Final Report, July 31, 2022, rev. 2
WORK ORDER UNDER THE CONTRACT BETWEEN TCEQ AND CONTRACTOR:
The University of Texas at Austin

Project Number 582-20-12731-008

Oxygenated Volatile Organic Compound (OVOC) Sampling for Biomass Burning Tracers Project

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Contents

1. Background

The purpose of this project has been to assess and evaluate the performance of a monitoring system designed to sample Oxygenated Volatile Organic Compounds (OVOCs) as indicators of biomass burning and to compare the measurements made by this system to independent measurements taken using aerosol absorption angstrom exponents.

On October 1, 2015, the U.S. Environmental Protection Agency (EPA) published a rule that

lowered the Ozone (O_3) National Ambient Air Quality Standard (NAAQS) to 0.070 parts per million (ppm) over an eight-hour average. With a more stringent standard, transport from areas outside the immediate airshed will account for a higher percentage of O_3 measured at regulatory monitors in Texas. States that can demonstrate a causal relationship between exceptional events such as wildfires or stratospheric intrusions for individual O_3 exceedances can have those exceedance days excluded from the NAAQS calculation. Air agencies must provide EPA with a technical demonstration that show a clear causal relationship between the event (e.g., wildfire, fireworks) and the monitored values. As exceptional events become more relevant, TCEQ staff have sought to develop new tools that can provide evidence of the required causal relationship.

Volatile organic compounds (VOCs) and oxygenated volatile organic compounds (OVOCs) contribute to the formation of O_3. Smoke is often present in the Western U.S. and can significantly influence ozone concentrations. However, proving the presence of transported smoke has been one of the biggest challenges in exceptional event demonstrations. The strongest evidence for smoke comes from:

- Satellite data showing fires and/or smoke transport,
- Trajectories linking fire locations with urban receptor,
- Surface observations of specific smoke tracers.

However, most urban areas do not have the means to detect specific smoke tracers.

The TCEQ is studying the usefulness of a new monitoring instrument developed by Dr. Dan Jaffe, at the University of Washington-Bothell (UW). Dr. Jaffe's instrument works by sampling ambient air for VOCs and OVOCs (e.g., Acrolein, 1,3-Cyclopentadiene, Acetonitrile, Furan, 2,3-Butanedione, Methacrolein, 2,5-Dimethyl furan, and Furfural) that are known to be indicators of biomass burning (BB). If effective, this instrument would provide important evidence that air quality at a receptor monitor was affected by an exceptional event. The system is experimental but has been successfully used in another application in 2019. These data can be used to better address the role of smoke in O_3 formation. Dr. Jaffe's instrument was installed to take measurements at the Houston Regional Monitor (HRM) Network site #3 in 2020 and 2021.

2. Summary of Recent Activities

The due dates for the completion for the project are:

- Final Report by July 31, 2022
- Completion date for the PGA is August 31, 2022.

Auxiliary data and OVOC/TAP comparison report were provided earlier in May 2022, although data analyses are ongoing. This is the final report on the project and contains summaries of the data and data collection activities over the project period.

UT was notified on Friday July 15, 2022, that all invoices need to be submitted by Friday July 22, 2022.

A Revised Final Report adding text at the end of Section 3.1 and Section 3.2, a graph in Section 3.5, tables in Section 3.6, and a new Section 3.7 was submitted on August 15, 2022.

3. Data Analyses

3.1 Project History

Significant problems were created during the COVID 19 pandemic, during which travel and working in teams were restricted. This prevented some maintenance and repairs on field and lab equipment, and the delays also led to turnover in personnel as graduate student researchers graduated. As pandemic conditions improved, more progress was made on sampling and analyses. On December 29, 2021, Dr. Jaffe reported on his group's progress:

> As I mentioned earlier, we now have all of our samples from this past summer analyzed by gas-chromatography – mass-spectrometry (GC-MS). This is a big milestone.
>
> The data will come in two parts. Set 1 (today attached) and Set 2, sometime in next two weeks. I consider Set 1 to be "near final" (Aug 6-Sept 10, 2021). I don't expect any changes, but it is always possible we will find a bug.
>
> As I mentioned, we have the analysis done on all samples, but are still doing integrations and quality control (QC) on Set 2 and we should be done very soon. Set 2 covers Sept 11-Oct 1, 2021.
>
> One issue that we had with Set 1 is that unfortunately Acetonitrile was not resolved, so we have only quantified Benzene, Toluene, Iso-pentane, and N-pentane from the GC-MS data in that set. This issue was fixed in Set 2 and so we will have the Acetonitrile in that group. Nonetheless, we expect the Benzene/Toluene and Isopentane/N-pentane ratios should still give us info on any biomass burning sources that might have been present.
>
> Once we have the dataset finalized, we will begin to look at the data for more interpretation.

As it turned out, although the original plan was to quantify furan, furfural, 2,5 dimethyl furan, methacrolein, acrolein, 2-butanone, 2,3-butanedione – the Group II oxygenated VOCs listed in the QAPP -- this was impractical owing to a larger number of VOCs and higher concentration of industrial VOCs in the area around HRM3. Peak separation and species identification were more difficult compared to earlier work. Prof. Jaffe stated by email on Aug. 12, 2020:

> It is possible with additional time and effort the Group II compounds could be identified and quantified in chromatograms from samples collected in Houston.

Furthermore, again because of the higher concentrations of VOCs around HRM3, concentrations for benzene, toluene, iso-pentane, and n-pentane were related to local sources to the extent that transported concentrations related to fires were difficult to discern, with the possible exception of one sample described in Section 3.5.

3.2 Ozone and $PM_{2.5}$ in the Houston Region, 2021

Ozone concentrations in the Houston Region historically have been elevated in the early summer and late summer/early autumn, with a lull in mid-summer owing to higher speed winds and greater dispersion of precursors. During 2021, this pattern was also evident. A list of the top four 8-hour average days for the Houston Region stations in 2021 appear in Table 1, with dates in the

month of September in red coloration. Of the four highest 8-hour O_3 days in the table, not all are actual exceedances of the National Ambient Air Quality Standard (NAAQS), and not all actual NAAQS exceedances in the Region are in the four highest 8-hour O_3 table. An illustration of the distribution of actual O_3 exceedance days by month in 2021 appears in Figure 1. A count of the number of monitor-exceedances among the 42 regulatory and non-regulatory stations in the Houston Region appears in Figure 2. Figure 3 shows the distribution by month for the days in the top four high ozone days in the Region in 2021. These three figures illustrate the late spring/early summer peak in high ozone days and late summer/early autumn peak in exceedances.

Figure 1. Count of the number of days on which one or more stations had an O_3 NAAQS exceedance in 2021

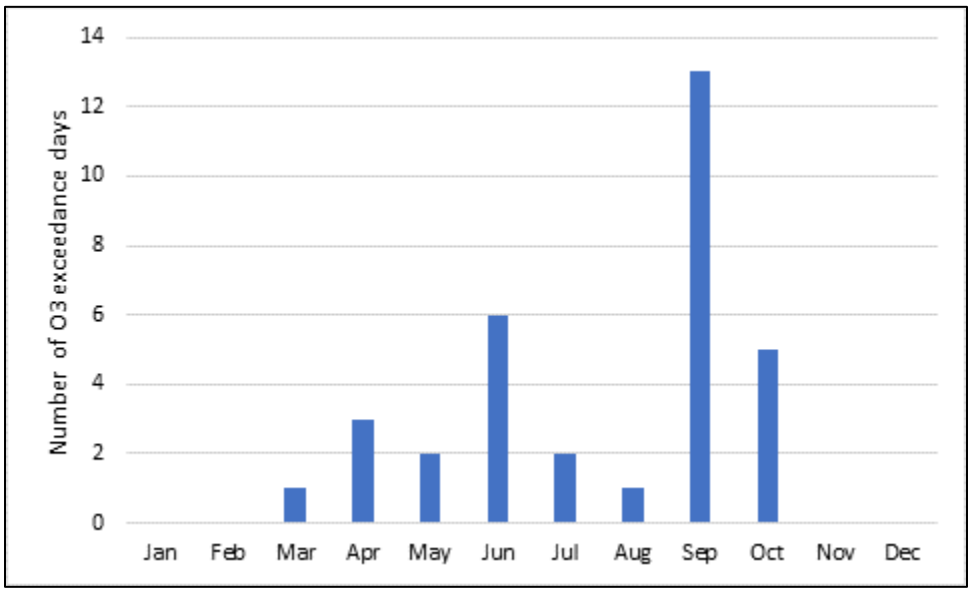


Figure 2. Count of the number of monitor exceedances by month in 2021

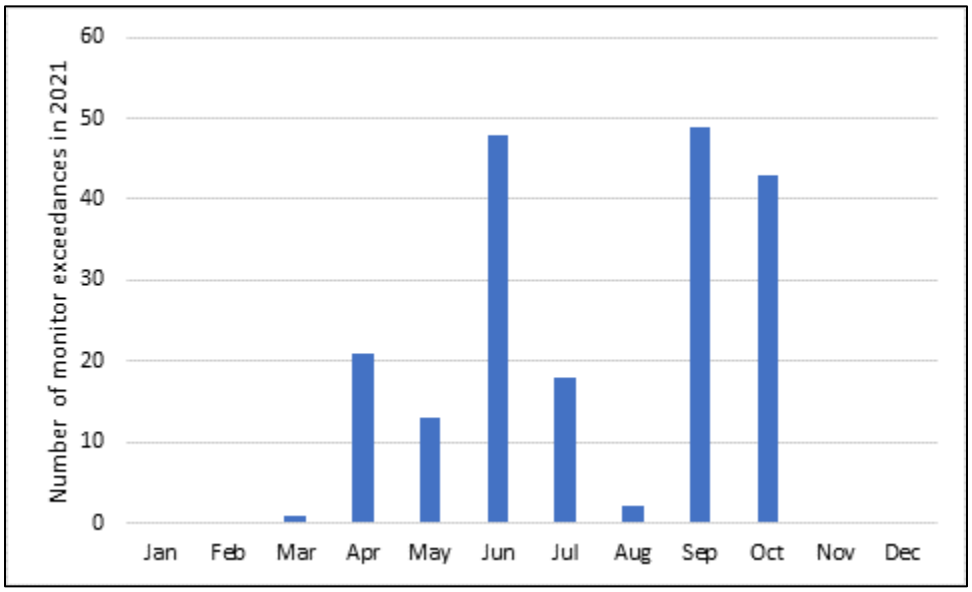


Figure 3 Count of the number of monitor days in top four 8-hour averages for 2021 (Table 1)

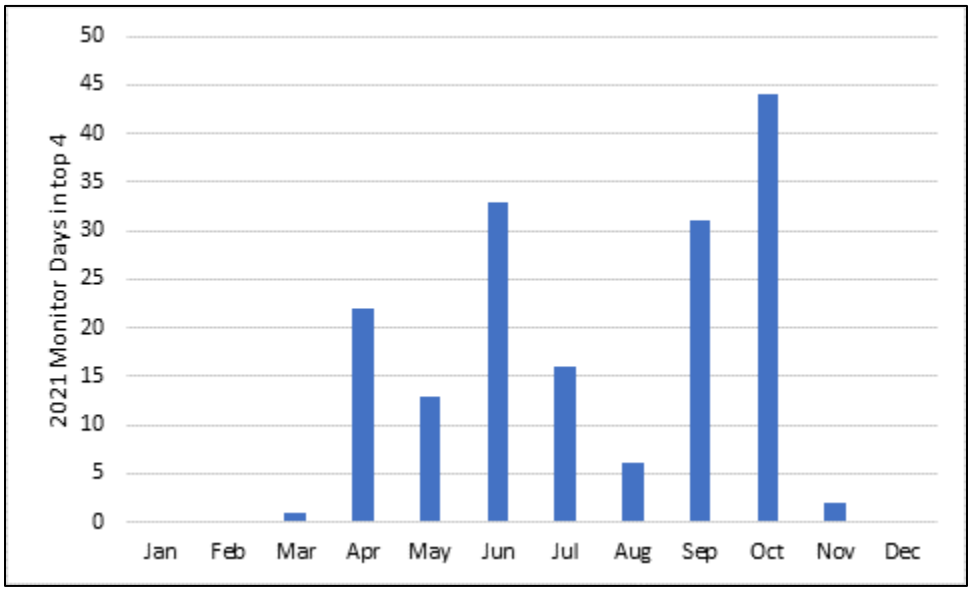


Table 1. Four highest 8-hour O3 days in Houston Region 2021, showing month number and day number of the days (e.g., 9/8 = September 8, 2021)

Monitoring Site	Flag	Date	ppb	Date	Value	Date	Value	Date	Value
Houston East C1	Reg	5/29	86	7/26	78	10/8	77	6/19	76
Houston Aldine C8	Reg	4/11	86	10/8	84	10/7	77	6/19	75
Channelview C15	Reg	5/29	90	7/26	81	10/8	74	7/27	68
Northwest Harris Co. C26	Reg	10/8	71	**9/11**	71	4/11	70	**9/26**	69
Hou.DeerPrk2 C35	Reg	7/26	97	6/19	89	10/7	84	5/29	74
Seabrook Friendship Park C45	Reg	10/7	83	6/19	79	7/26	71	6/18	60
Houston Bayland Park C53	Reg	10/7	92	6/18	86	**9/8**	83	7/28	78
Conroe Relocated C78	Reg	10/8	86	10/9	73	4/12	73	4/8	70
Manvel Croix Park C84	Reg	**9/8**	89	10/7	83	**9/9**	79	7/28	77
Clinton C403	Reg	7/26	78	5/29	75	6/19	70	4/11	70
Houston North Wayside C405	Reg	4/11	75	6/19	71	10/8	67	5/29	65
Houston Monroe C406	Reg	10/7	78	4/20	71	9/8	68	6/16	68
Lang C408	Reg	4/11	89	10/8	77	10/7	74	9/8	71
Houston Croquet C409	Reg	6/17	87	10/7	86	6/16	85	9/8	83
Houston Westhollow C410	Reg	6/18	82	7/28	74	9/8	73	10/7	71
Park Place C416	Reg	10/7	79	6/18	79	6/17	78	6/16	78
Houston Harvard Street C417	Reg	10/7	86	10/8	84	9/8	81	6/15	79
Sheldon C551	Non	10/8	73	4/20	63	9/11	57	6/19	57
Baytown Wetlands Ctr C552	Non	7/26	74	10/7	69	6/19	67	4/20	63
Crosby Library C553	Non	10/8	69	4/20	66	7/27	65	5/29	64
West Houston C554	Non	6/18	81	9/24	80	6/15	78	10/31	77
La Porte Sylvan Beach C556	Non	6/19	81	10/7	76	7/26	73	4/20	62
Mercer Arboretum C557	Non	6/19	60	5/7	60	4/12	59	4/20	58
Tom Bass C558	Non	10/7	83	9/25	81	9/8	81	6/16	76
Katy Park C559	Non	9/25	70	9/24	70	9/26	69	10/31	67

Monitoring Site	Flag	Date	ppb	Date	Value	Date	Value	Date	Value
Atascocita C560	Non	10/8	79	8/23	61	8/24	59	8/5	59
Meyer Park C561	Non	10/8	82	4/11	71	9/11	66	8/6	66
Bunker Hill Village C562	Non	10/7	76	9/8	75	6/18	75	6/15	73
Huffman Wolf Road C563	Non	10/8	73	4/20	65	8/24	63	8/5	62
HRM-3 Haden Road C603	Non	5/29	89	7/26	82	10/8	78	4/11	74
Wallisville Road C617	Non	5/29	76	7/26	75	4/20	73	10/8	67
Texas City 34th St. C620	Non	10/7	87	10/8	75	9/9	75	3/23	74
UH Moody Tower C695	Non	6/15	80	10/7	77	6/17	76	6/18	75
UH WG Jones Forest C698	Non	10/8	84	4/12	71	5/7	70	4/26	70
Lynchburg Ferry C1015	Reg	7/26	76	5/29	72	10/7	66	6/19	65
Lake Jackson C1016	Reg	9/9	79	9/8	74	5/5	70	9/7	69
Baytown Garth C1017	Reg	7/26	85	5/29	81	4/20	75	9/19	71
Galveston 99th St. C1034	Reg	6/14	77	9/18	75	9/9	71	10/6	70
UH Smith Point C1606	Non	10/7	77	6/19	77	9/18	74	9/19	72
Oyster Creek C1607	Non	9/9	81	9/7	72	9/8	70	10/6	66
UH Launch Trailer C1611	Non	6/15	78	10/7	76	4/11	76	6/17	75
Liberty Sam Houston Lib. C1626	Non	10/22	61	11/1	60	10/8	60	11/2	59

Figure 4 shows the times series for one-hour ozone concentrations in the Houston-Galveston-Brazoria (HGB) region in August and September 2021. These data, from 39 monitoring stations, show periods during which several if not most instruments recorded daytime ozone concentrations above 60 ppb and up to 100 ppb. Figure 5 takes up to 39 measurements per hour and averages them to show the HGB regional pattern of concentrations in August and September. Figure 6 through Figure 9 show the distribution of 24-hour rainfall accumulation (ending at 6 a.m. CST, 12 noon UTC) for the mornings of September 13 to 16, during which the maps show rainfall in the HGB region[1] on the first three days, coinciding with the low period of ozone on those dates.

