as motor vehicle activity may be lower overnight.

Of 34,687 hours of data since 2018, 28,217 hours have all 46 species. Using a simple principal component analysis on all 46 auto-GC species using all available hours produced a suggestion that five or six sources were present based on the eigenvalues, but the first principal component looked like a mix of all 46 species and explained 69 percent of total variance. Using only hours between 19 MST and 7 MST inclusive, the 14,151 observations suggested that five sources were present based on the eigenvalues but again the first principal component looks like a mix of all 46 species and explained 70 percent of total variance. The second principal component appeared to be C4 to C5 alkanes, the third appeared to be C2 to C4 alkenes, the fourth appeared to be dimethyl-pentane isomers and trimethyl-pentane isomers, and the fifth appeared to be natural gas (ethane and propane).

Next, a factor analysis with rotation was used on the 19 MST and 7 MST (five principal component) data. The first rotated factor included C2 to C4 alkenes, BTEX species, and trimethyl-benzene isomers. The second rotated factor included one alkene (1-pentene), and C6-C9 alkanes. The third rotated factor included C4 to C5 alkenes and alkanes. The fourth rotated factor was two dimethyl-pentane and two trimethyl-pentane isomers. The fifth rotated factor was natural gas (ethane and propane, some butane isomers).

Efforts to execute positive matrix factorization (PMF 5.0) are still underway and will be reported on in the final report.

Toluene at Delta Dr. and Chamizal Auto-GCs

For several years, the El Paso area has measured the highest concentrations of toluene in Texas. This remains true, despite the decline in toluene concentrations over the past quarter century. Toluene has a relatively high Maximum Incremental Reactivity (MIR) value of 4.0[2].

As noted above, the toluene concentrations in El Paso are still high compared to the balance of the State of Texas. Table 2 shows that over the past four years, the Chamizal station had the highest toluene concentration among Texas auto-GCs in three years and was second one year, and Delta was also highly ranked. The Delta station generally did not have complete years in all four years, however.

[2] See https://ww2.arb.ca.gov/sites/default/files/barcu/regact/2009/mir2009/mir10.pdf

Table 2. Rank among Texas Auto-GCs in annual mean toluene concentration

Station	2019	2019	2020	2020	2021	2021	2022	2022
	Rank	Total TX sites:36	Rank	Total TX sites: 40	Rank	Total TX sites:42	Rank	Total TX sites:44
Chamizal	2	2/36	1	1/40	1	1/42	1	1/44
Delta	3	3/36	2	2/40	2	1/42	5	5/44

Figure 14 shows a time series graph of hourly toluene values from the TCEQ's Chamizal auto-GC from April 1997 through July 2023. The most recent few months have not been validated yet but are unlikely to change. Values appear to be declining over time. Figure 15 shows the annual quarterly average concentrations, which more clearly shows the seasonal pattern for concentrations. Each year, the highest concentrations are in the 4th or 1st quarter, and the lowest are in the 2nd or 3rd quarter. This likely has to do with the generally lower mixing heights in the cooler late autumn and winter months keeping concentrations from diluting into a larger volume of air. Figure 16 fits a second order regression curve to the quarterly data suggesting that decline has flattened out in recent years. The regression explains 65 percent of the variation in quarterly means ($R^2 = 0.65$). The regression parameters are summarized in Table 3.

Figure 17 shows the mean wind-speed-adjusted toluene concentration from the Chamizal station by 10-degree wind direction bin. The original concentrations are adjusted per the Gausian dispersion model by multiplying the coincident wind speed by the concentration and then dividing by the mean wind speed. This helps to better represent the upwind emission sources. A similar graph is shown for the Delta Dr. station in Figure 18. There appears to be a key source upwind of Chamizal to the south; while a clear directional signal at Delta Dr. is not as obvious, and it could be that Delta is affected by a source to the north and a source to the south.

Figure 14. Hourly Toluene at Chamizal, April 1997 to July 2023

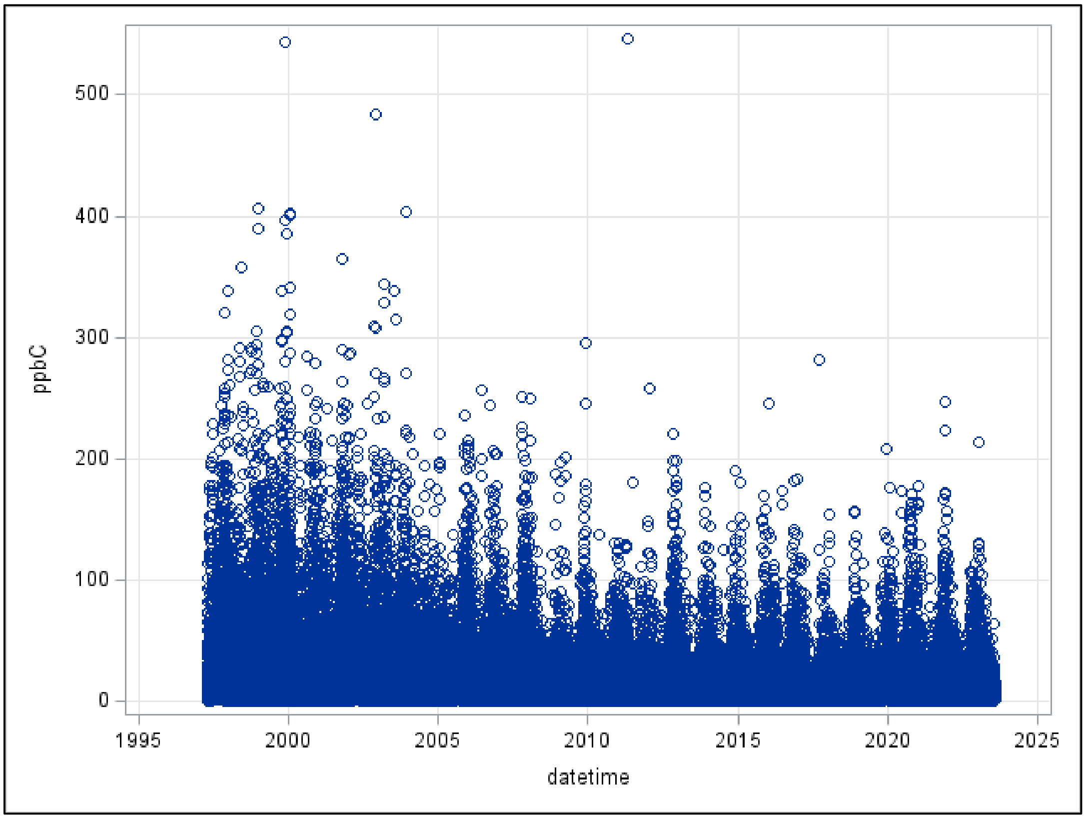


Figure 15. Annual quarterly Toluene at Chamizal, April 1997 to July 2023

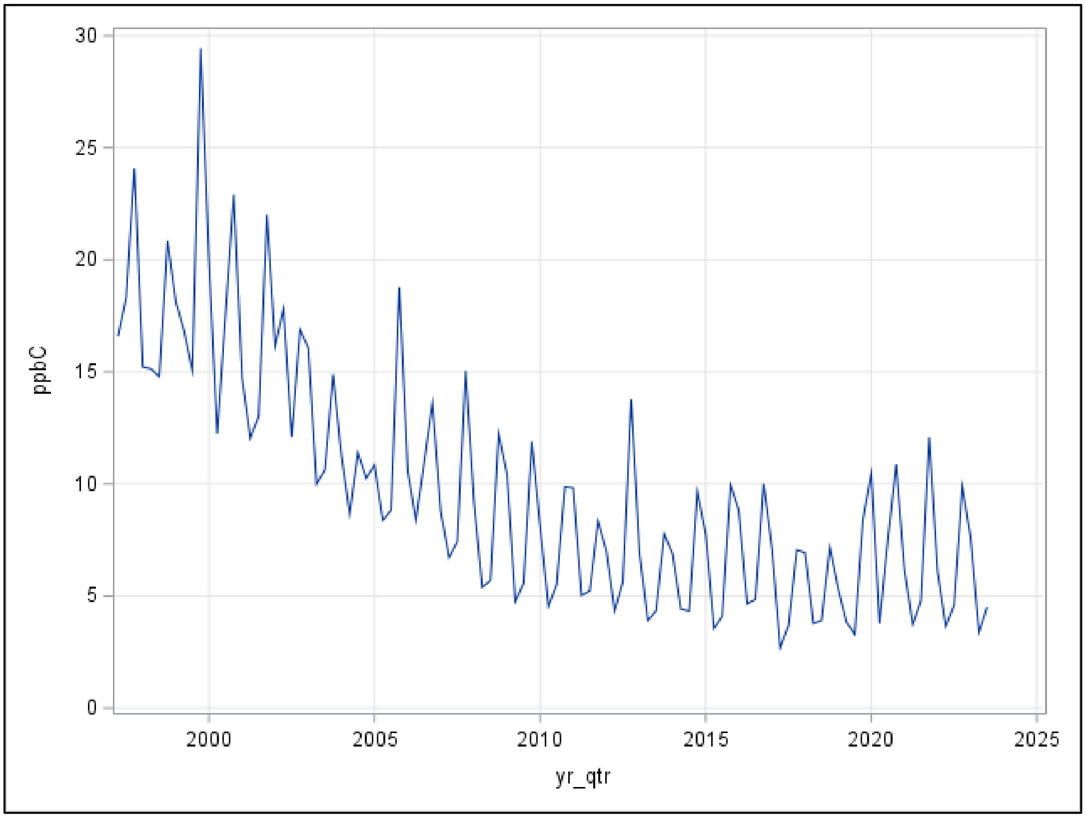


Figure 16. Quadratic regression fit to the quarterly mean toluene concentrations at Chamizal.