Figure 10 shows the times series for one-hour $PM_{2.5}$ concentrations in the Houston-Galveston-Brazoria (HGB) region in August and September 2021. Figure 11 takes these 12 measurements per hour and averages them to show the HGB regional pattern of fine PM concentrations in August and September. Contradicting the low ozone on September 13 is a spike in $PM_{2.5}$ that was measured in the Beaumont/Port Arthur Region as well as the HGB Region. The TCEQ Daily Air Quality Forecast for September 13 suggested that smoke from fires in the Western U.S. could affect East Texas on that day, but HYSPLIT back-trajectories suggest air movement from the Gulf of Mexico into Texas on that day.

[1] See https://www.wpc.ncep.noaa.gov/dailywxmap/index_20210916.html accessed June 2022

Figure 4 Time series one-hour ozone in the HGB Region Aug.-Sept. 2021

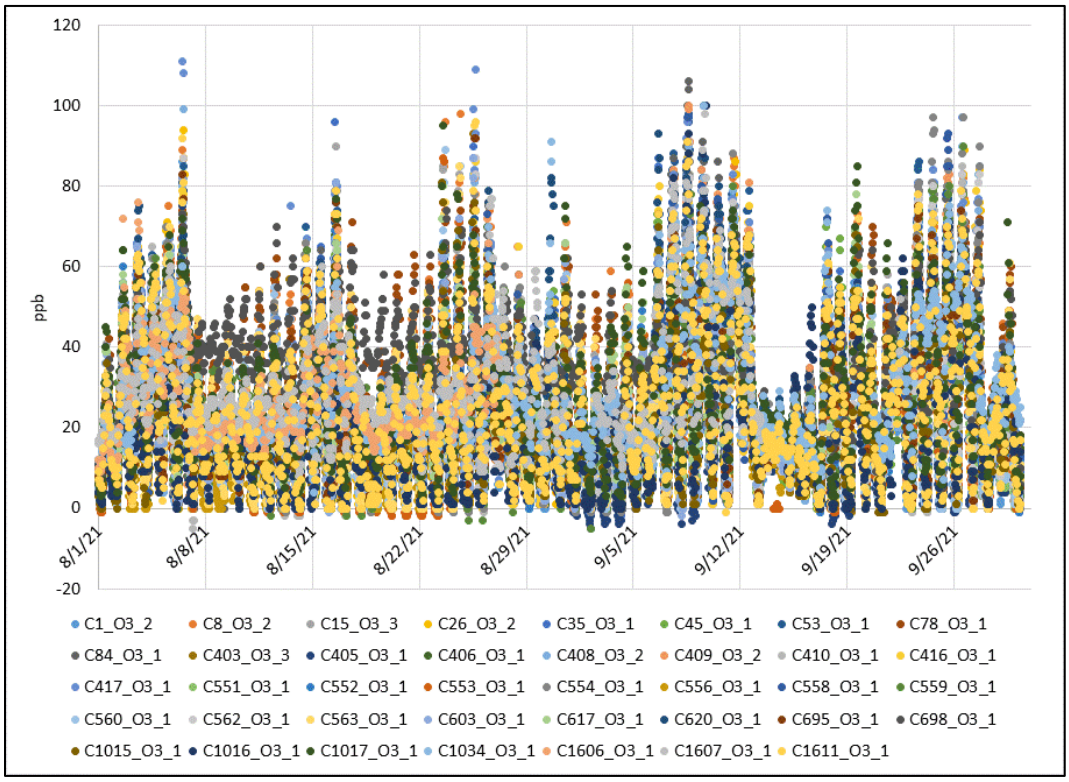


Figure 5 Time series HGB regional hourly average using up to 39 stations, Aug.-Sept. 2021, arrow indicating rainy period from Sept. 13 to Sept. 16, 2021

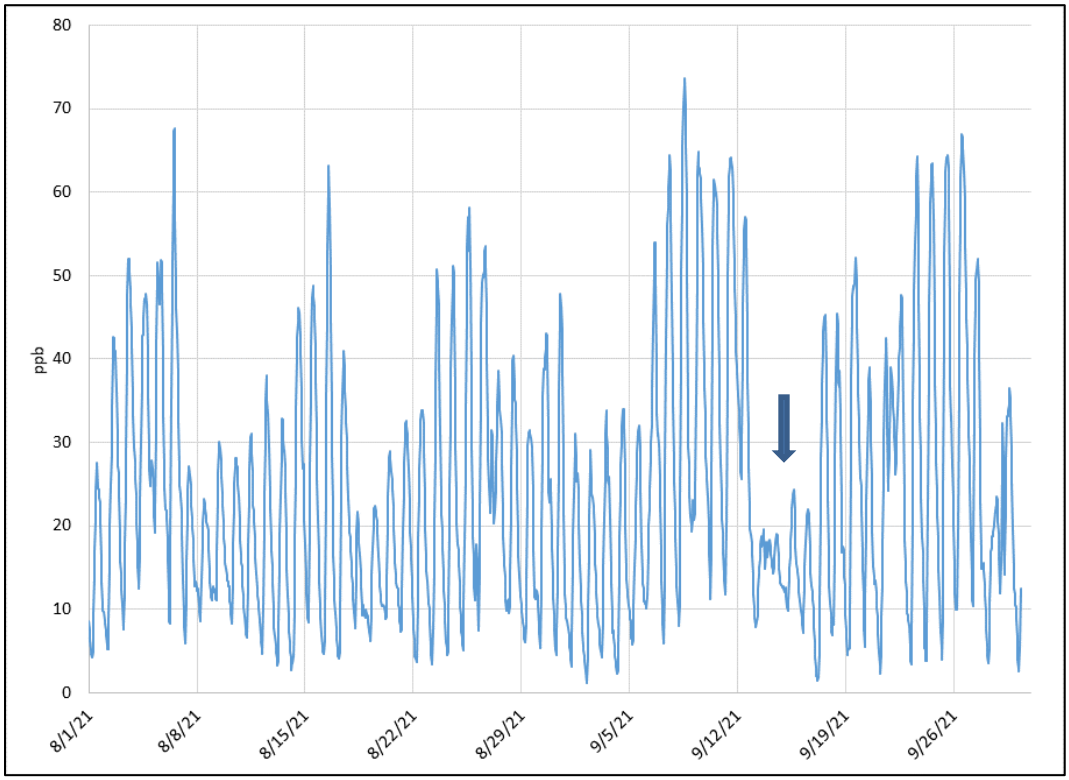


Figure 6 Sept. 13, 2021, rain map

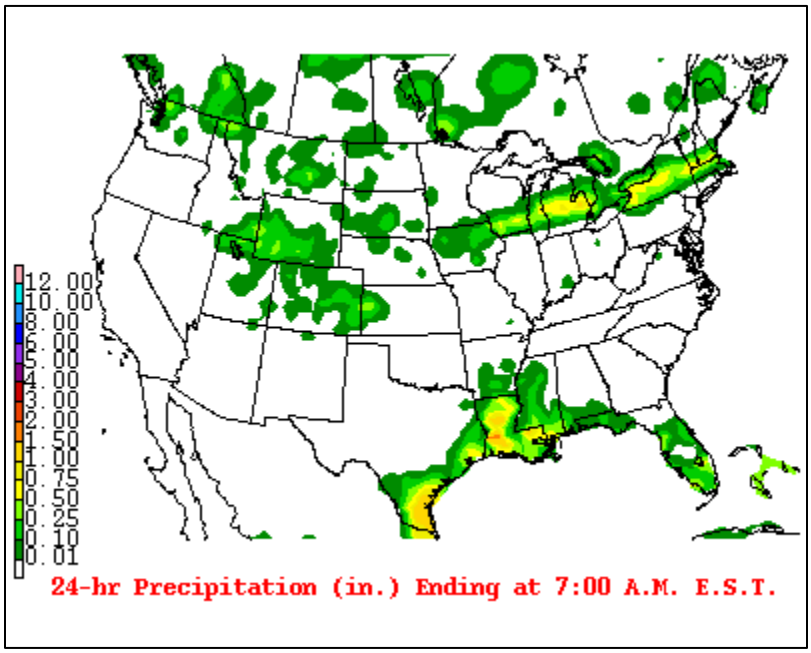


Figure 7 Sept. 14, 2021, rain map

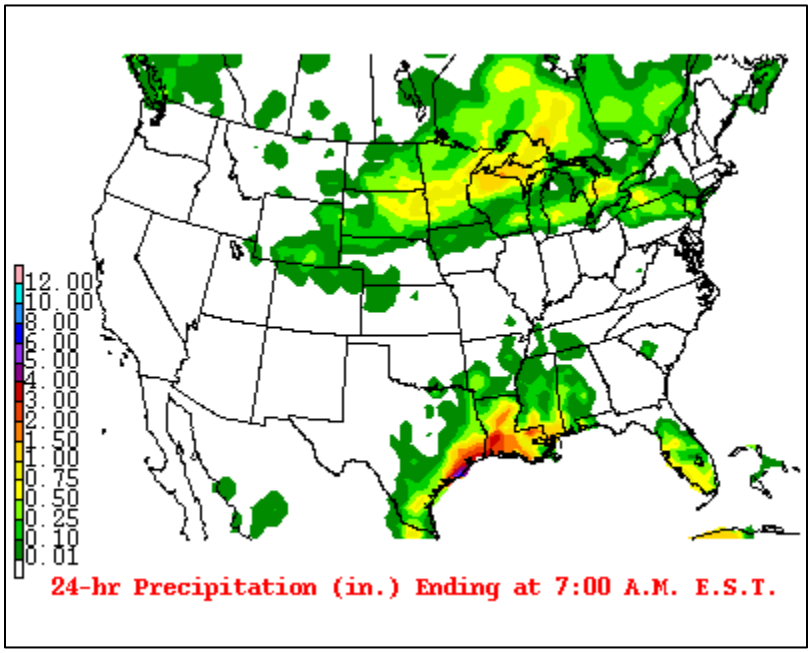


Figure 8 Sept. 15, 2021, rain map

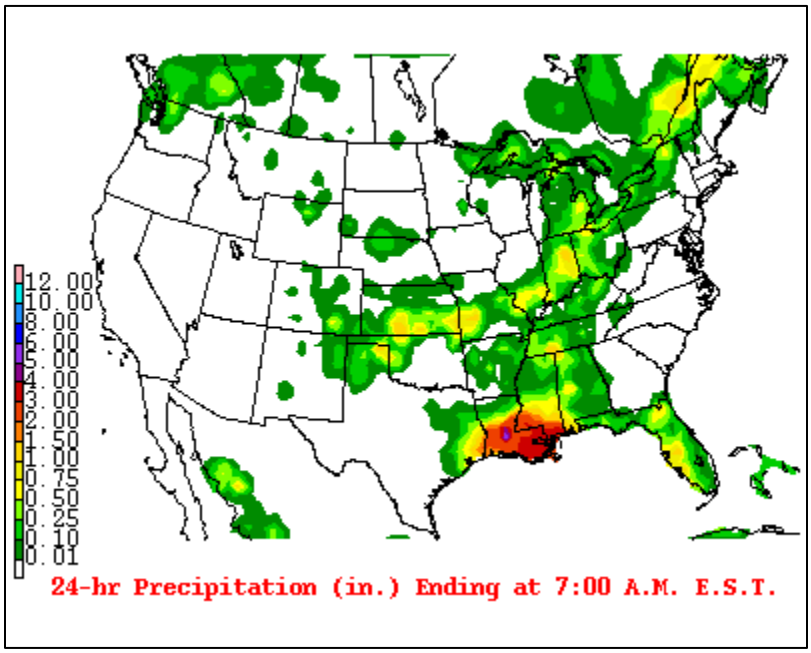


Figure 9 Sept. 16, 2021, rain map

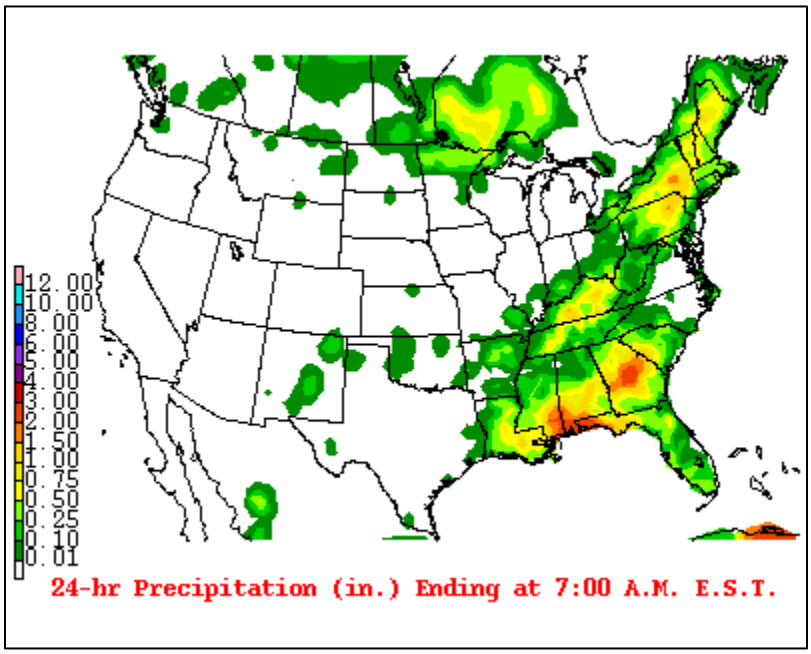


Figure 10 Time series one-hour $PM_{2.5}$ in the HGB Region Aug.-Sept. 2021

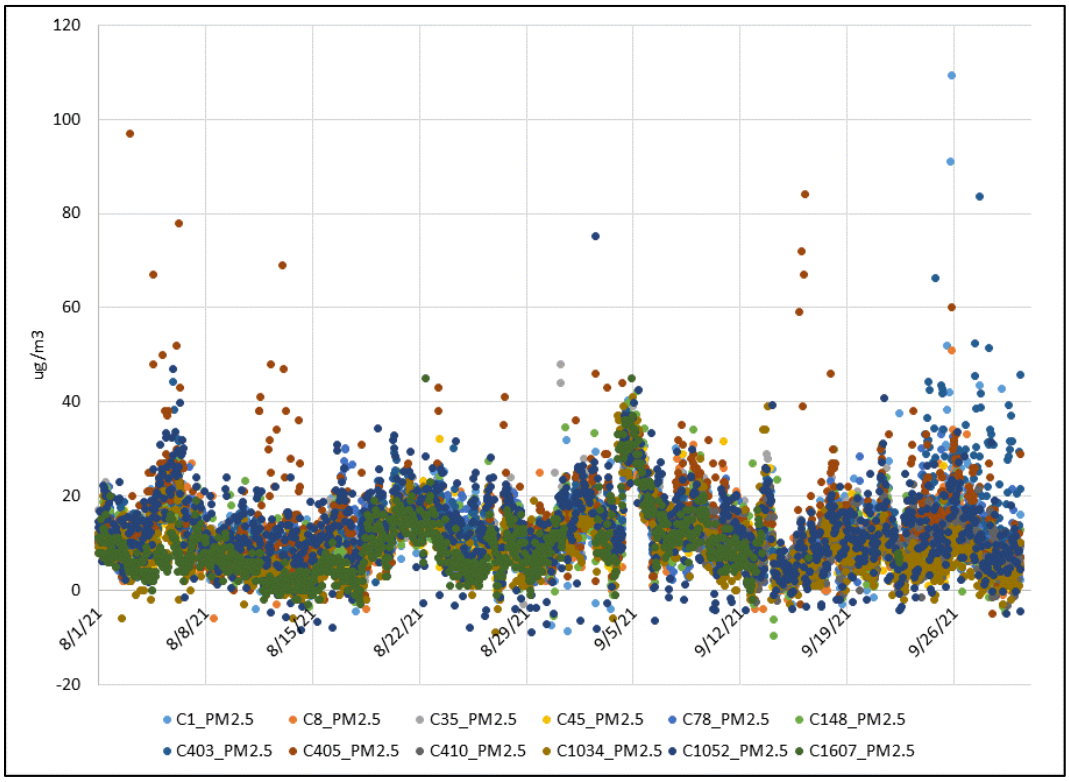
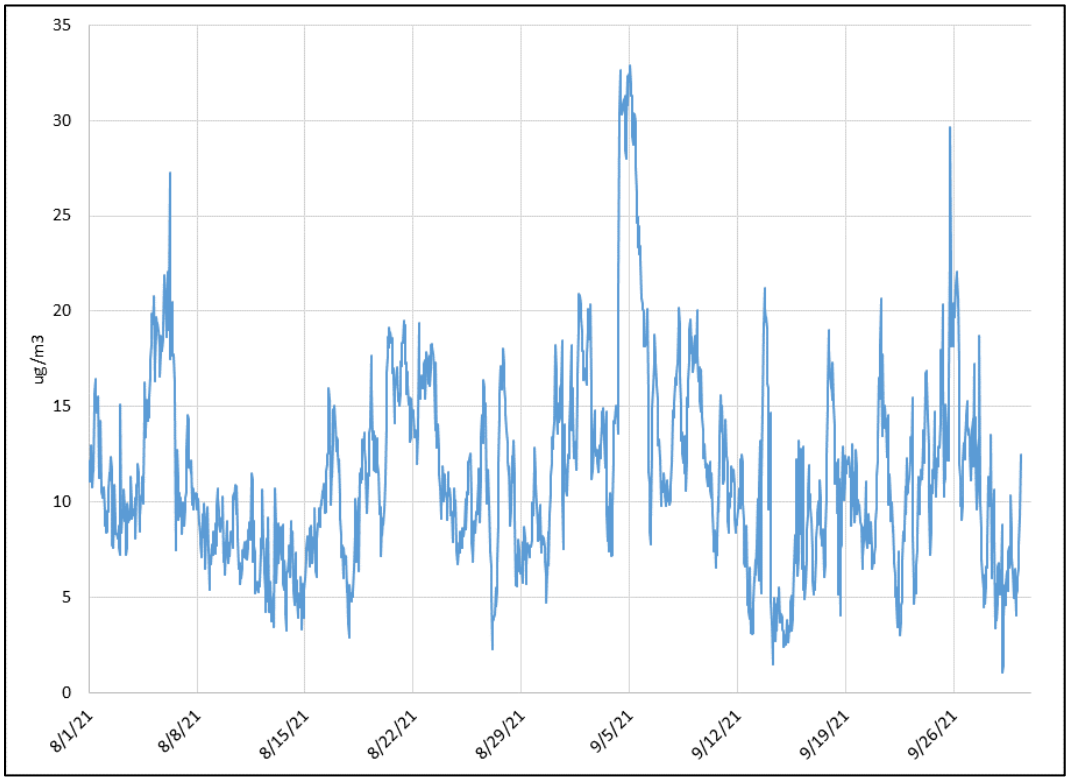


Figure 11 Time series HGB regional hourly average $PM_{2.5}$ using up to 12 stations, Aug.-Sept. 2021



3.3 OVOC and Hydrocarbon Comparisons

The UW data for August 6 through October 1, 2021, were received on January 14, 2022, and the HRM 3 auto-GC data for corresponding species had earlier been downloaded for the same period. The HRM data were averaged over 6-hour time periods to match the 6-hour integrated sampling period for the UW data. A point to consider is that the auto-GC hourly data represent a 40-minute sample within a 60-minute hour. This introduces some error in comparing the HRM data and UW data. However, given the high degree of autoregressive correlation in air quality and meteorological data hourly time series, this error is believed to be small. The following figures show the results of regressing the UW data (variables "Benzene", "Toluene", "Isopentane", and "Npentane") on the averaged HRM data (variables "benz6hr", "tolu6hr", "isopen6hr", "npen6hr"). Only HRM data for which at least 6 hours of data were available were used in the comparisons, which yielded 103 paired observations. In the December 2021 monthly report, an identical analysis had been carried out on the subset of the data with 65 matched pairs. The data set received in January also included Acetonitrile and Acetone. No corroborating data for Acetonitrile have been found in the TCEQ TAMIS database or in the U.S. EPA AQS database.

Each figure below shows the regression line for the model: $Y = a\,X + b$, where the Y variable is the UW variable, and the X variable is the TCEQ HRM 603 variable. The graphs also show the 95-percentile line prediction and data confidence intervals. All the regressions are statistically significant at p-values less than 0.0001, and not all the Y-intercept are statistically significant at $p < 0.05$.

Figure 12. Regressing UW Benzene on TCEQ HRM Benzene; UW = 0.95 TCEQ - 0.01, R^2 = 87%

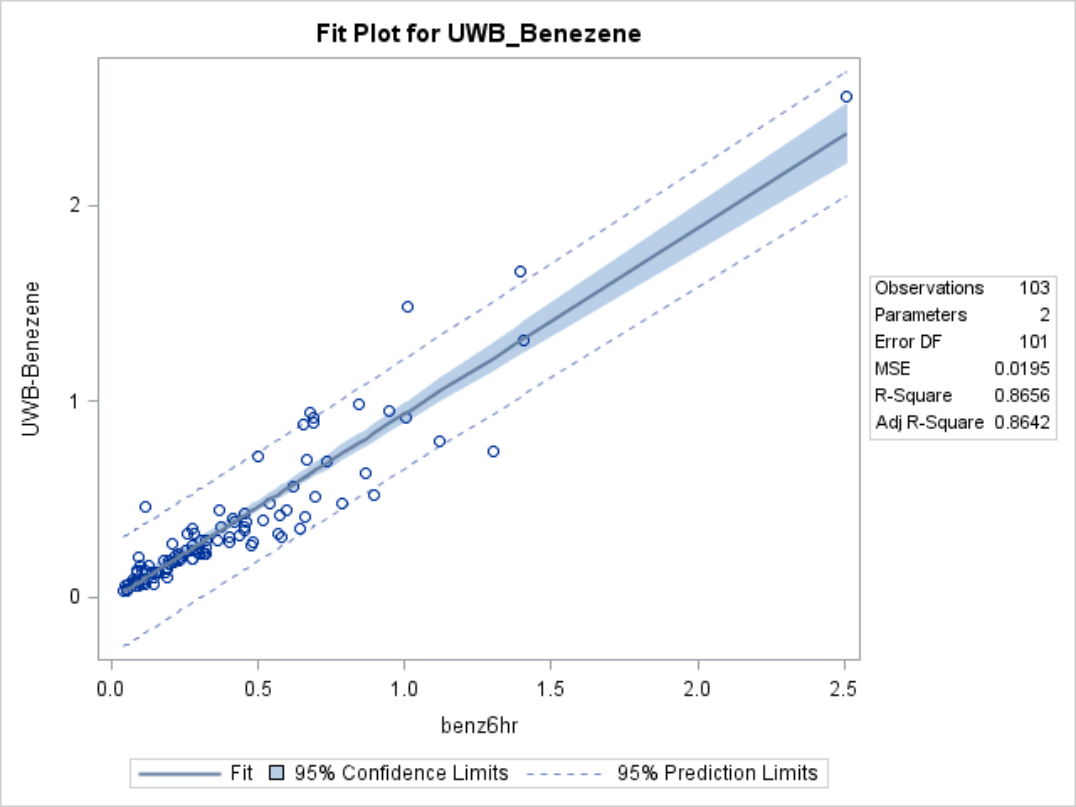


Figure 13. Regressing UW Toluene on TCEQ HRM Toluene; UW = 0.70 TCEQ + 0.062, R^2 = 77%

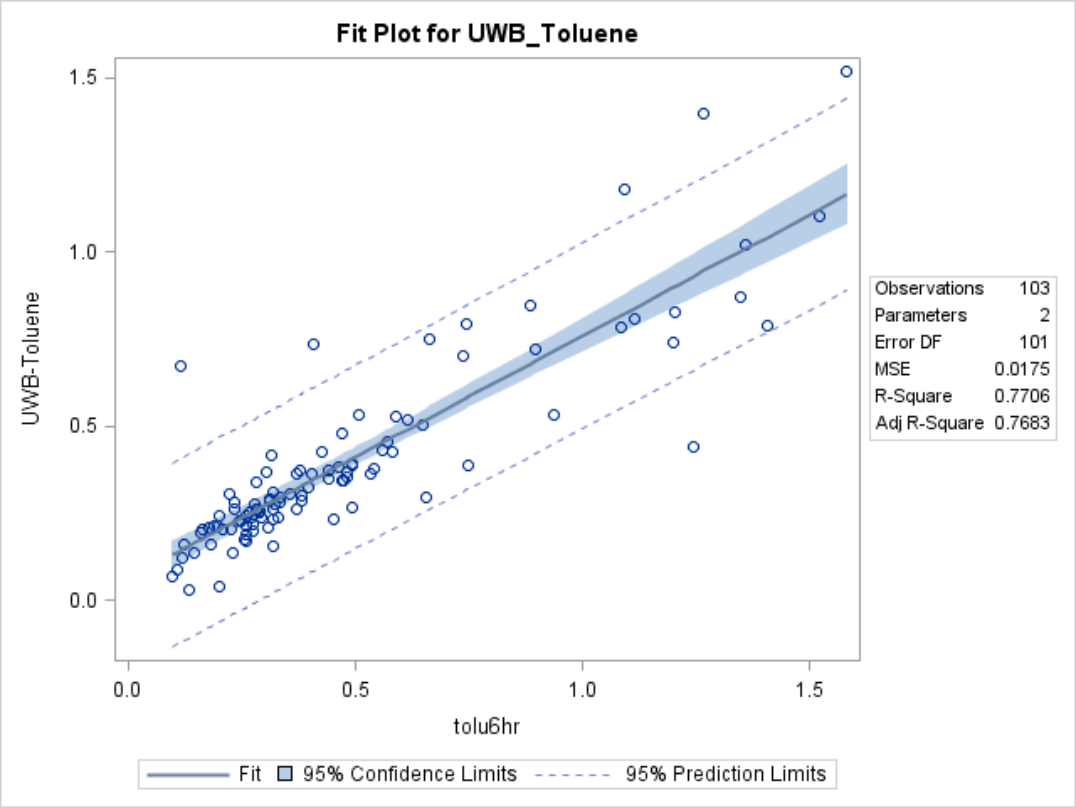


Figure 14. Regressing UW Isopentane on HRM Isopentane; UW = 0.47 TCEQ + 0.24, R^2 = 71%

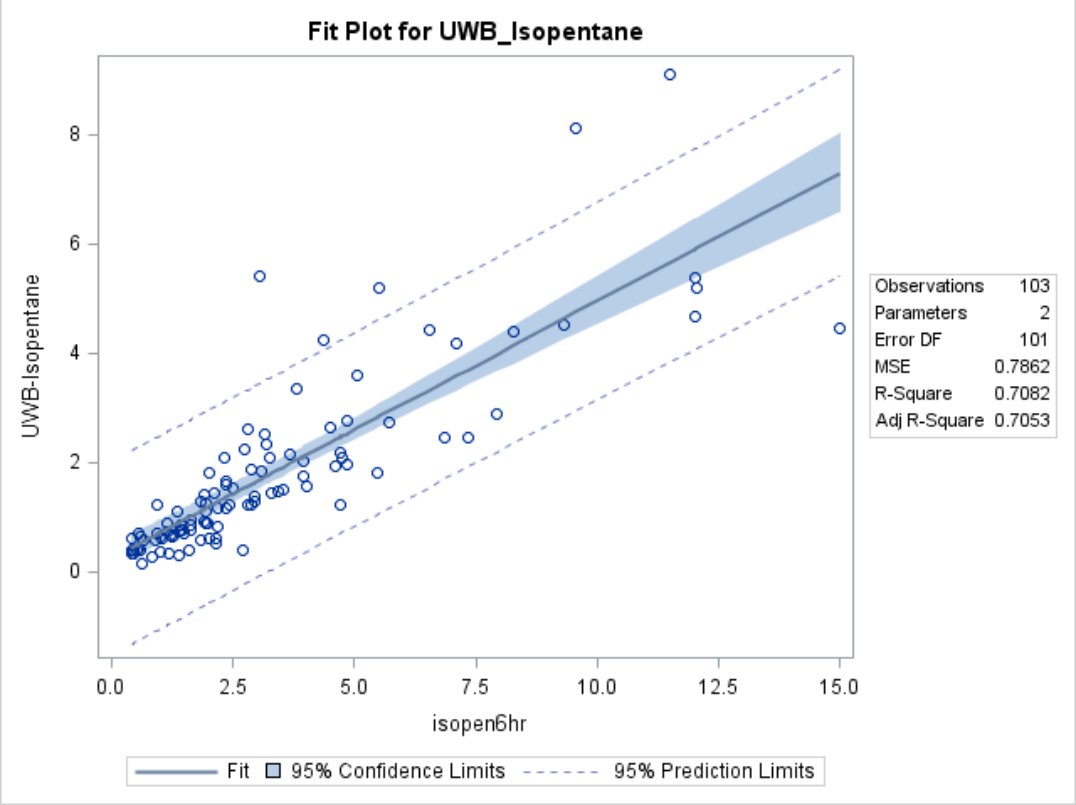
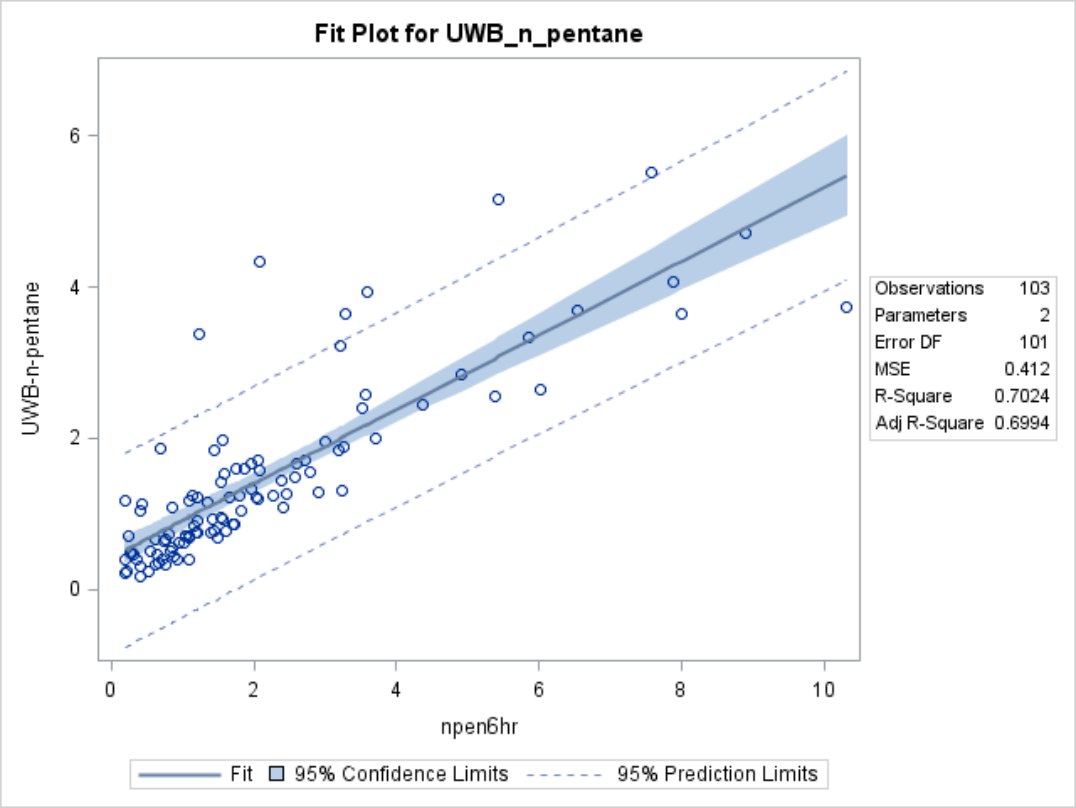