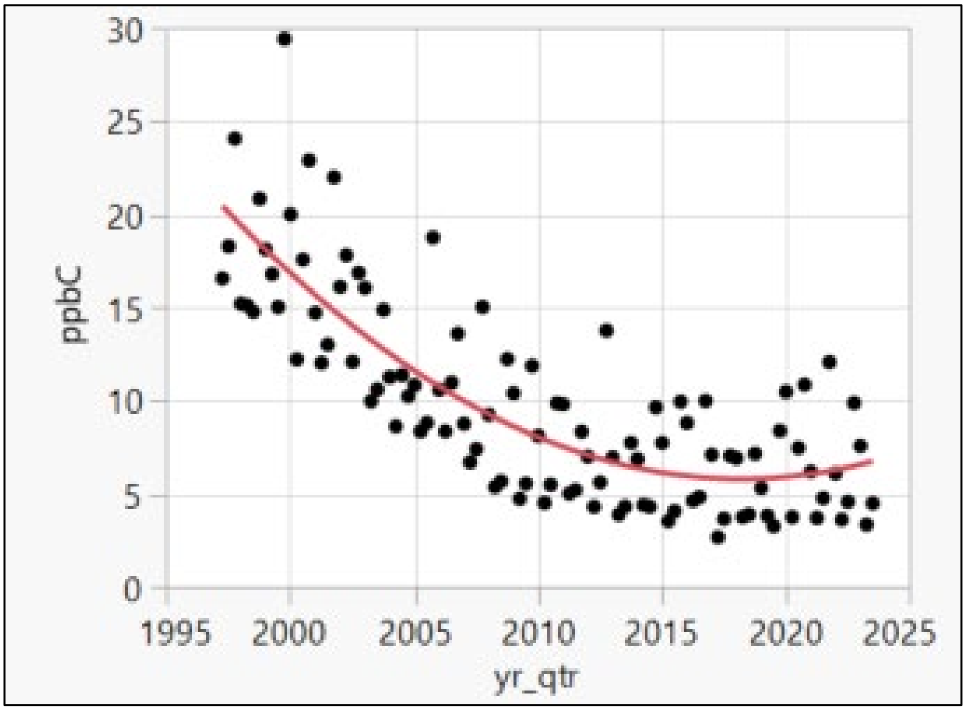


Table 3. Regression fit statistics from the model in Figure 14

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	14.837	0.714	20.78	<.0001*
yrs since 1997	-0.522	0.041	-12.88	<.0001*
(yrs since 1997-13.375)*(yrs since 1997-13.375)	0.033	0.006	5.64	<.0001*

Figure 17. Wind speed-adjusted mean toluene by wind direction at Chamizal, 2018 - 2022

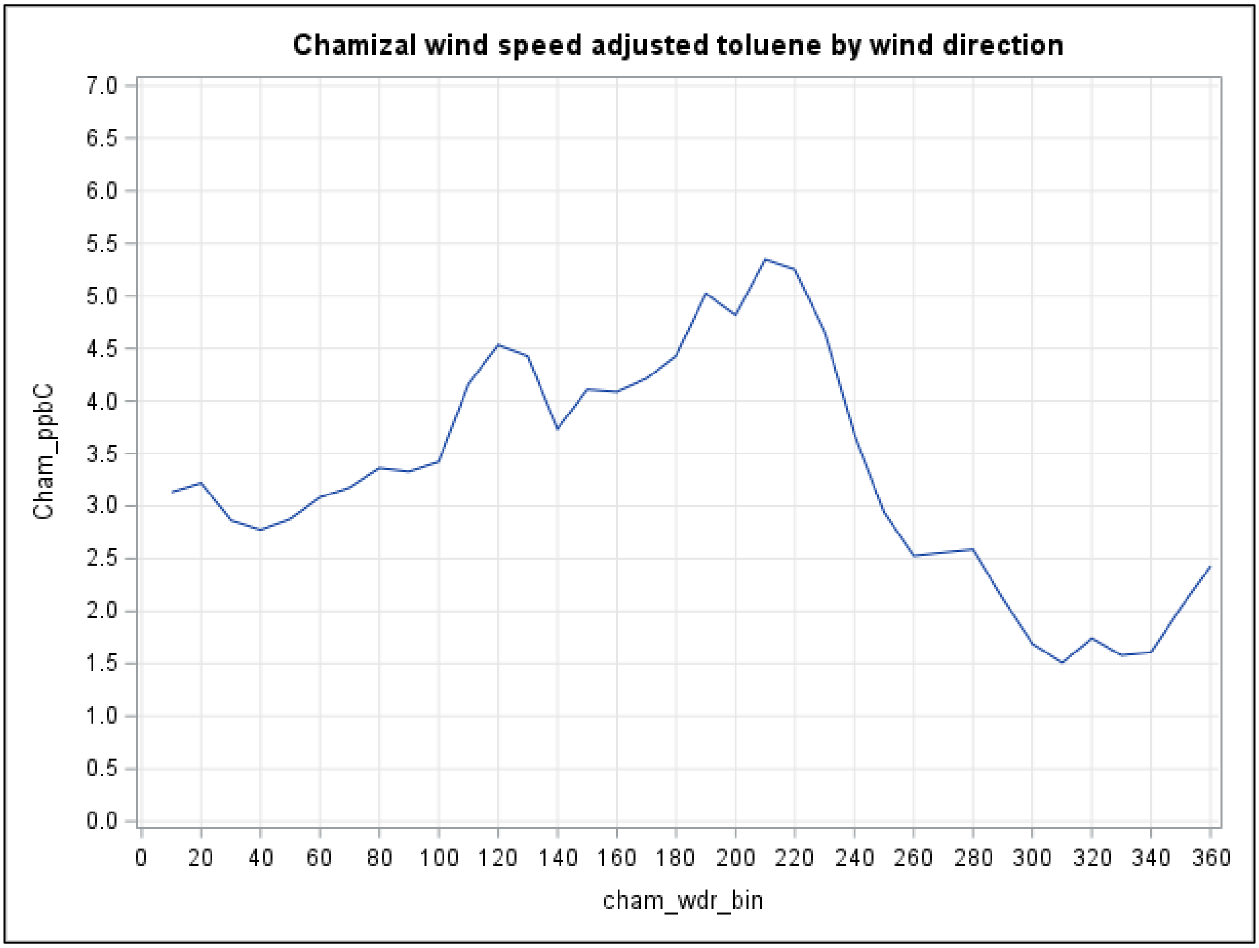
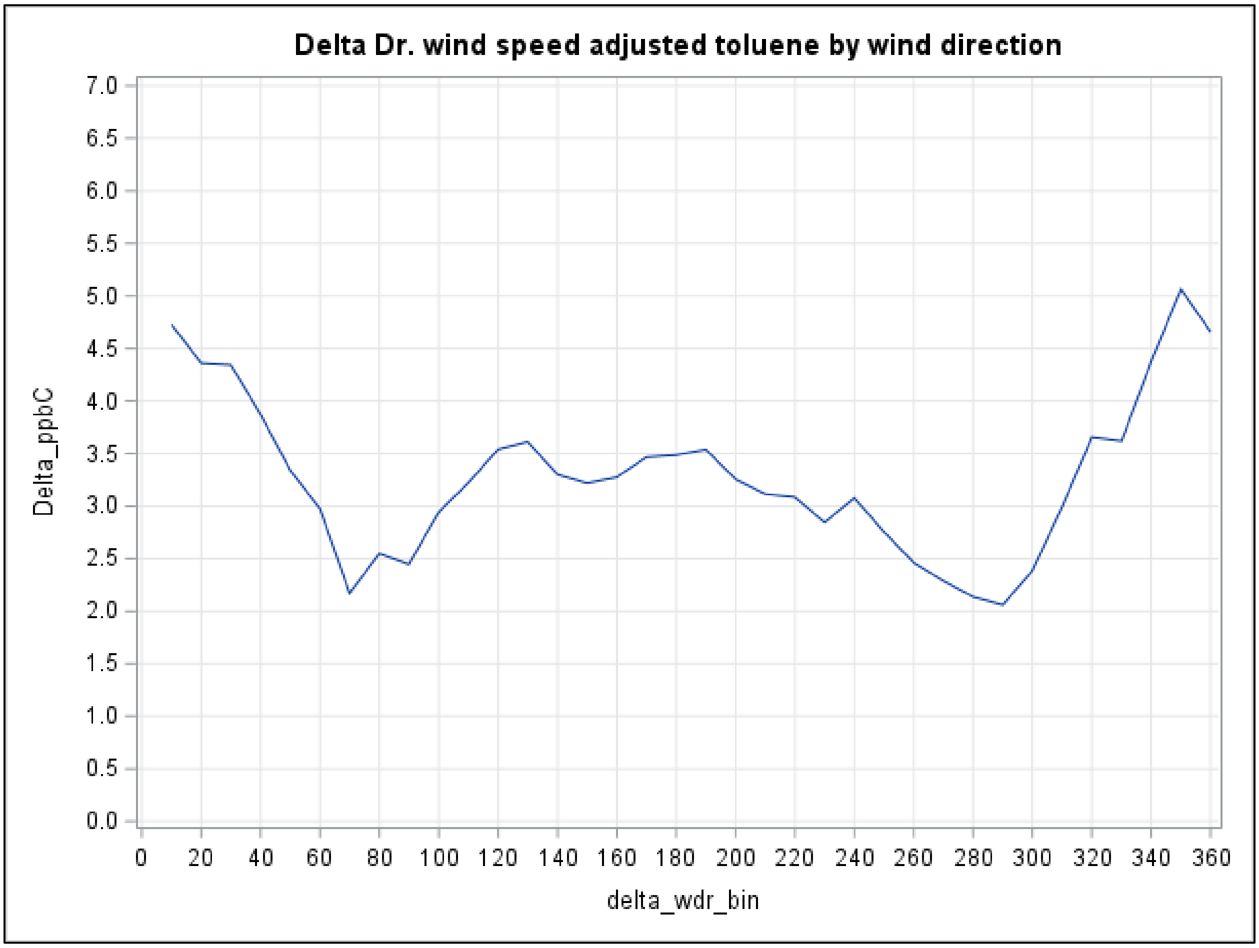


Figure 18. Wind speed-adjusted mean toluene by wind direction at Delta Dr., 2018 - 2022



Toluene in El Paso Canister Samples

Hydrocarbon data recorded for canister samples use parts per billion volume (ppbV) units, as these are used for toxicological evaluations, which are generally done in ppbV units. Canister samples are generally taken for 24 hours on a once every sixth day schedule. Only the Womble station has continuous every sixth day 24-hour samples from 2000 to 2022, and Womble shows a significant decline in concentrations over that period. In Figure 19 through Figure 24 the quarterly mean toluene concentrations from the Community Air Toxics Monitoring Network (CATMN) sites in El Paso. Figure 25 to Figure 36 show graphs resulting from merging wind direction data on the 24 hours from sampling days with the canister toluene values and calculating the mean concentration by wind direction. This is not as accurate approach as with the hourly auto-GC data, but in many cases, given several years of data, some directional conclusions can be drawn. No adjustment is made for wind speed in these graphs. Also in this set of graphs are frequency graphs of the count of wind direction readings in each 10-degree wind direction bin. To a large extent, winds from stations closer to the Rio Grande / Rio Bravo are channelized to follow the river's course, so most winds are either from upstream or downstream directions. It appears that the Chamizal canister directional graph in Figure 27 is very similar to the Chamizal auto-GC directional graph in Figure 17. In addition, the UTEP canister directional graph in Figure 25 appears to point to the south.