Figure 15. Regressing UW N-pentane on HRM N-pentane; UW = 0.49 TCEQ + 0.43, R^2 = 70%

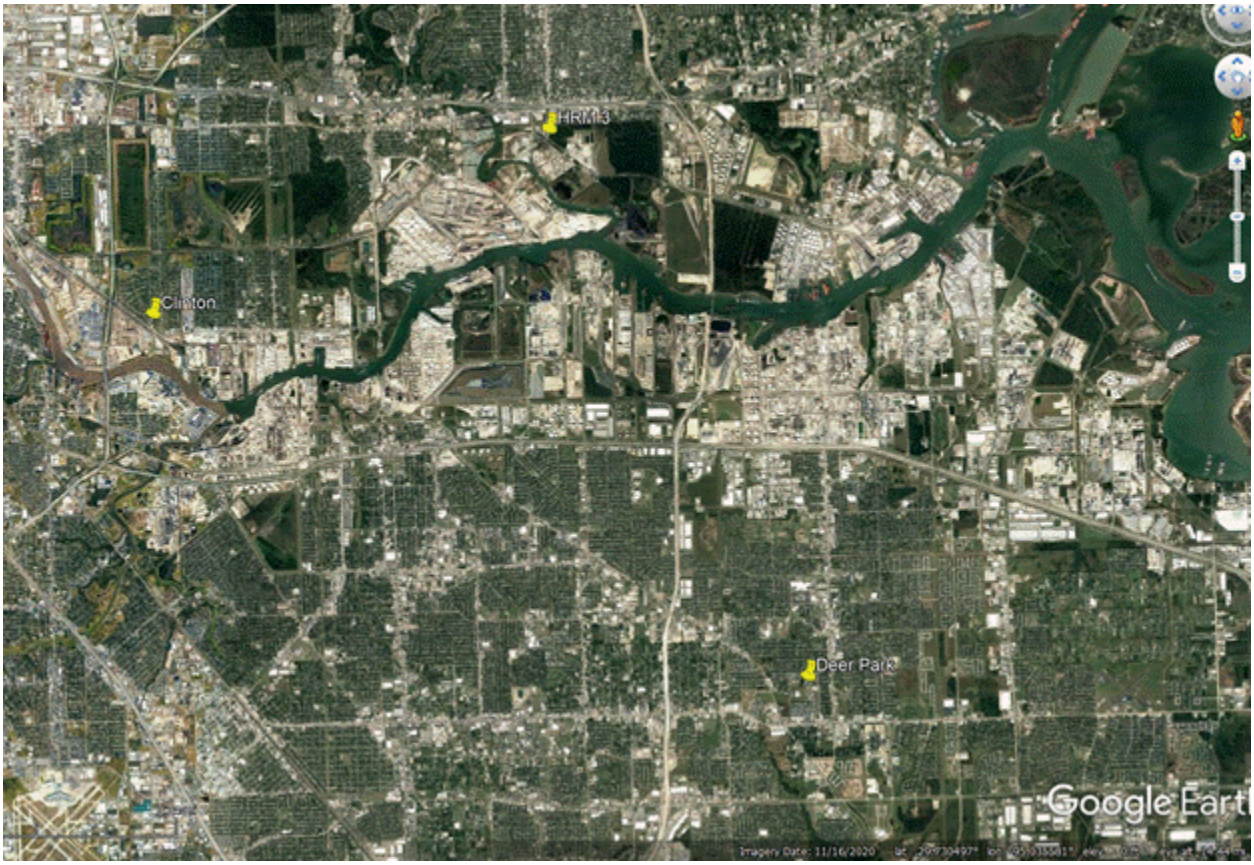


3.4 Comparing Acetone Concentrations

The acetone data from Harris County at two stations from August 2021 through October 2021 were downloaded from the TCEQ TAMIS database. No acetonitrile data could be found in the TAMIS database. Acetone is a carbonyl species measured using absorption in 2,4-dinitrophenylhydrazine (DNPH) cartridges. Acetone samples were collected on an every-6th-day schedule at the Clinton Drive station as 24-hour integrated samples based on a CST time scale. Acetone samples were collected on an every-3rd-day schedule at the Deer Park station as 8-hour integrated samples on a CST time scale in June, July, and August, and on every 6th-day schedule in other months. The CST vs CDT time stamps implies an inability to exactly match up the TCEQ acetone concentrations with the UW acetone concentrations in time. Figure 16 shows a map of the Houston area with the HRM 3, Clinton Drive, and Deer Park stations. Clinton Drive is 5 miles west-southwest of HRM 3 and Deer Park is 7 miles south-southeast of HRM 3

The UW data were collected on 6-hour time periods timed to match integral multiples of 6 on the Central Standard time scale (12 mid., 6 a.m., 12 noon, 6 p.m., CDT). The CDT values were converted to the Central Standard Time scale used by U.S. EPA and state agencies including TCEQ. UW acetone values were provided from Aug. 6, 2021, through Sept. 9, 2021, for 91 total values. Following Sept. 9, acetonitrile values were provided from Sept. 12 through Oct. 1, 2021.

Figure 16 Three acetone sampling location in Harris County TX



The UW measured acetone concentrations were significantly greater than the concentrations at the two TCEQ stations. This begged the question as to what are typical summertime acetone concentrations? To examine this, data from the U.S. Environmental Protection Agency (EPA) Air Quality System (AQS) were downloaded for 2019 from the entire lower 48 states. The average acetone concentration from 1,377 samples at 122 stations reporting to EPA AQS from August and September 2019 was 3.4 ppbV, which is much higher than the TCEQ stations. In August and September 2019, the Dallas Hinton average was only 0.58 ppbV. The average 24-hour concentration at Clinton in 2021 for August and September 2021 was only 0.083 ppbV and Deer Park in August 2021 was 0.24 ppbV. The UW average at HRM 3 in August and September 2021 was 1.54 ppbV, which is more in line with the average from EPA AQS. These results are shown in Table 2.

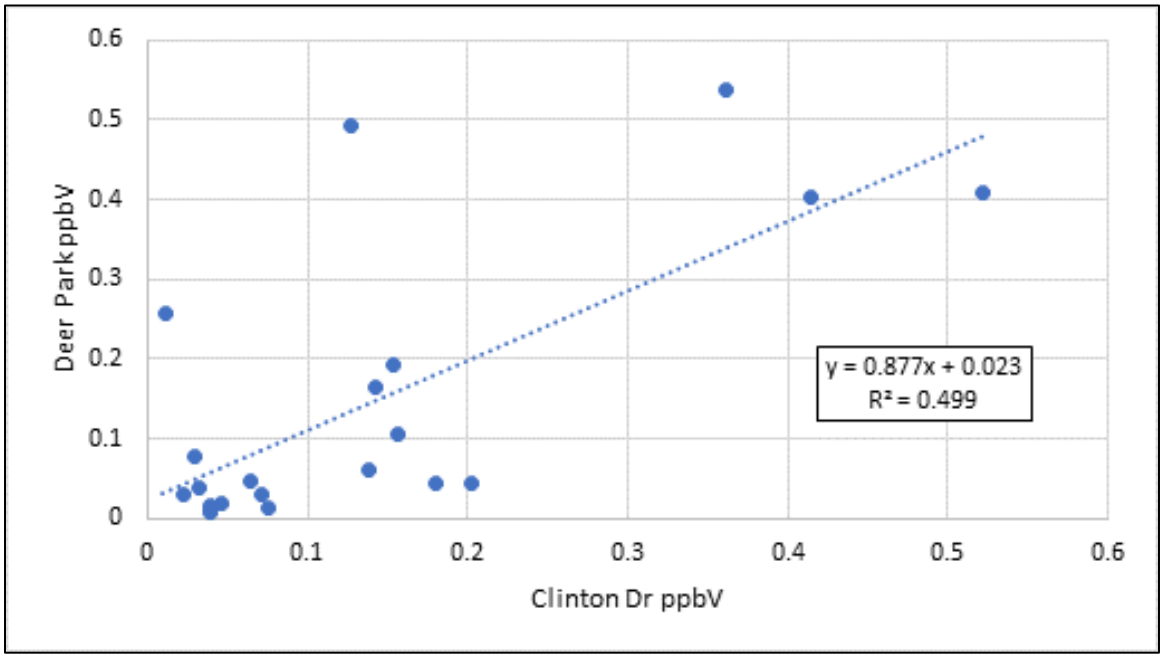
Table 2 Some information on mean acetone concentrations, ppbV units

Data Source	Mean ppbV	Samples
Deer Park Aug.-Sept 2021	0.235	five 24-hour and 30 8-hour samples
Clinton Dr. Aug.-Sept 2021	0.083	ten 24-hour samples
U.S. 2019 122 stations, Aug.-Sept. 2021	3.41	1,377 samples at 122 stations at 3, 8, and 24-hour duration
UW Aug.-Sept. 2021	1.54	91 six-hour samples, 4 per day

Figure 17 shows a comparison of the 2021 24-hour acetone values at Clinton Dr. and Deer Park. The Clinton Dr. samples were taken every sixth day from April 4, 2021, to October 31, 2021. Deer Park samples were taken in every sixth day in April, May, September, and October only.

This provided 21 days for comparison. The regression is significant at $p<0.001$, the y-intercept is not significant, and 1.0 lies within a 95 percent confidence interval on the slope. For the 21 paired dates, the mean at Clinton was 0.137 and at Deer Park was 0.143, with no statistically significant difference between the two. During June, July, and August the Deer Park sampler switched to taking 8-hour samples every third day. When these values were averaged for each date and added to the regression, the agreement between the two stations worsened, which was most likely owing to the low concentrations during these three months that diminished the leverage the joint higher concentrations had, and the two-sample t-test suggested that the concentrations at Deer Park were statistically significantly higher although in fact the numeric difference was only 0.082 ppbV (0.093 ppbV mean at Clinton and 0.175 ppbV mean at Deer Park) which was a small value relative to the AQS and UW means.

Figure 17 Comparison of 2021 coincident 24-hour Acetone measurements at Clinton and Deer Park



Overall, it appears that the 24-hour averaged UW data are one or two orders of magnitude higher than the two TCEQ stations, though all the correlations are positive. Not all UW daily averages have four 6-hour observations included. TCEQ reported on August 3, 2022, that Monitoring Division staff had investigated their carbonyl measurements and came to the following conclusion:

> Monitoring Division reviewed and found that acetone QC meets data quality objectives but did observe that recoveries on matrix spikes indicate data may be biased low at times. They also made note that acetone is not a required compound for the PAMS[2] program, but TCEQ is reporting as an optional carbonyl.

[2] Photochemical Assessment Monitoring Station

3.5 Suspected Smoke Episodes Likely Affecting Ozone Concentrations

An examination for the collected UW data suggests several days may have been impacted by transported smoke. Based on an elevated acetone concentration, Prof. Jaffe cited Sept. 8, 2021. The four highest acetone values were consecutive starting at 23 CST on Sept. 8 through the sample ending at 23 CST on Sept. 9. No sample had been started on Sept. 7. The time series graph for the 6-hour acetone and subsequent acetonitrile concentrations appears in Figure 18. On Sept. 8, monitors in Dallas/Fort Worth, Waco, Austin, Houston/Galveston, Corpus Christi, and Harlingen – a total of 28 monitoring stations in East Texas – all had one of the top four 8-hour ozone averages for 2021. On Sept. 9, five stations had one of the top four 8-hour ozone averages for 2021. Figure 19 shows a map from the National Aeronautics and Space Administration (NASA) fire detection program of the location of detected fires on Sept. 7 & 8, 2021 (https://firms.modaps.eosdis.nasa.gov/ accessed July 2022.). A 96-hour HYSPLIT back trajectory from Houston started at 14 CST on Sept. 8, 2021, is shown in Figure 20. (https://www.ready.noaa.gov/HYSPLIT.php accessed July 2022) The evidence, which includes the elevated $PM_{2.5}$ shown earlier in Figure 11 suggests that fires in northern Louisiana may have played a role in the elevated ozone in East Texas on Sept. 8 and Sept. 9, 2021.