Figure 19. Quarterly mean toluene from UTEP canister samples

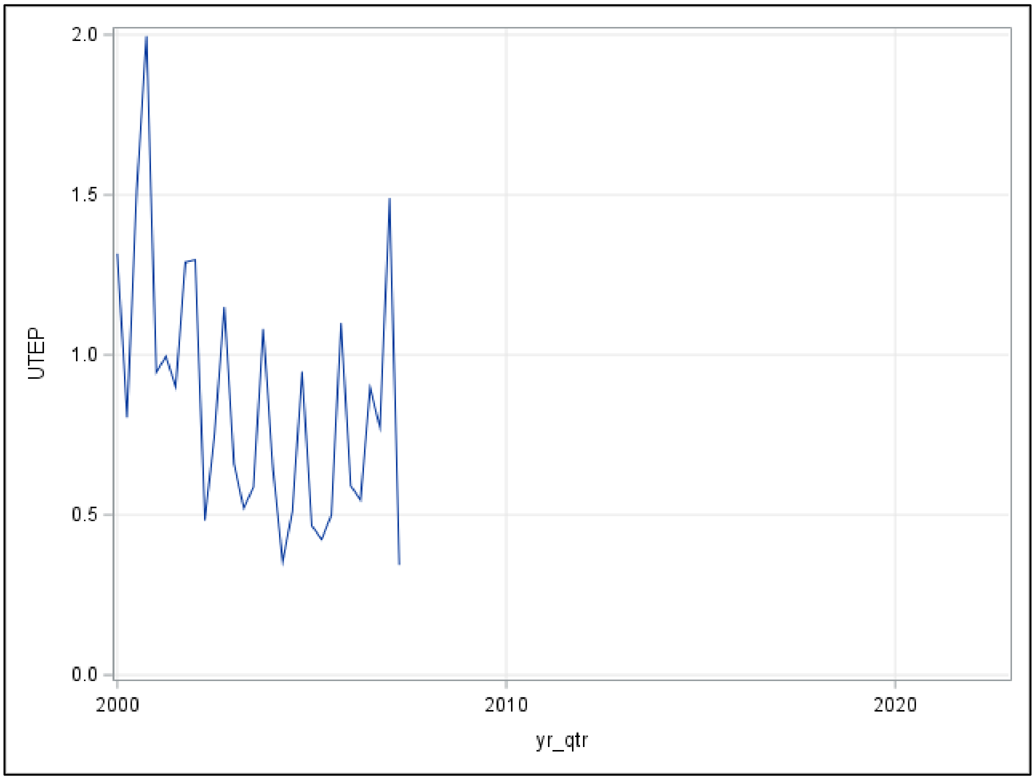


Figure 20. Quarterly mean toluene from Chamizal canister samples

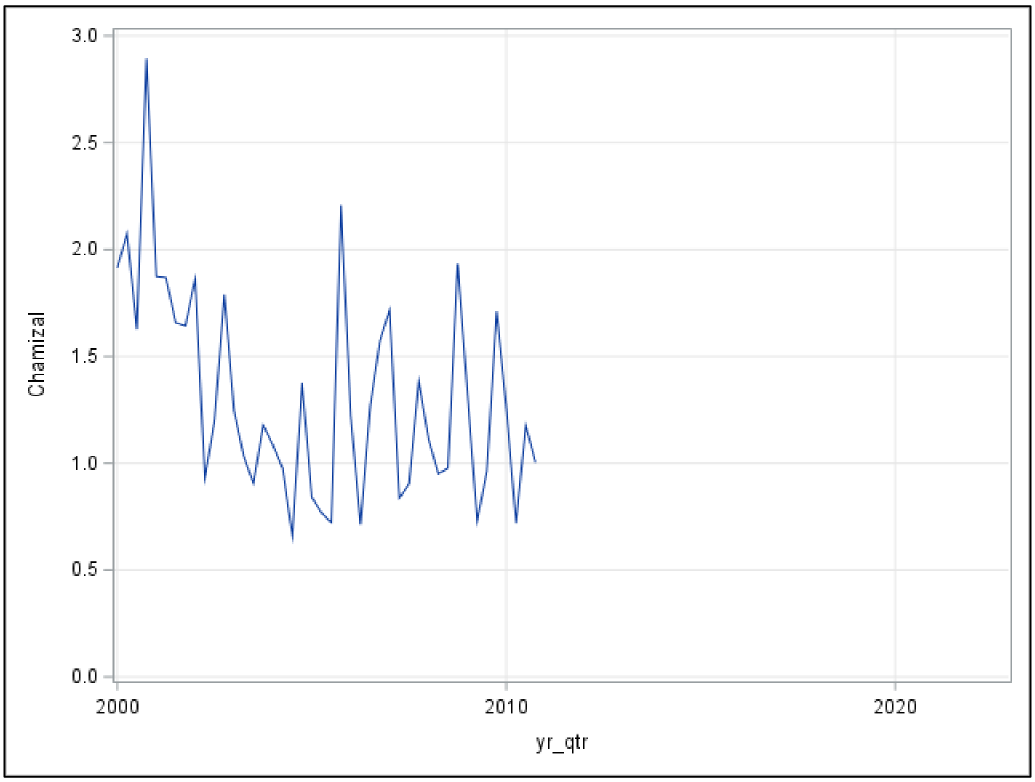


Figure 21. Quarterly mean toluene from Womble canister samples

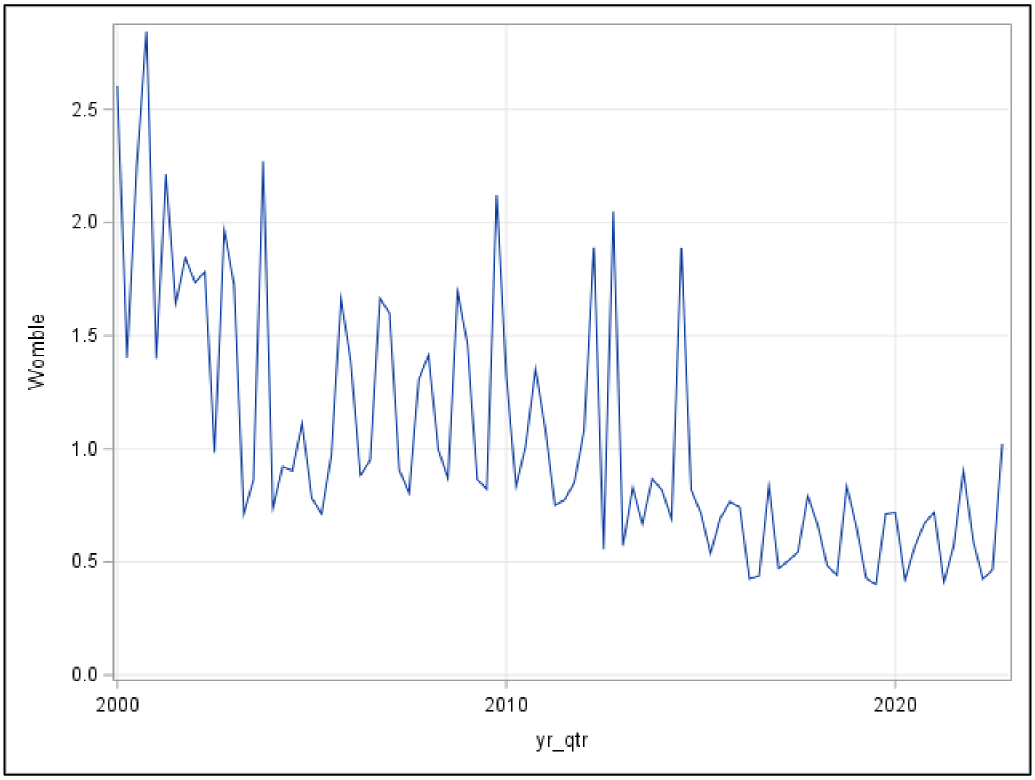


Figure 22. Quarterly mean toluene from Sun Metro canister samples

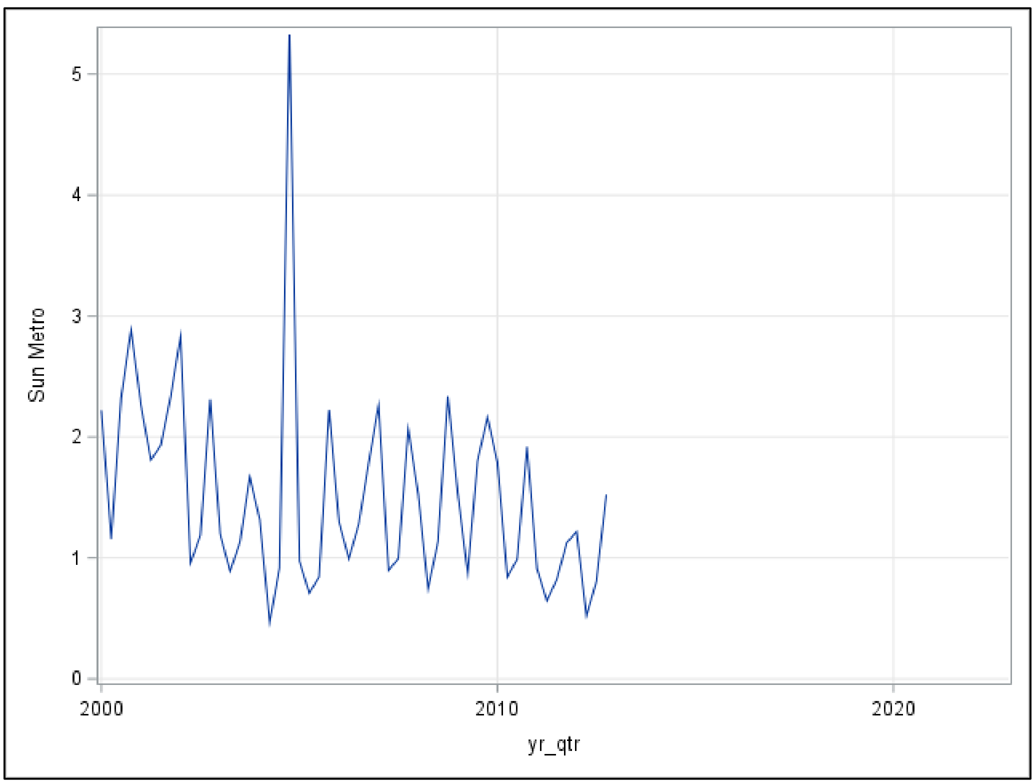


Figure 23. Quarterly mean toluene from Ascarate canister samples (note missing data)

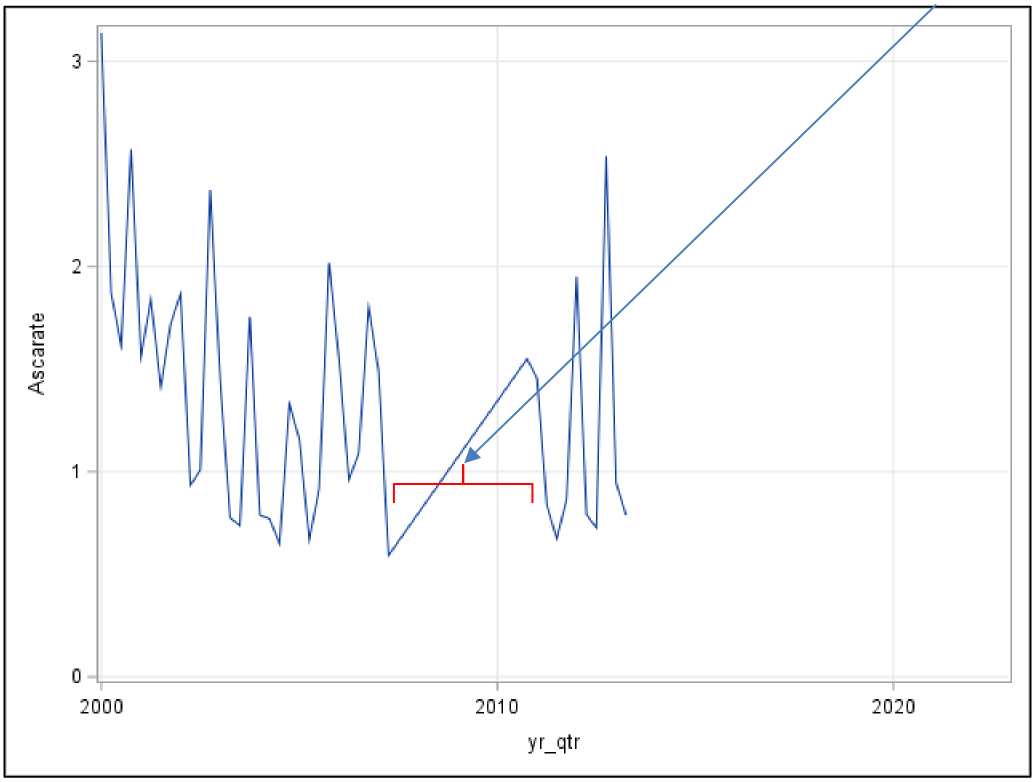


Figure 24. Quarterly mean toluene from Socorro Hueco canister samples

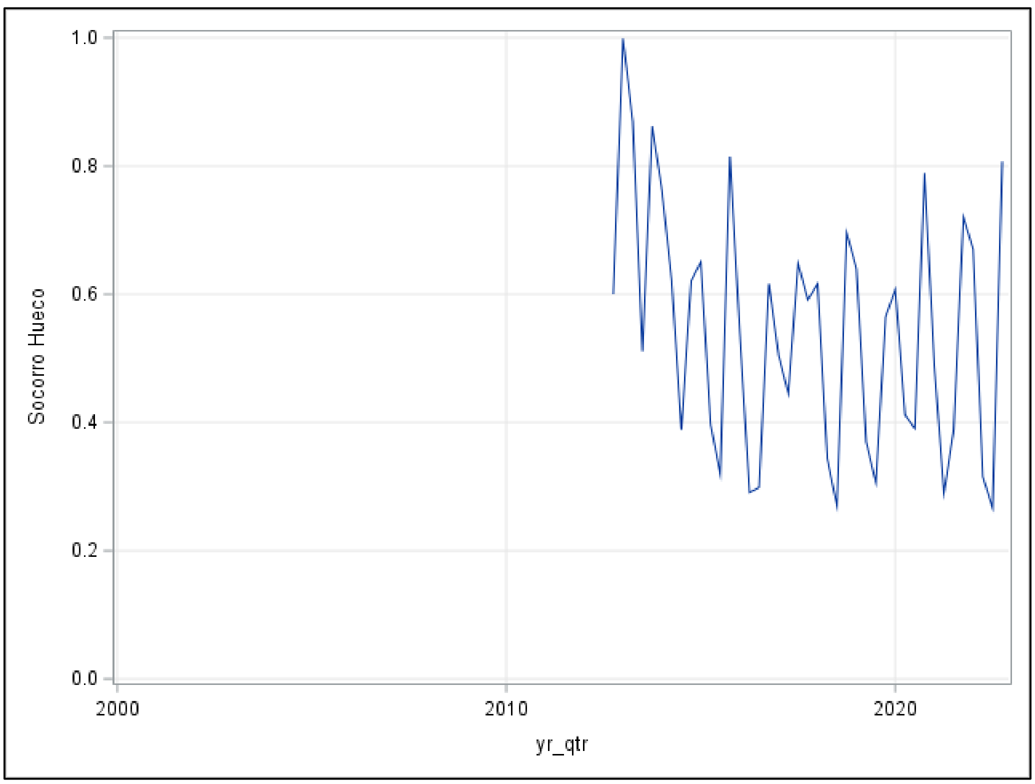


Figure 25. UTEP mean toluene in canister samples, ppbV units, by wind direction

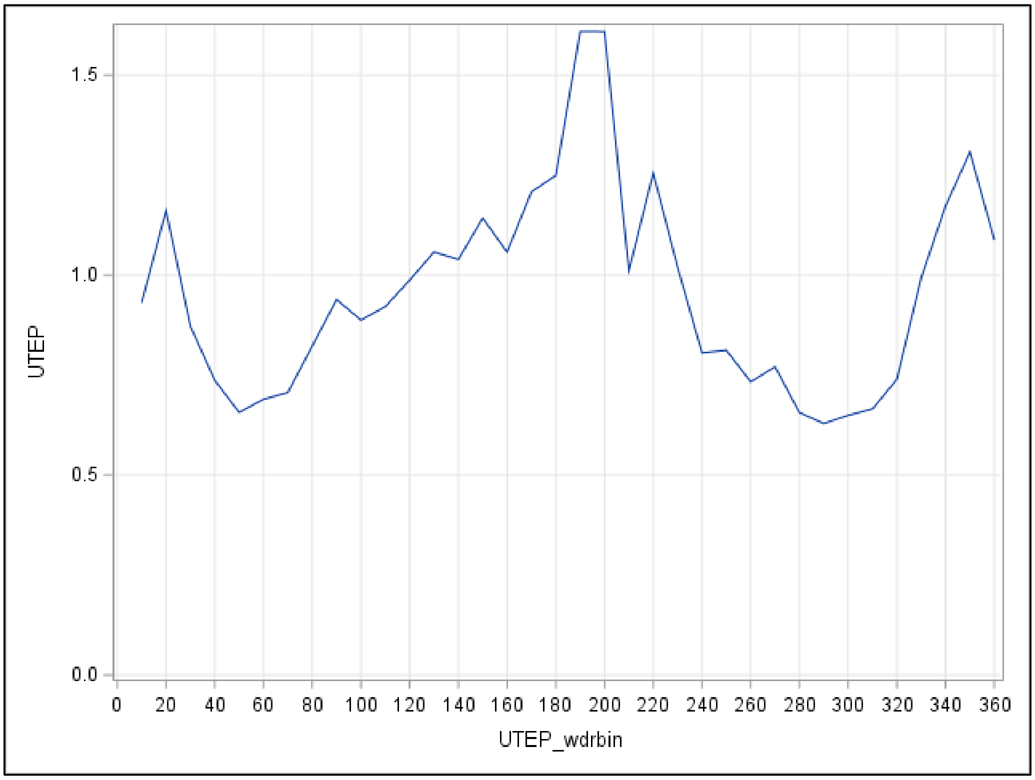


Figure 26. Wind direction frequency at UTEP

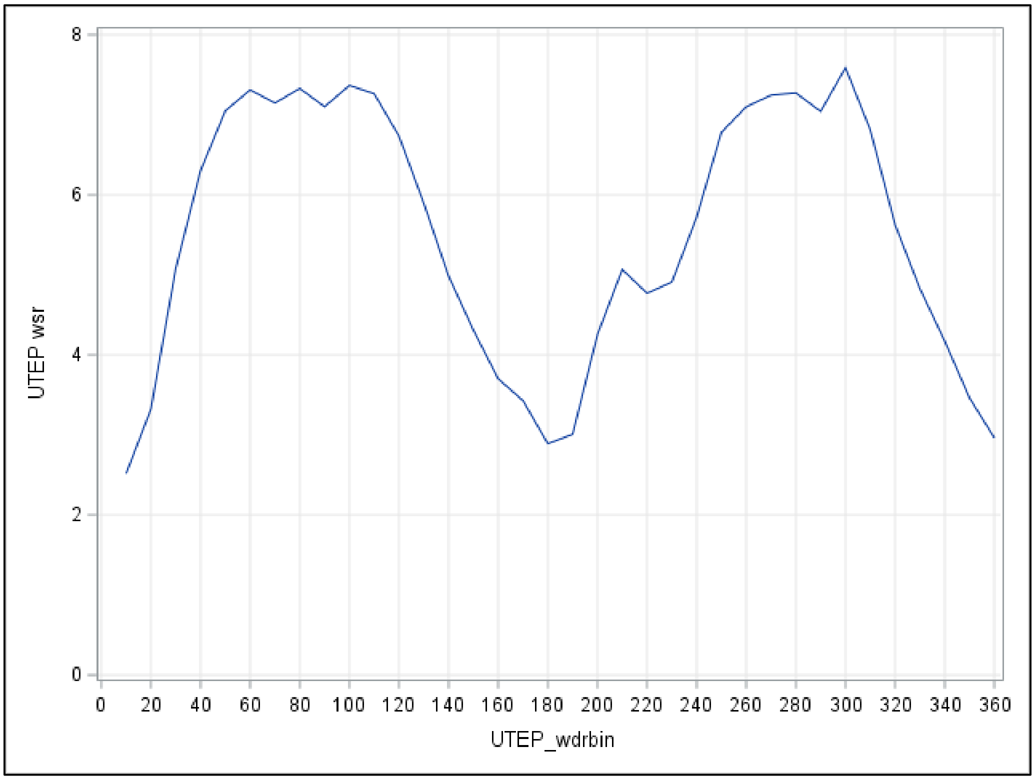


Figure 27. Chamizal mean toluene in canister samples, ppbV units, by wind direction