Figure 18 Time series for UW acetone (Aug. 6 – Sept. 9) and acetonitrile (Sept. 12 – Oct. 1)

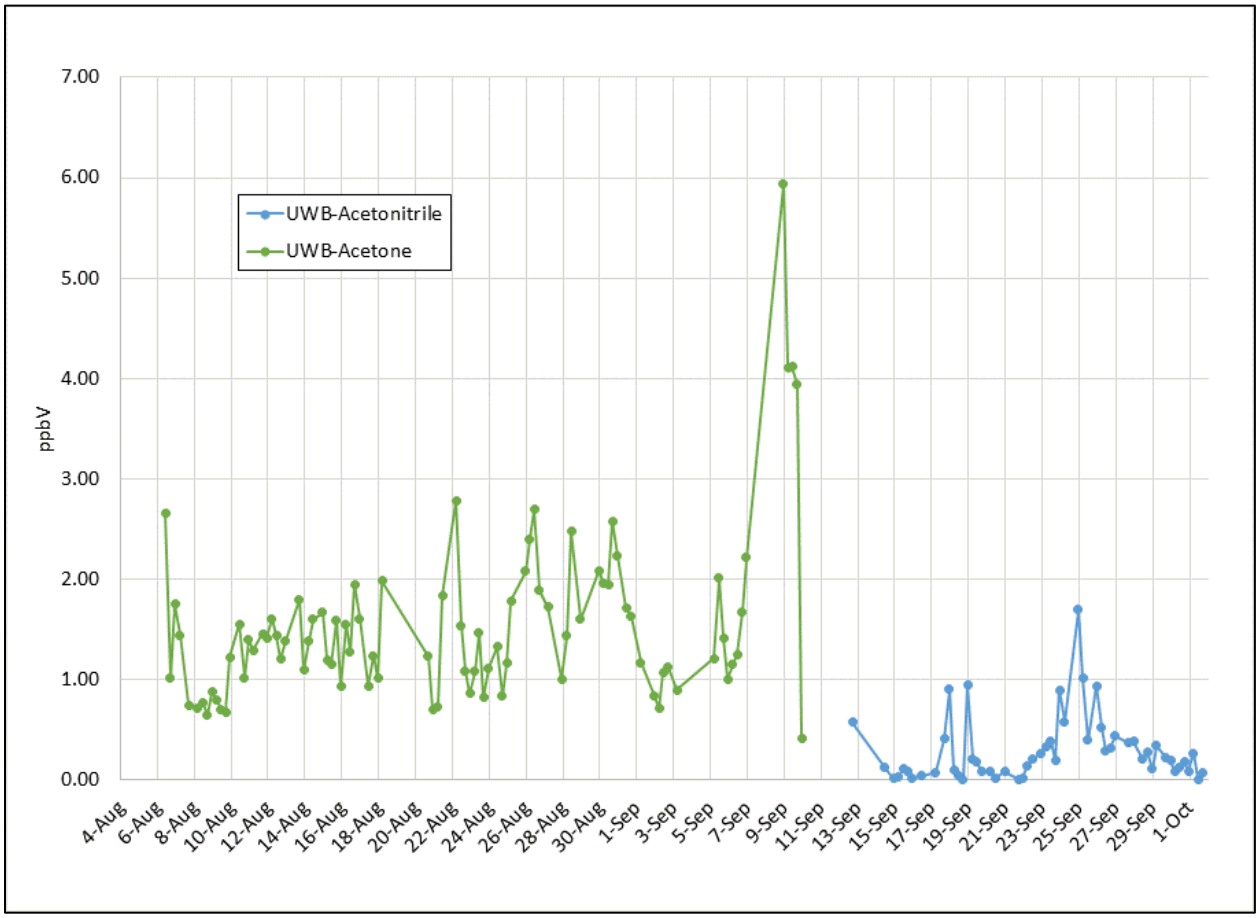


Figure 19 NASA fire detection locations of fires on Sept. 7, 8, and 9, 2021

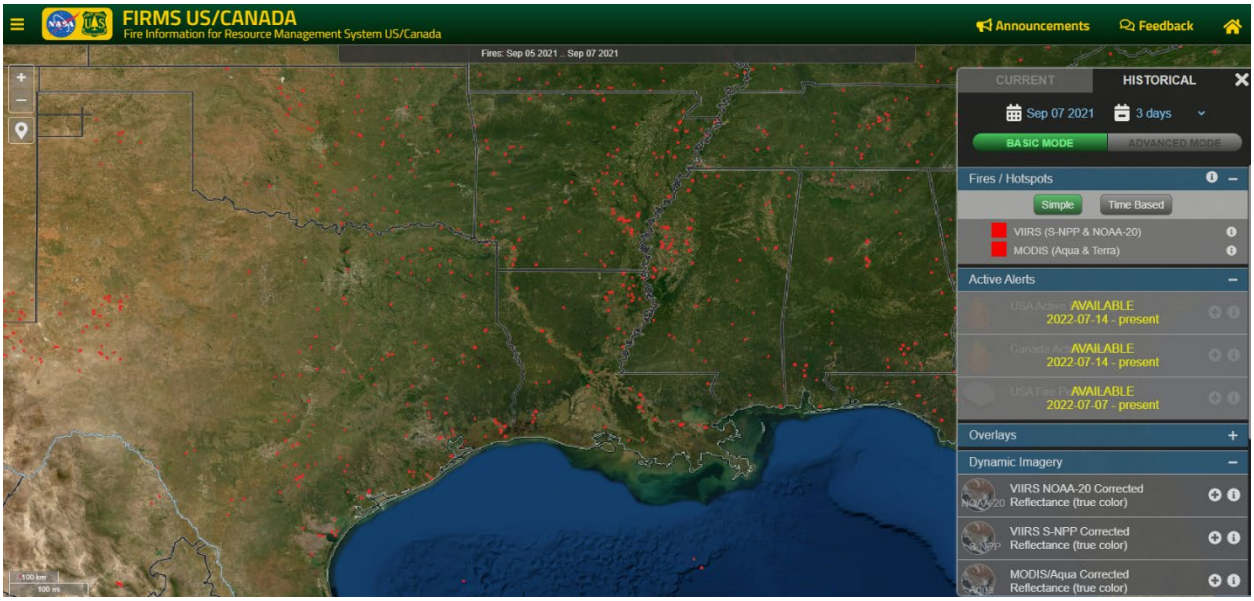


Figure 21 is a plot of $PM_{2.5}$ for the HGB region along with the measured acetonitrile data, suggested by Prof. Jaffe. Figure 22 is a time series plot of the ratios of benzene to toluene and isopentane to n-pentane, which are also smoke indicators according to Prof. Jaffe. The agreement of elevated acetonitrile, benzene to toluene ratio, and $PM_{2.5}$ concentrations for the latter half of September strongly suggests a smoke source for some of this $PM_{2.5}$, especially around Sept. 25, 2021. Two stations in the Region had Sept. 25 among the top two high ozone dates in 2021: Tom Bass C558 and Katy Park C559. The NASA Fire Map appears in Figure 22 and the HYSPLIT back Trajectory appears in Figure 23, again suggesting fires in Louisiana could have been the source of advected smoke and ozone precursors.

Figure 20 HYSPLIT 96-hour back trajectory from 100 m 14 CST (20 UTC) on 9/8/2021

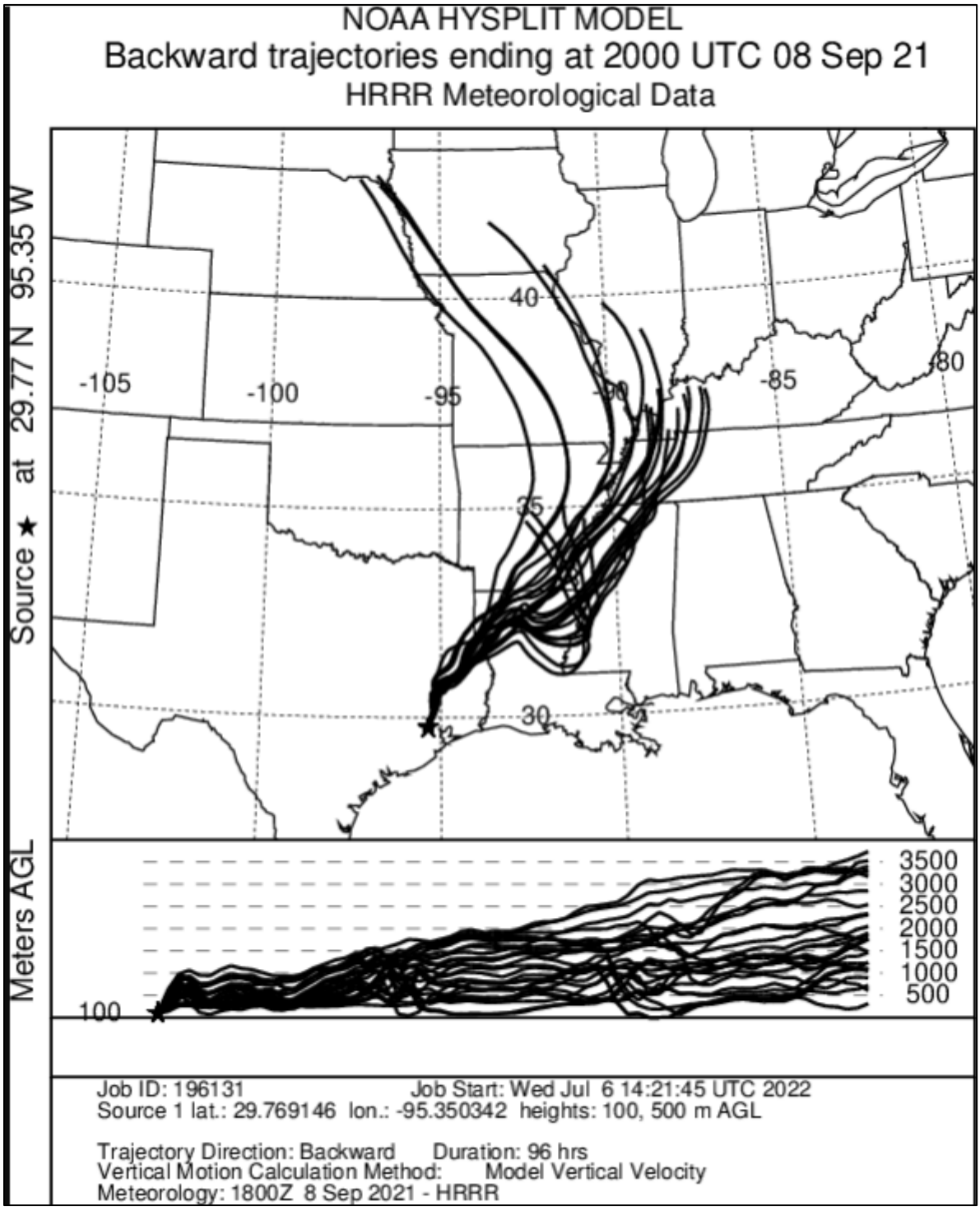


Figure 21 Houston Region 6-hour $PM_{2.5}$ and coincident Acetonitrile concentrations