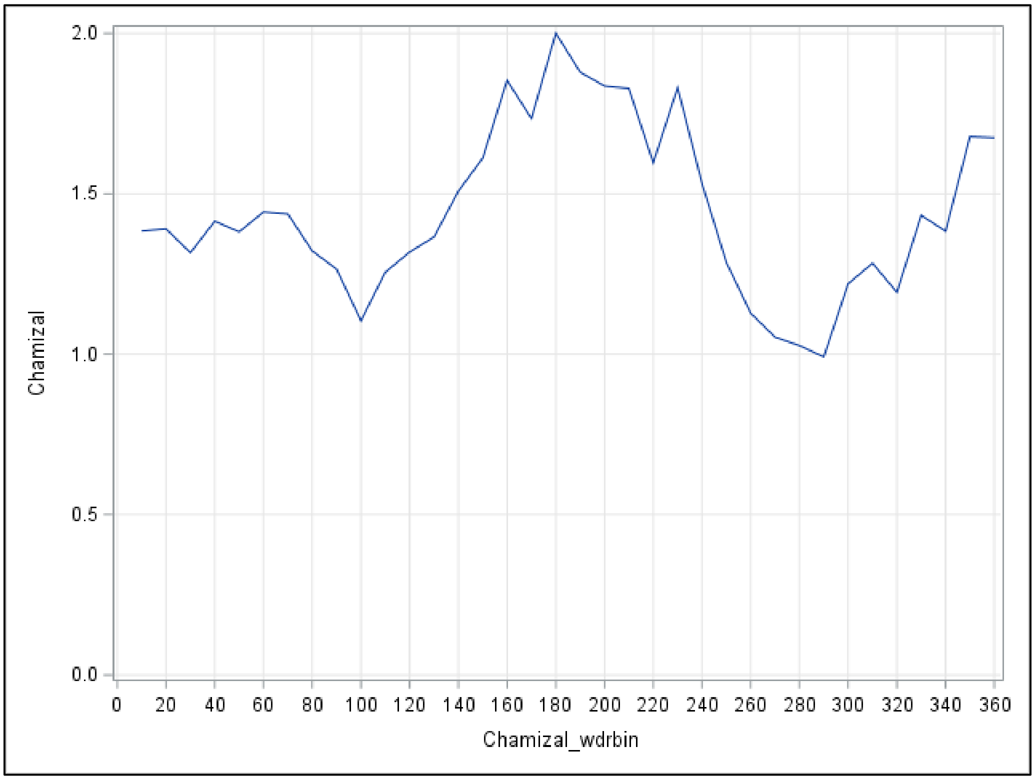


Figure 28. Wind direction frequency at Chamizal

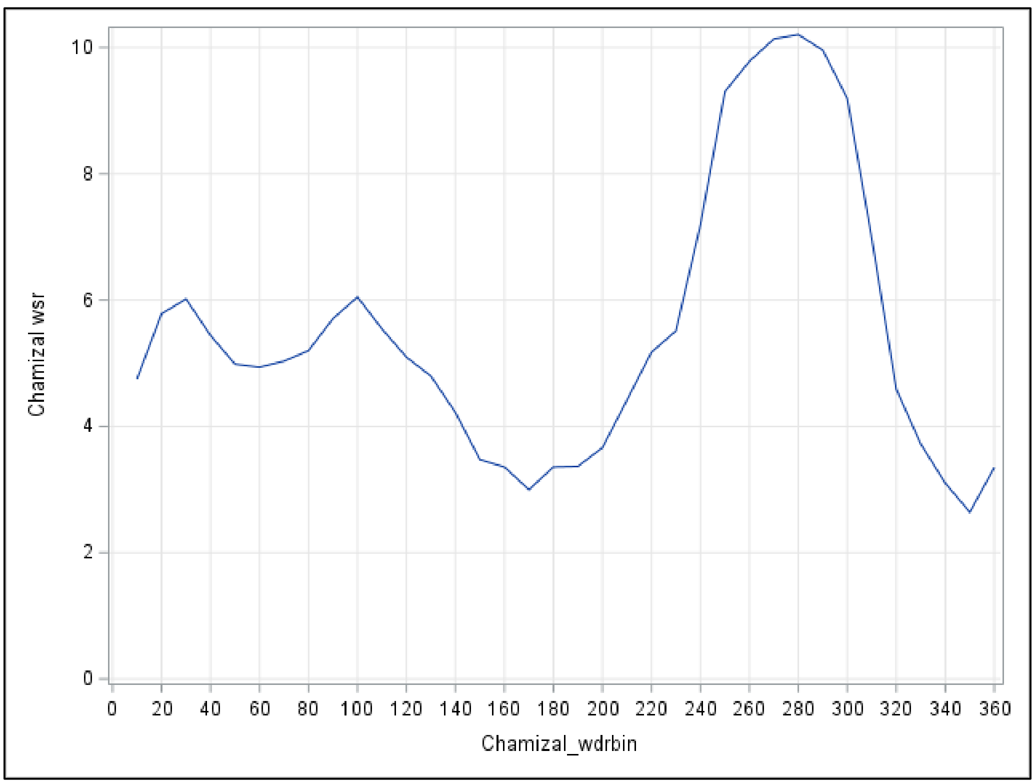


Figure 29. Womble mean toluene in canister samples, ppbV units, by wind direction

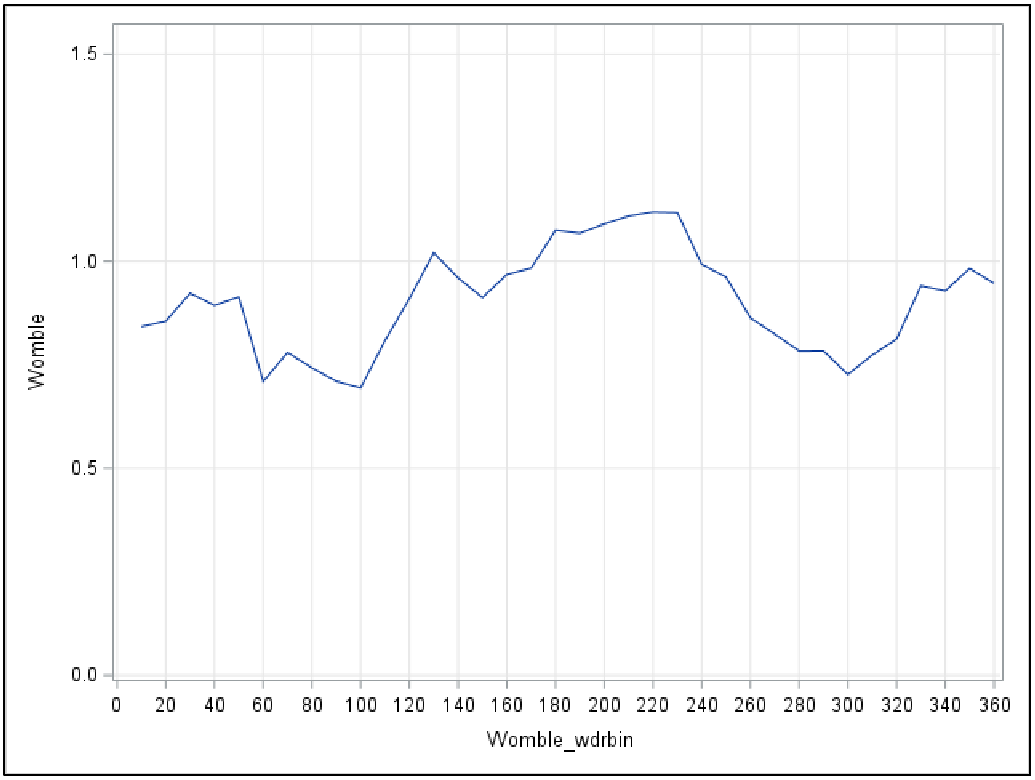


Figure 30. Wind direction frequency at Womble

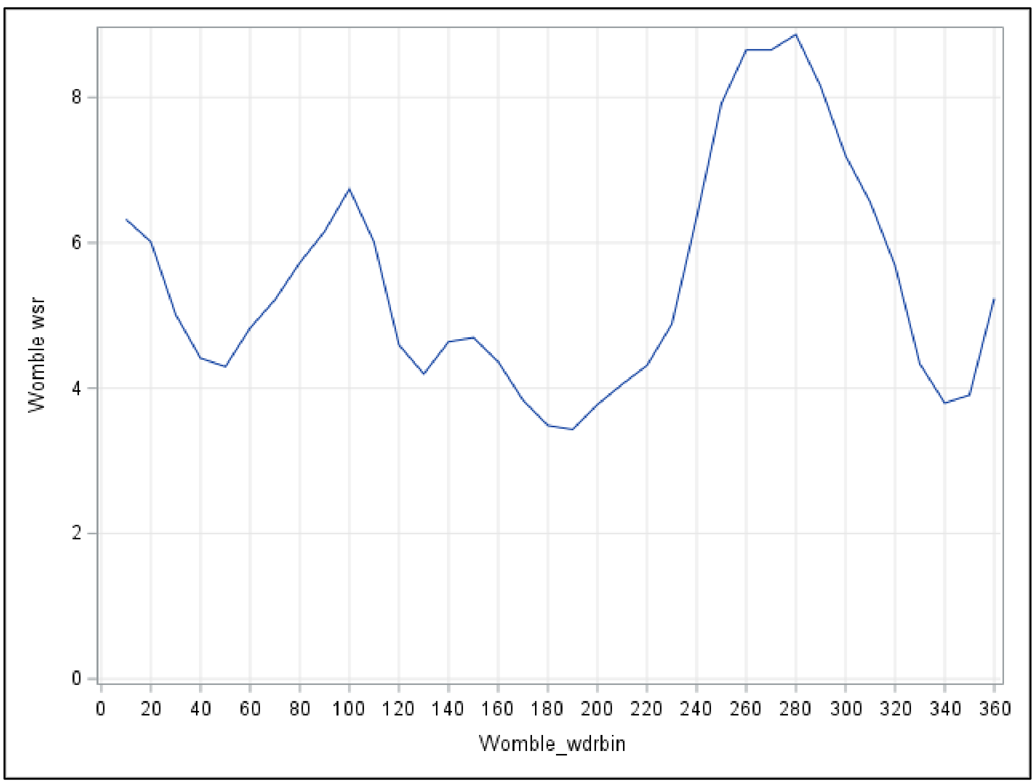


Figure 31. Sun Metro mean toluene in canister samples, ppbV units, by wind direction