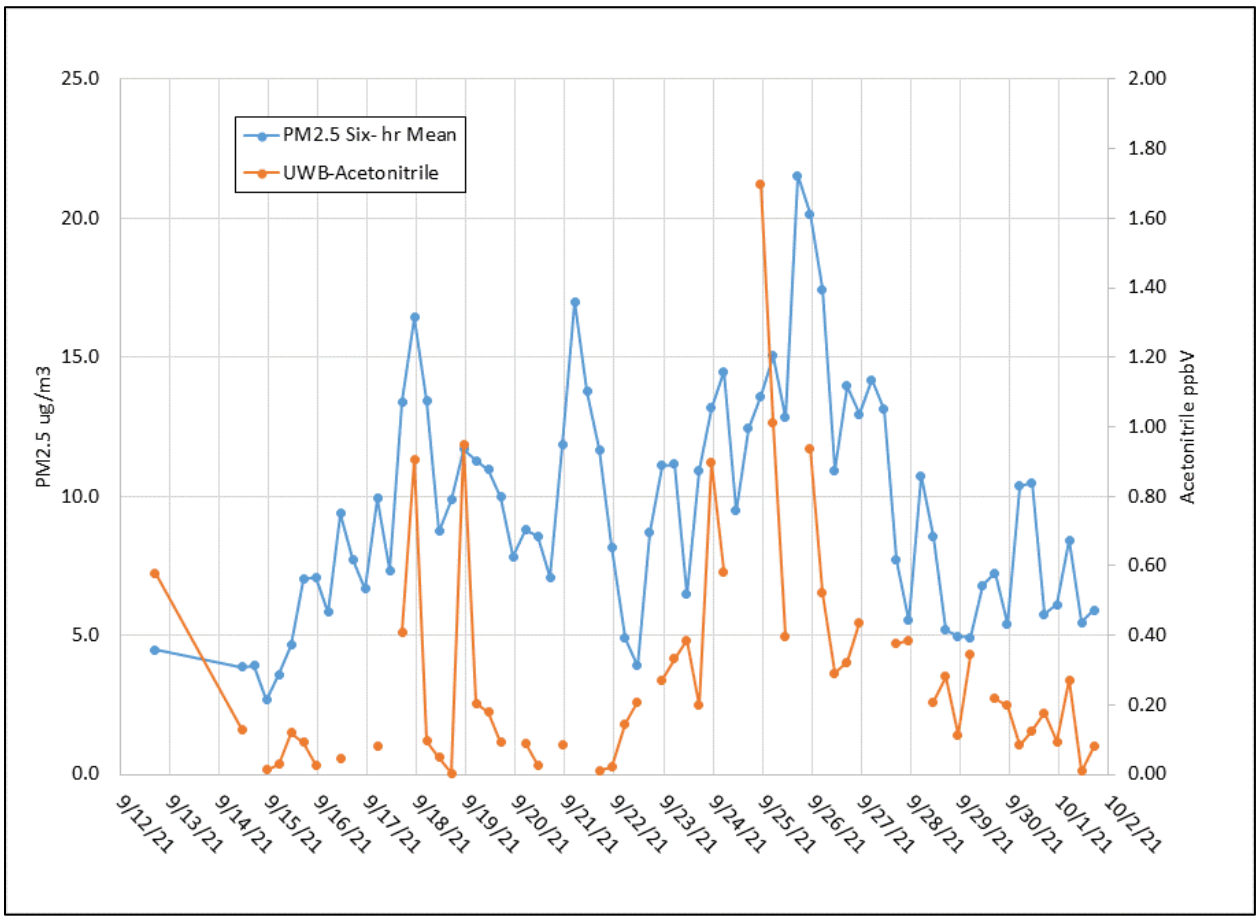


Figure 22 Benzene to toluene and isopentane to n-pentane ratios from UW sampling

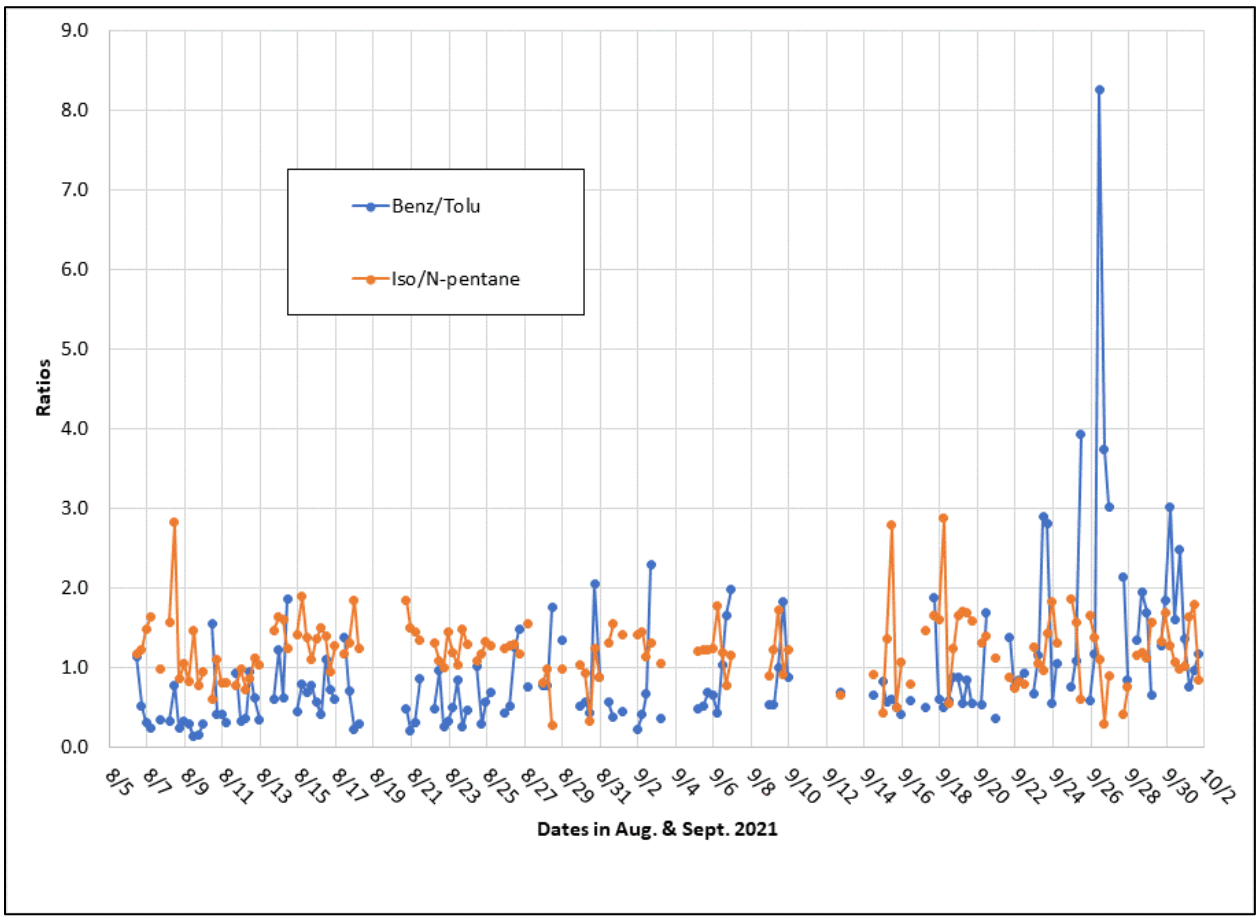


Figure 23 NASA fire detection locations of fires on Sept. 24, 25, and 26, 2021

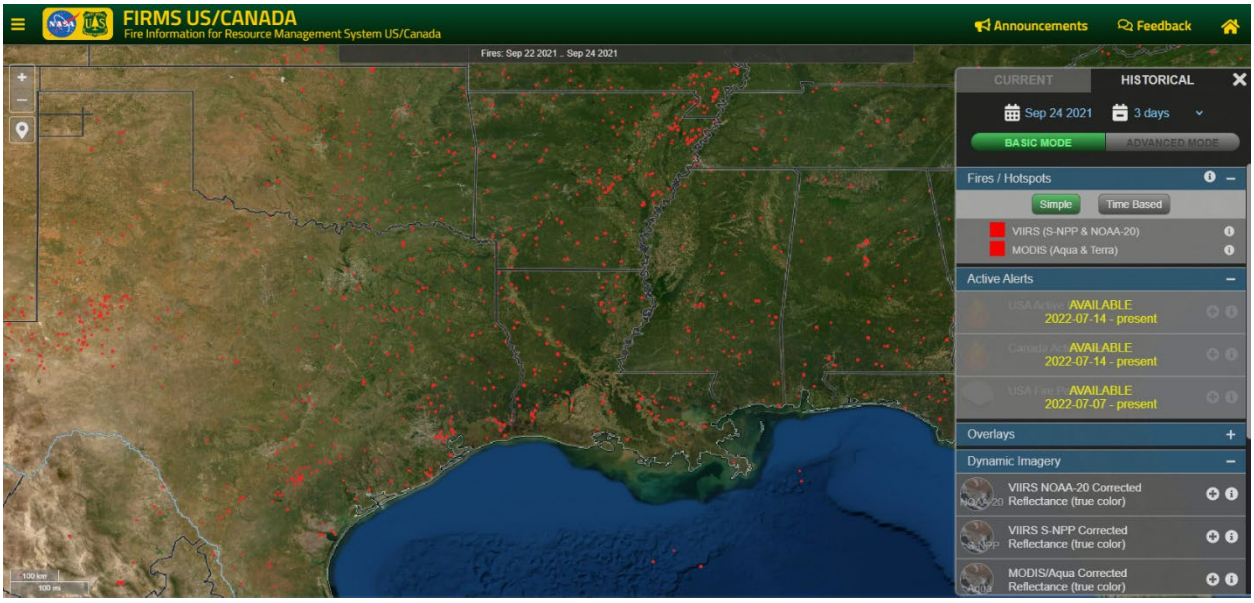
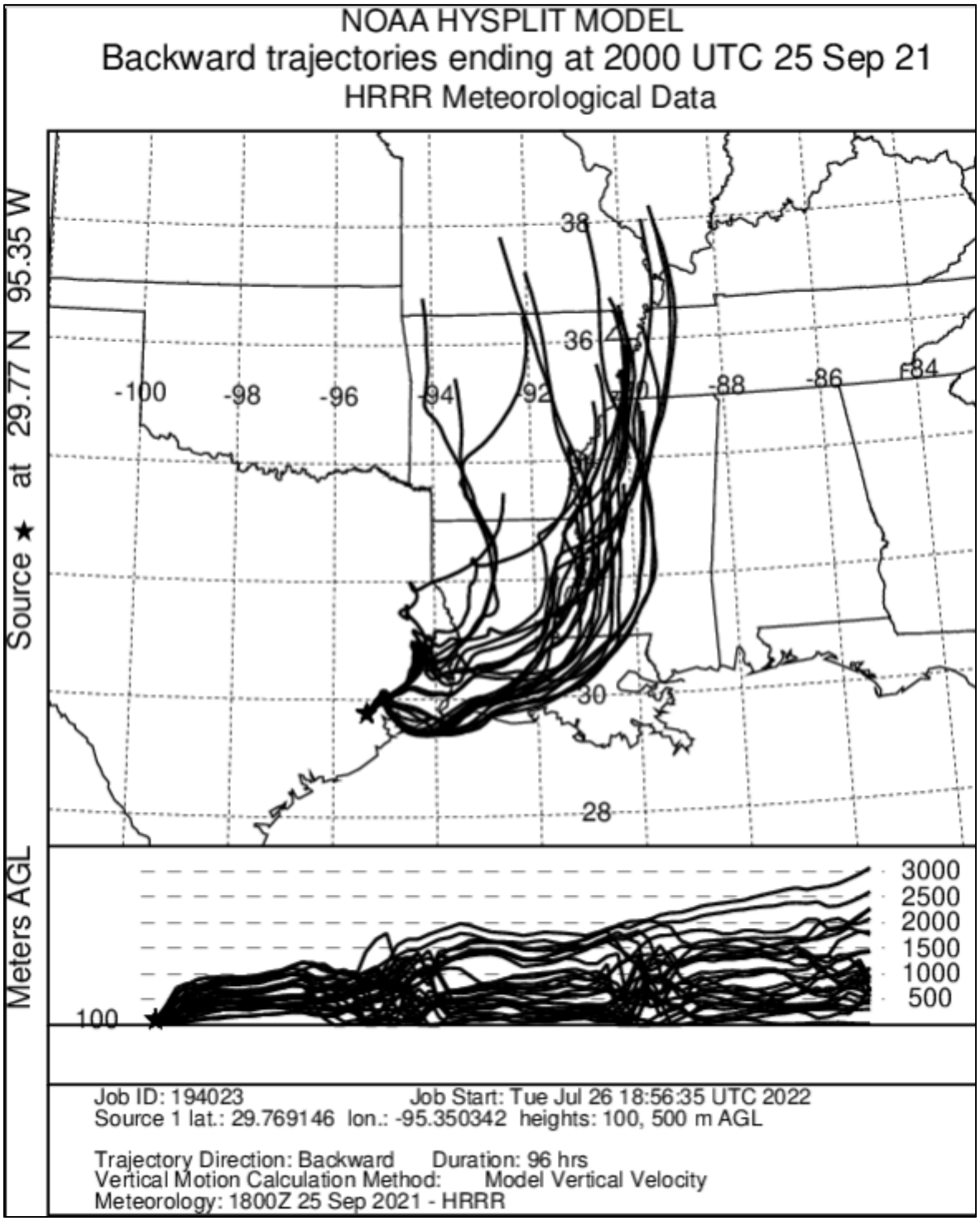


Figure 24 HYSPLIT 96-hr back trajectory from 100m 14 CST (20 UTC) on 9/25/2021



3.6 Data Analyses for TAP and Nephelometer to VOC/OVOC Comparison

The Baylor University (BU) data were downloaded from the TCEQ's FTP server. These data were taken at 5-minute data samples, whereas the UW data are at 6-hour samples. The Baylor data were taken in Liberty County, Galveston County, and at Aldine in Harris County. Aldine being the closest location, its data were used in the tricolor absorption photometer (TAP) and nephelometer comparisons to the UW data. To facilitate comparison, the BU data were converted to 6-hour averages of 72 five-minute values, using the same start-times as the UW 6-hour samples. This allowed direct one to one comparison for the 145 UW values to a subset of the BU Aldine data. A statistical summary of the combined data set from August 6, 2021, through October 1, 2021, appears in Table 3. Table 4 follows with the Pearson correlations among the 6 UW species and the 8 TAP/nephelometer 6-hour averages. For VOC measurements, units are ppbV. For the TAP, the absorption coefficient (AC) units are Mm^{-1}, and for the nephelometer, the scattering coefficients (SC) units are Mm^{-1}. Scattering coefficients are measured at: 635 nm, 525 nm, and 450 nm, and the absorption coefficient are measured at 640 nm, 520 nm, and 365 nm. AAE stands for absorption ångström exponent and SAE for scattering ångström exponent, both of which are unitless

Table 3 Statistical summary of UW HRM3 and BU Aldine data from Aug. 6 – Oct. 1, 2021

Variable	N	Mean	Std Dev	Minimum	Maximum
UWB-Benzene	145	0.387	0.395	0.016	2.553
UWB-Toluene	145	0.455	0.377	0.018	2.712
UWB-Isopentane	145	2.332	3.093	0.047	19.215
UWB-n-pentane	145	1.801	1.895	0.038	11.565
UWB-Acetonitrile	54	0.293	0.328	0.003	1.699
UWB-Acetone	91	1.538	0.842	0.423	5.944
AC 640 nm	237	4.800	3.131	0.592	17.969
AC 520 nm	237	5.924	3.879	0.756	22.740
AC 365 nm	237	9.087	6.380	1.221	39.121
AAE	237	1.102	0.165	0.721	1.673
SC 635 nm	237	23.995	13.428	4.978	72.435
SC 525 nm	237	31.163	18.363	6.425	98.043
SC 450 nm	237	38.154	23.378	7.558	120.053
SAE	237	1.260	0.522	0.029	2.160

Table 4 Pearson correlation coefficients, with associated p-value: Prob > |r| under H0: ρ=0

	Benzene	Toluene	Isopentane	N-pentane	Acetonitrile	Acetone	AC640 nm	AC520 nm	AC365 nm	AAE	SC635 nm	SC525 nm	SC450 nm	SAE
Benzene		**0.715**	0.582	0.570	0.604	0.409	0.482	0.490	0.511	0.162	0.163	0.224	0.257	0.260
		<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	0.0523	0.0508	0.0068	0.0018	0.0016
Toluene	0.715		0.790	0.744	0.815	0.334	0.705	0.717	0.747	0.288	0.392	0.447	0.472	0.259
	<.0001		<.0001	<.0001	<.0001	0.0012	<.0001	<.0001	<.0001	0.0005	<.0001	<.0001	<.0001	0.0016
Isopentane	0.582	0.790		0.966	0.831	0.170	0.574	0.590	0.641	0.400	0.389	0.413	0.422	0.159
	<.0001	<.0001		<.0001	<.0001	0.1069	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	0.0555
N-pentane	0.570	0.744	0.966		0.833	0.283	0.535	0.549	0.594	0.376	0.381	0.400	0.408	0.140
	<.0001	<.0001	<.0001		<.0001	0.0066	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	0.0935
Acetonitrile	0.604	0.815	0.831	0.833		.	0.709	0.720	0.748	0.489	0.535	0.535	0.546	0.245
	<.0001	<.0001	<.0001	<.0001		.	<.0001	<.0001	<.0001	0.0002	<.0001	<.0001	<.0001	0.0748
Acetone	0.409	0.334	0.170	0.283	.		0.203	0.196	0.206	-0.107	0.407	0.512	0.553	0.359
	<.0001	0.0012	0.1069	0.0066	.		0.054	0.0628	0.0506	0.314	<.0001	<.0001	<.0001	0.0005
AC640nm	0.482	0.705	0.574	0.535	0.709	0.203		**0.999**	**0.978**	0.092	0.537	0.608	0.644	0.411
	<.0001	<.0001	<.0001	<.0001	<.0001	0.054		**<.0001**	**<.0001**	0.1568	<.0001	<.0001	<.0001	<.0001
AC520nm	0.490	0.717	0.590	0.549	0.720	0.196	**0.999**		**0.986**	0.125	0.533	0.602	0.639	0.403
	<.0001	<.0001	<.0001	<.0001	<.0001	0.0628	**<.0001**		**<.0001**	0.0555	<.0001	<.0001	<.0001	<.0001
AC365nm	0.511	0.747	0.641	0.594	0.748	0.206	**0.978**	**0.986**		0.227	0.530	0.598	0.635	0.388
	<.0001	<.0001	<.0001	<.0001	<.0001	0.0506	**<.0001**	**<.0001**		0.0004	<.0001	<.0001	<.0001	<.0001
AAE	0.162	0.288	0.400	0.376	0.489	-0.107	0.092	0.125	0.227		0.123	0.041	0.006	-0.367
	0.0523	0.0005	<.0001	<.0001	0.0002	0.314	0.1568	0.0555	0.0004		0.0594	0.5288	0.9253	<.0001
SC635nm	0.163	0.392	0.389	0.381	0.535	0.407	0.537	0.533	0.530	0.123		**0.977**	**0.945**	0.086
	0.0508	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	0.0594		**<.0001**	**<.0001**	0.1896
SC525nm	0.224	0.447	0.413	0.400	0.535	0.512	0.608	0.602	0.598	0.041	**0.977**		**0.993**	0.274
	0.0068	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	0.5288	**<.0001**		**<.0001**	<.0001
SC450nm	0.257	0.472	0.422	0.408	0.546	0.553	0.644	0.639	0.635	0.006	**0.945**	**0.993**		0.375
	0.0018	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	0.9253	**<.0001**	**<.0001**		<.0001
SAE	0.260	0.259	0.159	0.140	0.245	0.359	0.411	0.403	0.388	-0.367	0.086	0.274	0.375	
	0.0016	0.0016	0.0555	0.0935	0.0748	0.0005	<.0001	<.0001	<.0001	<.0001	0.1896	<.0001	<.0001	

The data show very tight agreement among the wavelength bands among the absorption coefficients (AC) and very tight agreement among the wavelength bands among the scattering coefficients (SC). Out of 91 paired comparisons between pairs of variables, 61 are significant at $p < 0.0001$. Taking out the 6 comparisons just noted (3 AC and 3 SC), that is 55 out of 85 or 65 percent of the variables have very significant correlations.

This examination only included the UW data from HRM #3 and the Aldine Baylor data. It may be valuable in examining the associations among the Aldine, Liberty, and Galveston data with the UW HRM #3 data to diagnose mesoscale smoke/fire as opposed to what in some cases may be local micro-scale events.

Table 5 lists the pairwise correlations between the AC and SC values, the large majority of which are strongly significant, and Table 6 lists the few pairs that are less well related. The highest correlations, which would be expected, are AC with AC and SC with SC variables, with a large drop in correlation (rho) in Table 5 indicated by a darker line after the sixth row in the table.