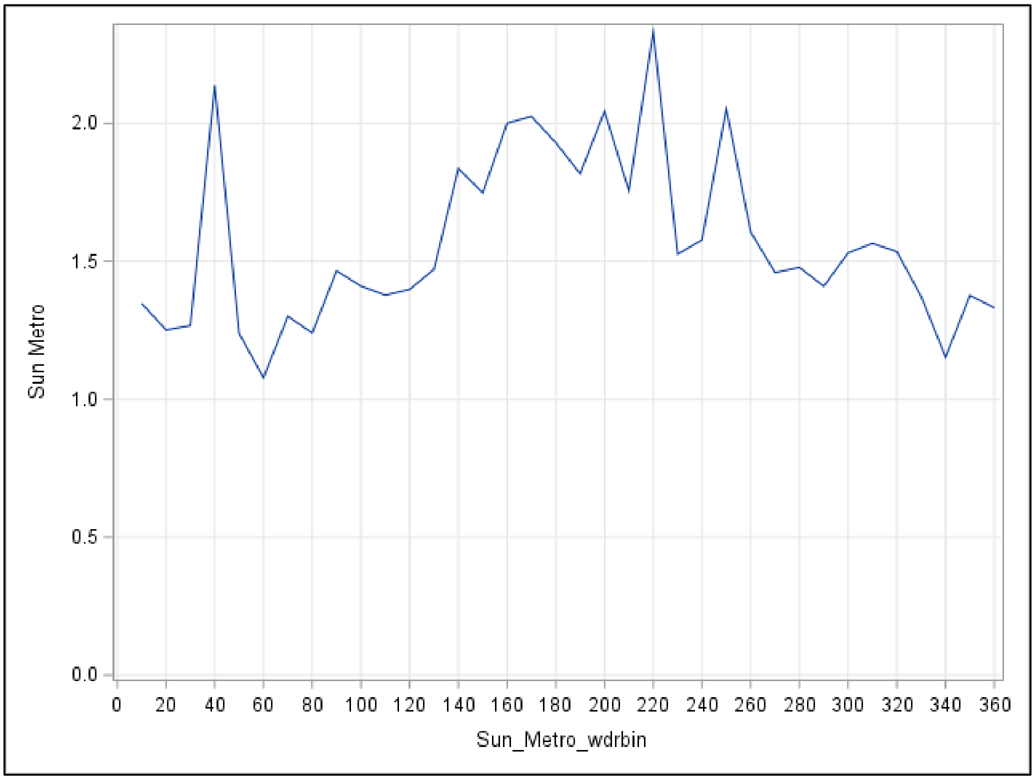


Figure 32. Wind direction frequency at Sun Metro

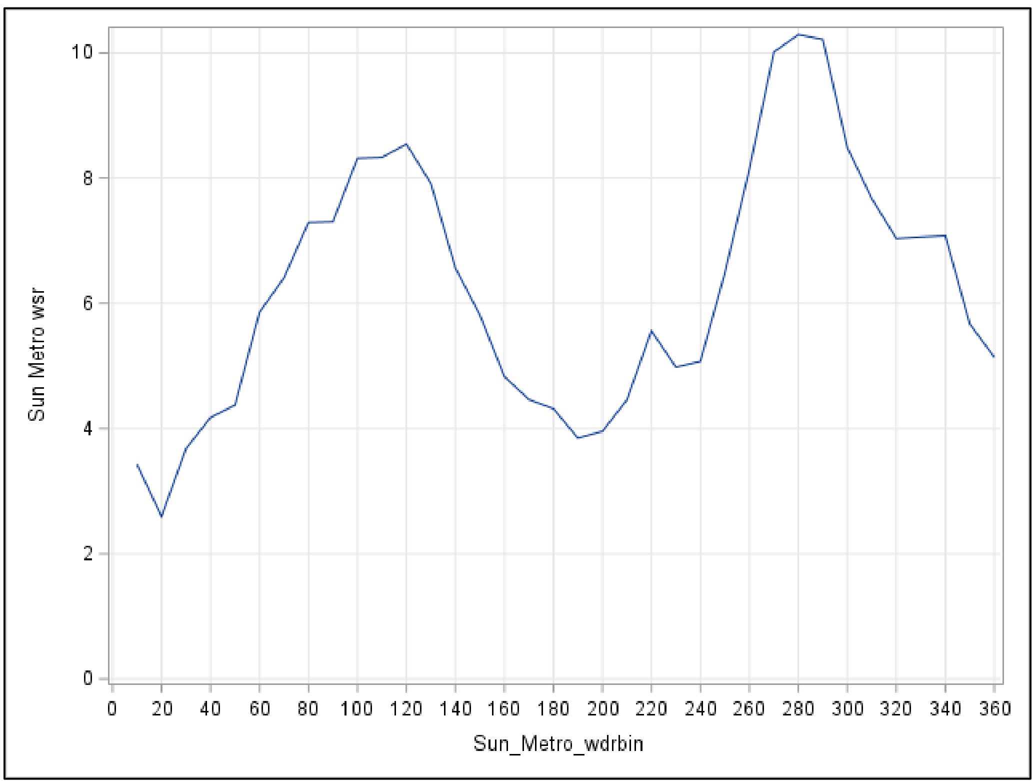


Figure 33. Ascarate mean toluene in canister samples, ppbV units, by wind direction

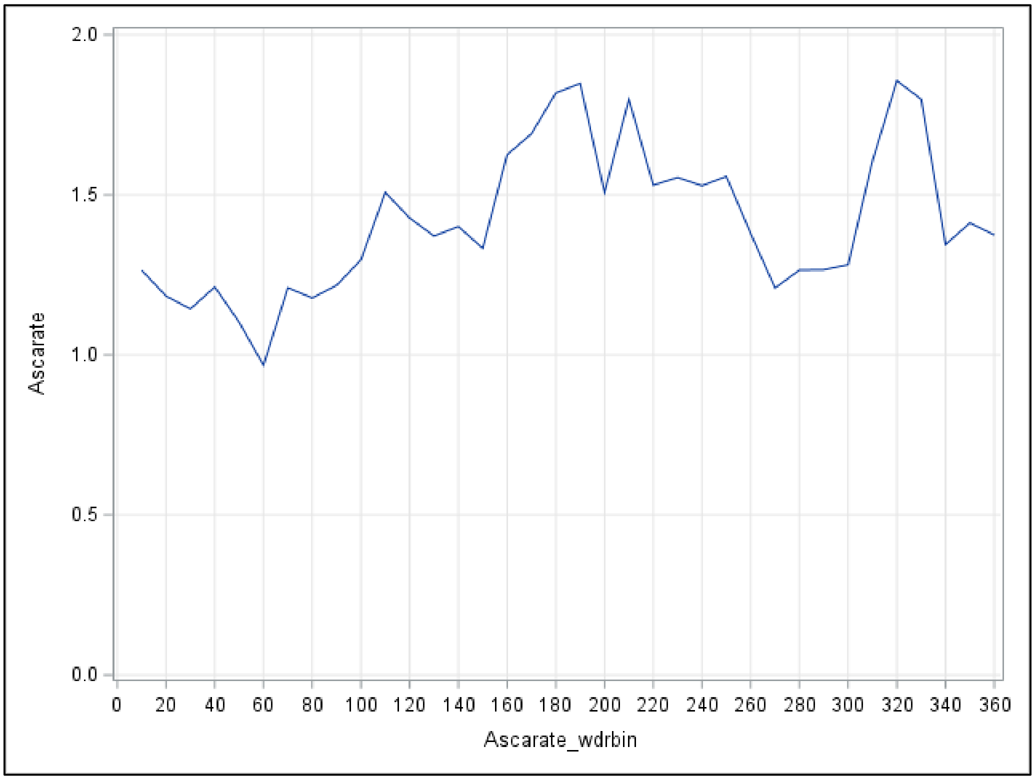


Figure 34. Wind direction frequency at Ascarate

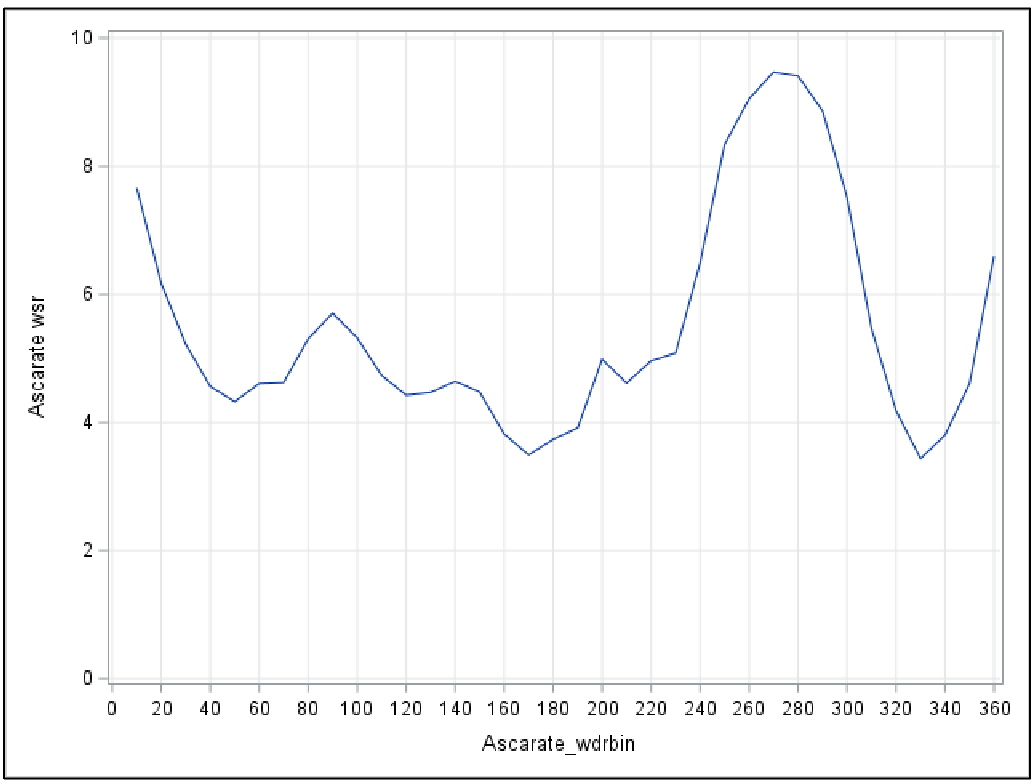


Figure 35. Socorro Hueco mean toluene in canister samples, ppbV units, by wind direction