Table 5 Pairwise Pearson correlations and very low P-values for AC and SC variables

Var 1	Var 2	Rho	Signif.
AC640nm	AC520nm	0.999	<.0001
SC525nm	SC450nm	0.993	<.0001
AC520nm	AC365nm	0.986	<.0001
AC640nm	AC365nm	0.978	<.0001
SC635nm	SC525nm	0.977	<.0001
SC635nm	SC450nm	0.945	<.0001
AC640nm	SC450nm	0.644	<.0001
AC520nm	SC450nm	0.639	<.0001
AC365nm	SC450nm	0.635	<.0001
AC640nm	SC525nm	0.608	<.0001
AC520nm	SC525nm	0.602	<.0001
AC365nm	SC525nm	0.598	<.0001
AC640nm	SC635nm	0.537	<.0001
AC520nm	SC635nm	0.533	<.0001
AC365nm	SC635nm	0.530	<.0001
AC640nm	SAE	0.411	<.0001
AC520nm	SAE	0.403	<.0001
AC365nm	SAE	0.388	<.0001
SC450nm	SAE	0.375	<.0001
SC525nm	SAE	0.274	<.0001
AC365nm	AAE	0.227	0.0004

Table 6 Pairwise Pearson correlations and less significant P-values or negative correlations for AC and SC variables

Var 1	Var 2	Rho	Signif.
AC520nm	AAE	0.125	0.0555
AAE	SC635nm	0.123	0.0594
AC640nm	AAE	0.092	0.1568
SC635nm	SAE	0.086	0.1896
AAE	SC525nm	0.041	0.5288
AAE	SC450nm	0.006	0.9253
AAE	SAE	-0.367	<.0001

Table 7 lists the pairwise correlations among the VOCs and OVOCs, all of which are statistically significant with low p-values except for the pair isopentane and acetone with correlation 0.17 and p-value 0.11.

Table 7 Pairwise Pearson correlations and very low P-values for VOC and OVOC variables

Var 1	Var 2	Rho	Signif
Isopentane	N-pentane	0.966	<0.0001
N-pentane	Acetonitrile	0.833	<0.0001
Isopentane	Acetonitrile	0.831	<0.0001
Toluene	Acetonitrile	0.815	<0.0001
Toluene	Isopentane	0.790	<0.0001
Toluene	N-pentane	0.744	<0.0001
Benzene	Toluene	0.715	<0.0001
Benzene	Acetonitrile	0.604	<0.0001
Benzene	Isopentane	0.582	<0.0001
Benzene	N-pentane	0.570	<0.0001
Benzene	Acetone	0.409	<0.0001
Toluene	Acetone	0.334	0.0012
N-pentane	Acetone	0.283	0.0066

Finally, Table 8 lists the highest correlations for VOC/OVOC variables with AC/SC variables, and Table 9 lists the lowest correlations for VOC/OVOC variables with AC/SC variables.

Table 8 Highest correlations of VOC/OVOC variables with AC/SC variables

Var 1	Var 2	Rho	Signif
Acetonitrile	AC365nm	0.748	0.00007
Toluene	AC365nm	0.747	0.00007
Acetonitrile	AC520nm	0.702	0.00007
Toluene	AC520nm	0.717	0.00007
Acetonitrile	AC640nm	0.709	0.00007
Toluene	AC640nm	0.705	0.00007
Isopentane	AC365nm	0.641	0.00007
N-pentane	AC365nm	0.594	0.00007
Isopentane	AC520nm	0.590	0.00007
Isopentane	AC640nm	0.574	0.00007
Acetone	SC450nm	0.553	0.00007
N-pentane	AC520nm	0.549	0.00007
Acetonitrile	SC450nm	0.546	0.00007
N-pentane	AC640nm	0.535	0.00007
Acetonitrile	SC635nm	0.535	0.00007
Acetonitrile	SC525nm	0.535	0.00007
Acetone	SC525nm	0.512	0.00007
Benzene	AC365nm	0.511	0.00007
Benzene	AC520nm	0.490	0.00007
Acetonitrile	AAE	0.489	0.0002
Benzene	AC640nm	0.482	0.00007
Toluene	SC450nm	0.472	0.00007
Toluene	SC525nm	0.447	0.00007
Isopentane	SC450nm	0.422	0.00007
Isopentane	SC525nm	0.413	0.00007
N-pentane	SC450nm	0.408	0.00007
Acetone	SC635nm	0.407	0.00007
Isopentane	AAE	0.400	0.00007
N-pentane	SC525nm	0.400	0.00007
Toluene	SC635nm	0.392	0.00007
Isopentane	SC635nm	0.389	0.00007
N-pentane	SC635nm	0.381	0.00007
N-pentane	AAE	0.376	0.00007
Acetone	SAE	0.359	0.0005
Toluene	AAE	0.288	0.0005
Benzene	SAE	0.260	0.0016
Toluene	SAE	0.259	0.0016
Benzene	SC450nm	0.257	0.0018
Benzene	SC525nm	0.224	0.0068

Table 9 Lowest correlations of VOC/OVOC variables with AC/SC variables

Var 1	Var 2	Rho	Signif
Acetonitrile	SAE	0.245	0.0748
Acetone	AC365nm	0.206	0.0506
Acetone	AC640nm	0.203	0.054
Acetone	AC520nm	0.196	0.0628
Benzene	SC635nm	0.163	0.0508
Benzene	AAE	0.162	0.0523
Isopentane	SAE	0.159	0.0555
N-pentane	SAE	0.14	0.0935
Acetone	AAE	-0.107	0.314

3.7 TAP and Nephelometer time series

In the figures that follow, the Aldine 5-minute TAP and nephelometer data are graphed. The only notable point may be that the TAP and nephelometer variables do reflect higher values during the two September episodes of Sept. 8-9 and Sept. 25-26, especially Figure 29 through Figure 31 for the nephelometer data and the negative values in Figure 32.