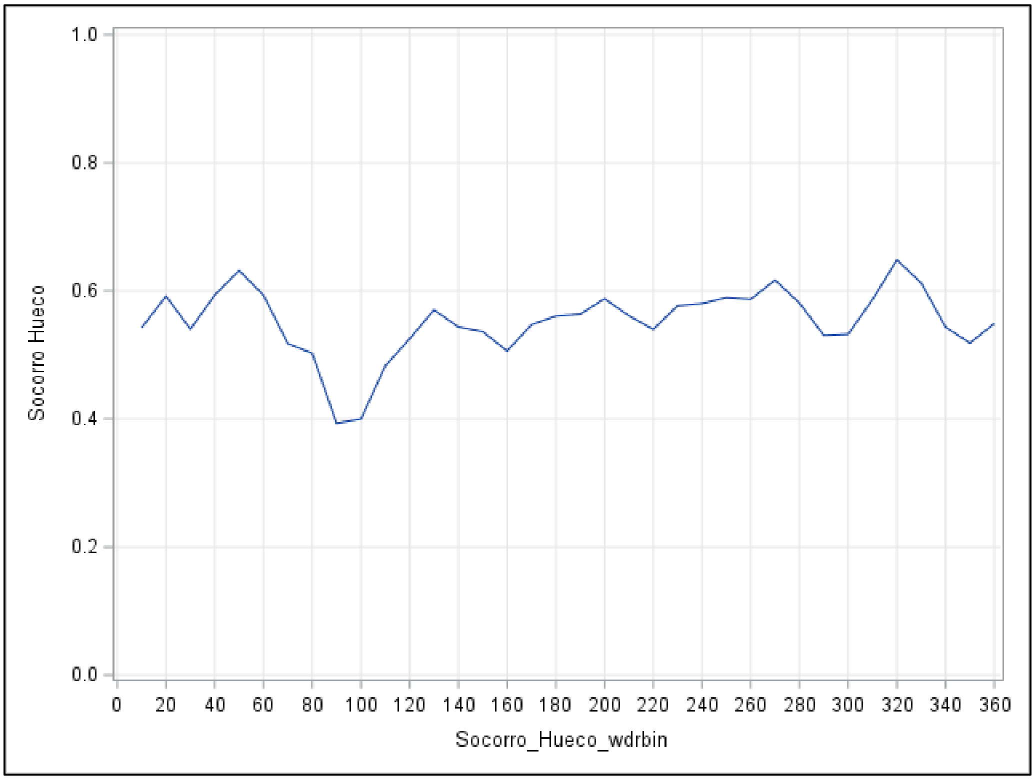
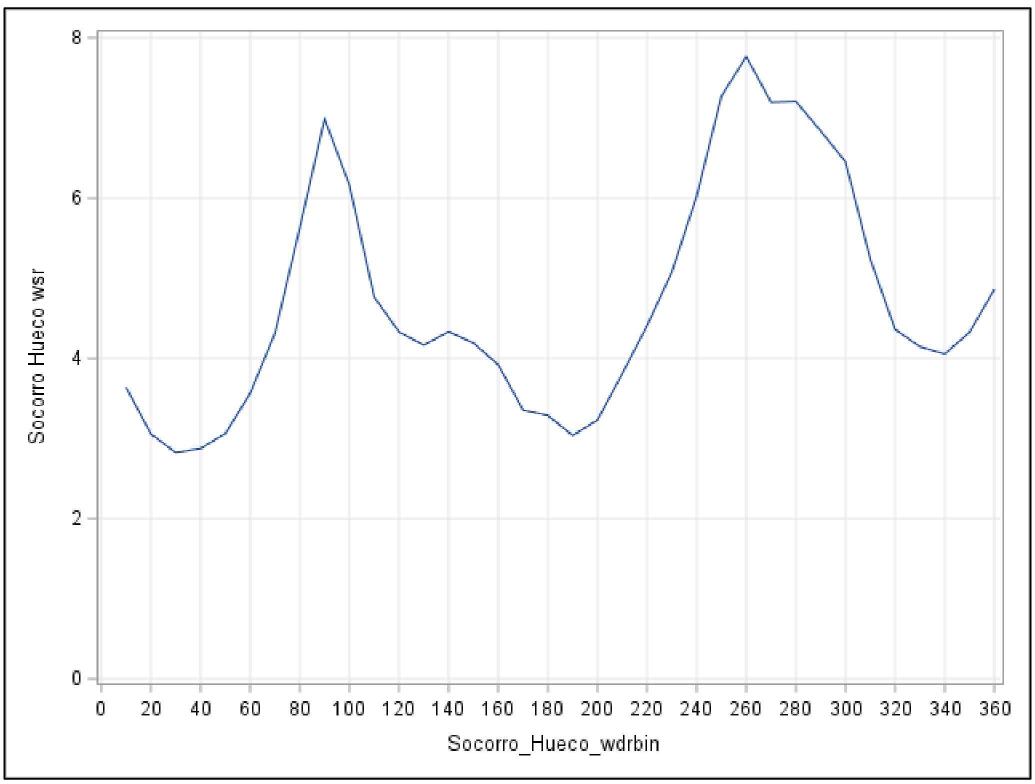


Figure 36. Wind direction frequency at Socorro Hueco



VOC to NOx Ratios

From Seinfeld and Pandis, 2006[3], pages 235-236:

"The hydroxyl radical is the key reactive species in the chemistry of ozone formation. The VOC—OH reaction initiates the oxidation sequence. There is competition between VOCs and NOx for the OH radical. At a high ratio of VOC to NOx concentration, OH will react mainly with VOCs; at a low ratio, the NOx reaction can dominate. Hydroxyl reacts with VOC and NO_2 at an equal rate when the VOC:NO_2 concentration ratio is a certain value; this value depends on the particular VOC or mix of VOCs present, as the OH rate constants of VOCs differ for each VOC species…. When the VOC:NO_2 concentration ratio is approximately 5.5 to 1, with VOC concentration expressed on a carbon atom basis, the rates of reaction of VOC and NO_2 with OH are equal. If the VOC:NO_2 ratio is less than 5.5 to 1, reaction of OH with NO_2 predominates over reaction of OH with VOCs. The OH—NO_2 reaction removes OH radical from the active VOC oxidation cycle, retarding the further production on O_3. On the other hand, when the ratio exceeds 5.5 to 1, OH reacts preferentially with VOCs. At a minimum, no new radicals are produced or destroyed; however, in actuality, photolysis of intermediate products generated by the OH—VOC reactions generates new radicals, accelerating O_3 production."

In 2023 through early August, hourly O_3 exceeded 70 ppb at the three O_3 stations closest to the Delta Dr. station on 16 days. These stations are Ivanhoe CAMS 414, Chamizal CAMS 41, and Ascarate Park CAMS 37. On these 16 days, there were 52 hours during which at least one station had a value of 70 ppb or above. At the Delta Dr. station, the mean VOC:NO_2 in 2023 during those hours was 12.0 and ranged from 5.8 to 24.4.

On the 16 days, taking the earliest hour on which one of the three stations had a value of 70 or higher, Table 4 shows the VOC to NO_2 ratios at Delta Dr. for one through six hours earlier. The fairly large difference between the median and mean rows is in part explained by the large values in the maximum row, which are attributable to one date, July 16, 2023, when the peak O_3 occurred late in the afternoon at 16:00 MST. On the other 15 days, the earliest O_3 value at or above 70 ppb ranges from 11:00 to 14:00 MST. Table 5 contains a modified 2023 summary, for 15 days excluding July 16. The point is that in the hours preceding elevated O_3 in central El Paso, it appears the VOC to NO_2 ratio suggests mixed VOC/NO_2 limitation, tending on the VOC limited direction.

Table 4. VOC to NO_2 ratios at Delta Dr. for one to six hours before a 70 ppb or higher nearby O_3 measurement

16 days	1hr Earlier	2hr Earlier	3hr Earlier	4hr Earlier	5hr Earlier	6hr Earlier
Mean	11.59	10.35	9.60	9.63	10.02	10.49
Median	9.17	8.11	7.46	6.61	6.21	5.42
Min	3.67	3.41	2.74	2.30	2.58	2.40
Max	25.28	31.60	37.66	51.87	60.79	71.66

[3] Seinfeld, J.H. and S.N. Pandis, Atmospheric Chemistry and Physics, From Air Pollution to Climate Change, John Wiley & Sons, 2006.

Table 5. VOC to NO_2 ratios at Delta Dr. for one to six hours before a 70 ppb or higher nearby O_3 measurement excluding July 16, 2023

15 days	1hr Earlier	2hr Earlier	3hr Earlier	4hr Earlier	5hr Earlier	6hr Earlier
Mean	10.63	8.83	7.59	6.81	6.64	6.41
Median	8.95	7.86	6.62	6.48	5.65	5.26
Min	3.67	3.41	2.74	2.30	2.58	2.40
Max	25.28	23.10	14.59	15.50	16.11	16.94

4. Conclusions

This draft final report is being submitted on August 15, 2023, and a final report will be submitted on August 31, 2023. Among the findings from this project are the following points:

- El Paso has seen significant improvement in air quality over the past few decades.
- A multivariate analysis of hydrocarbon data from the Delta Dr. station suggests five to 6 factors affect the site, and this work is ongoing.
- Among continuing air quality issues, toluene levels are still among the highest in Texas, despite a strong downward trend that appears to have flattened out.
- Ozone levels still show noncompliance with the 2005 EPA NAAQS.
- An examination of VOC to NO2 ratios in 2023 suggest that El Paso is mixed in terms of limitation, leaning to being VOC limited.