Figure 25 TAP 640 nm time series for August and September 2021

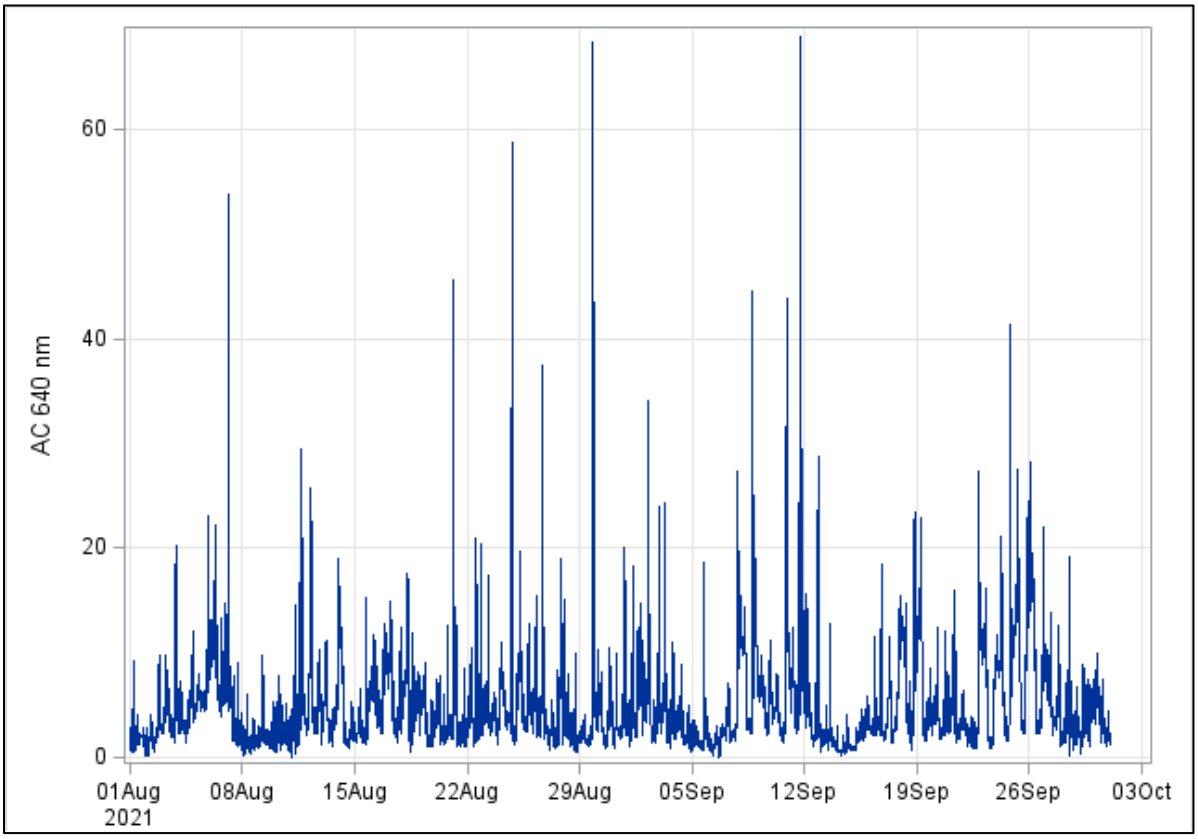


Figure 26 TAP 520 nm time series for August and September 2021

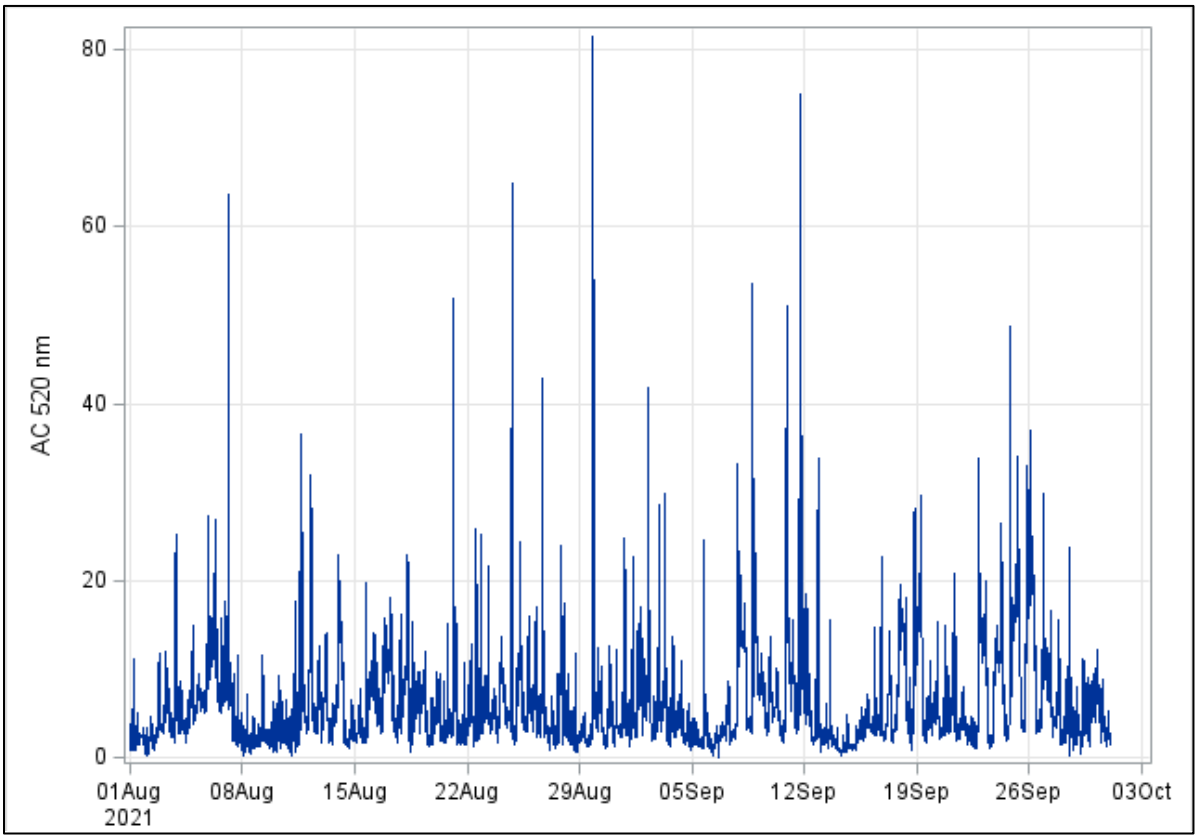


Figure 27 TAP 365 nm time series for August and September 2021

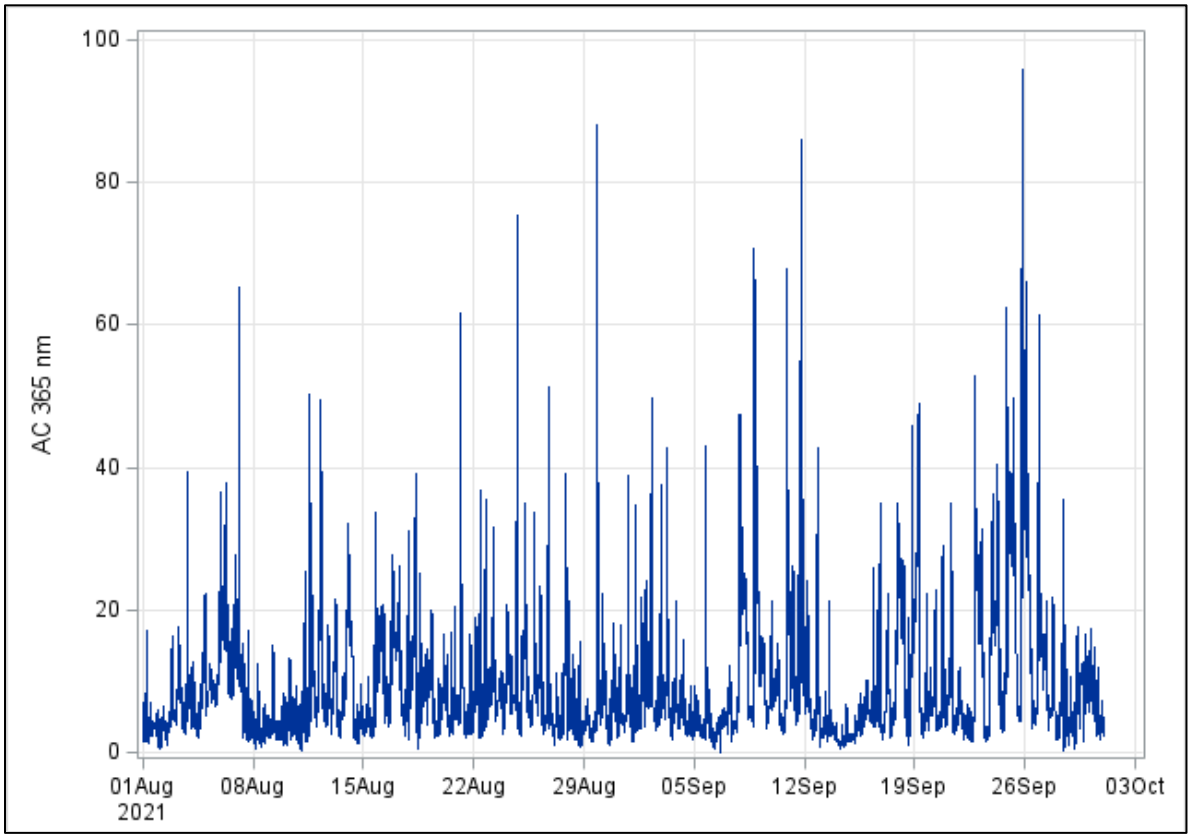


Figure 28 TAP AAE time series for August and September 2021

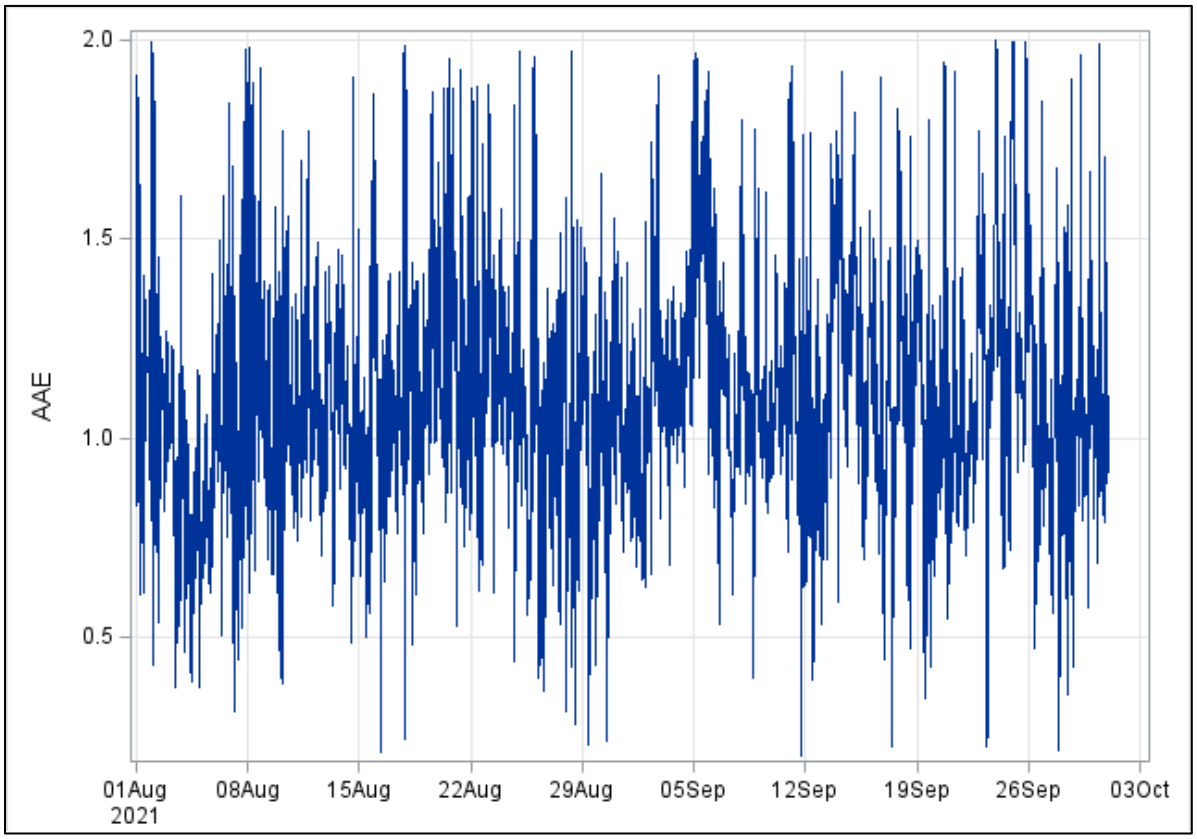


Figure 29 Nephelometer 635 nm time series for August and September 2021

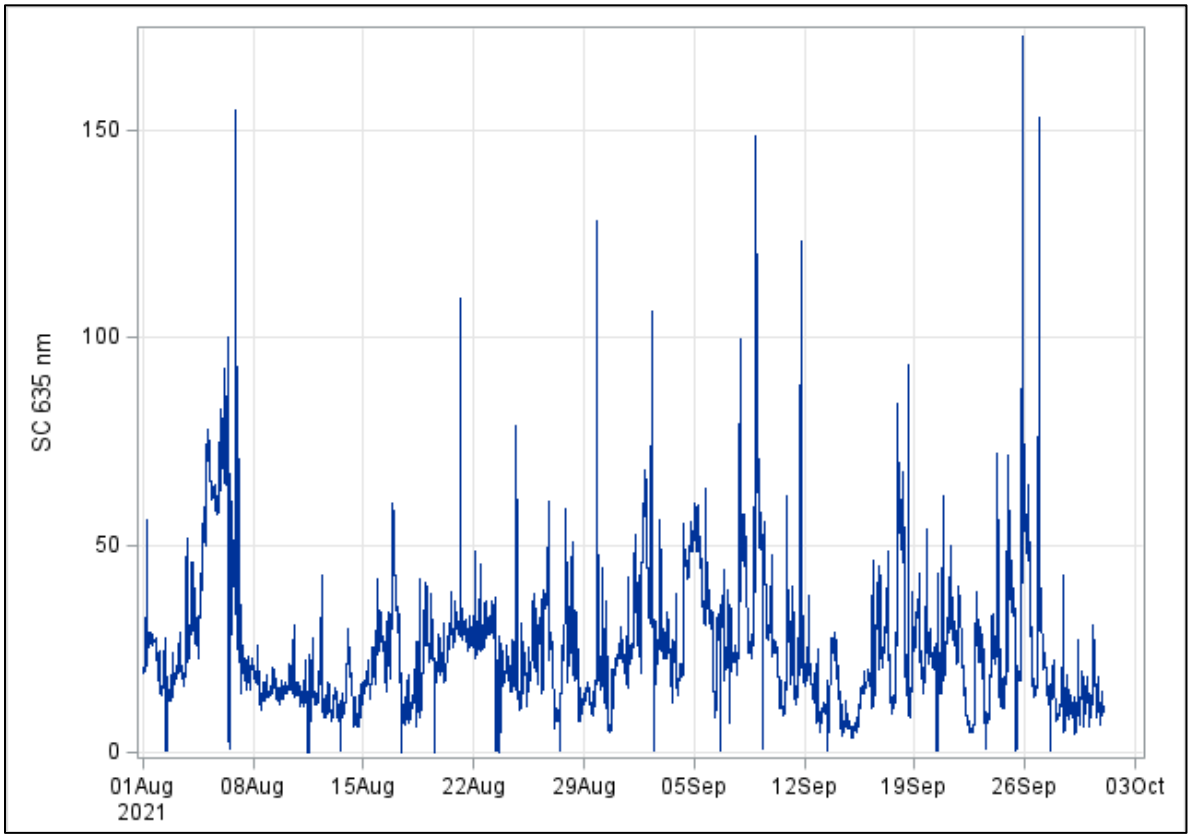


Figure 30 Nephelometer 525 nm time series for August and September 2021

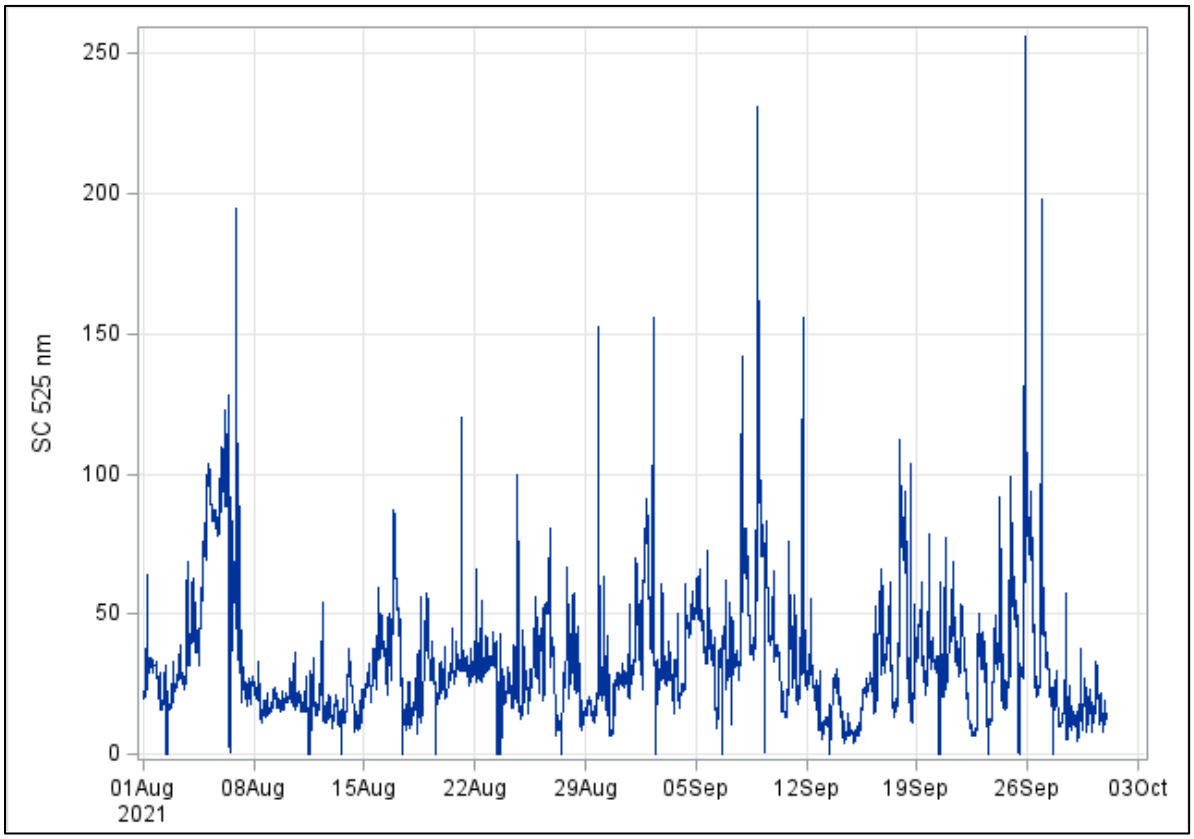


Figure 31 Nephelometer 450 nm time series for August and September 2021

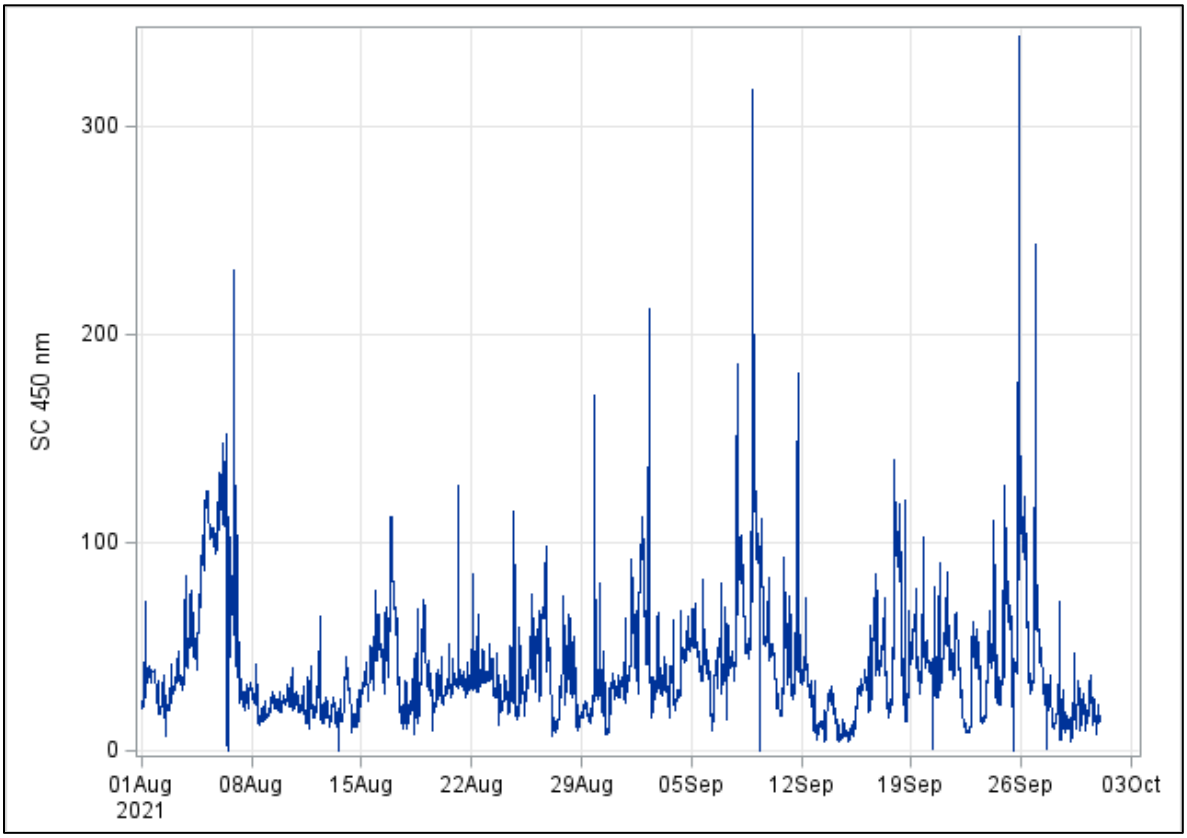
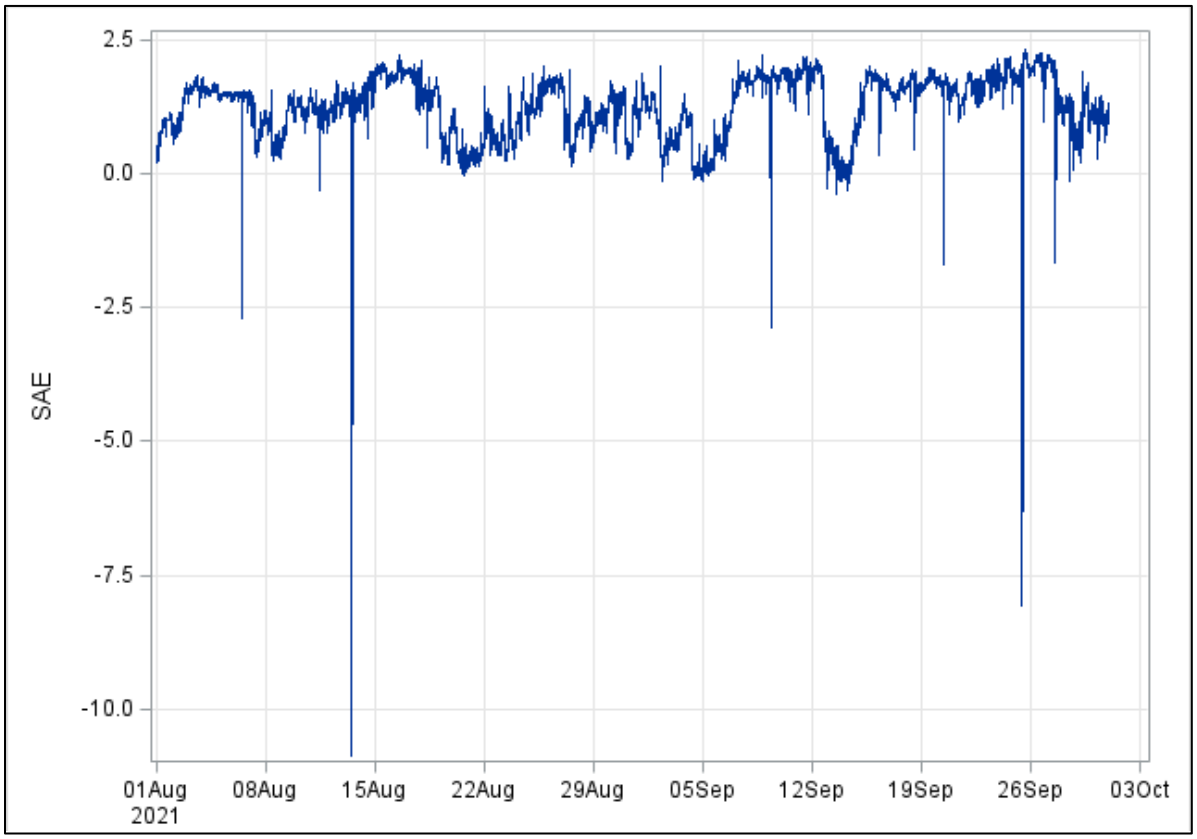


Figure 32 Nephelometer SAE time series for August and September 2021



4. Conclusions

Overall, the best comparison among species was with benzene measurements. Several dates were identified as having smoke effects, which likely affected ozone concentrations, these being Sept. 8-9 and 25-26, 2021 and possibly surrounding dates.