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The University of Texas at Austin

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Biogenic Isoprene Monitoring Study

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1. Background

The Texas Commission on Environmental Quality (TCEQ) and other organizations have found that biogenic emission computer models over-predict isoprene (C_5H_8) concentrations compared with measurements from urban surface Automated Gas Chromatograph (auto-GC) monitors. TCEQ's existing network of auto-GCs are in urban areas or locations without significant isoprene emitters (oak forests). Accurate information as to isoprene concentrations is important in accurately computer-modeling ozone concentrations. This project will provide hourly, or higher frequency, biogenic isoprene and meteorological observations at a monitoring site for two summer ozone seasons. The monitoring location is sited where TCEQ's biogenic emission model predicts elevated concentrations, which will help evaluate the performance of the biogenic and photochemical computer model results. Summary of Activities from July 2015 to February 2018 is shown in Section 2. The original project description appears in Section 3. A summary of the collected isoprene data appears in Section 4. Section 5 is a detailed description of the isoprene instrument and how it operates. A short summary of findings appears in Section 6.

1.1 Monitoring Instruments

UT is responsible for site operation and maintenance and data collection for the instruments listed in Table 1.

Table 1 Measurements taken for this project

Instruments	Parameter	Time resolution	Planned period of operation
Peak Performer 1 Reducing Compound Photometer (RCP) 910-132 isoprene instrument	Isoprene (C_5H_8), parts per billion carbon (ppbC)	5-minutes & 1-hour	Mar. 2016 – Oct. 2016, Mar. 2017 – Oct. 2017
Meteorology Climatronics 460	Wind speed mph, wind direction degrees, ambient temperature, degrees F	5-minute & 1-hour	Mar. 2016 – Oct. 2016, Mar. 2017 – Oct. 2017
Photosynthetically active radiation (PAR) instrument	Spectral range from 400 to 700 nm, in $\mu\text{mol (photons)} \text{ m}^{-2} \text{ s}^{-1}$	5-minute & 1-hour	Mar. 2016 – Oct. 2016, Mar. 2017 – Oct. 2017
Solar radiation pyranometer	Solar energy in the visible range in langleys/min.	5-minute & 1-hour	Mar. 2016 – Oct. 2016, Mar. 2017 – Oct. 2017

1.2 Big Thicket Radio Tower Site

This remote monitoring site at 30.5445, -94.3455 has electricity and unimproved road access. Figure 1 shows a topographic map of the area and Figure 2 and Figure 3 show Google Earth Pro

aerial images of the site and the surrounding area. The site is 5 miles south of FM 1943 off the Bumstead Cemetery Rd (CR 4800), or 3 miles east of Hwy 69 on the Triple D Ranch Rd (CR 4780). Much, if not all, of the county roads in the area are unpaved. Figure 4 is a photo of the monitoring station and fenced pad site. At the end of the project the site will be restored to its original condition.

Figure 1 Topographic and land cover map of the area around the monitoring site

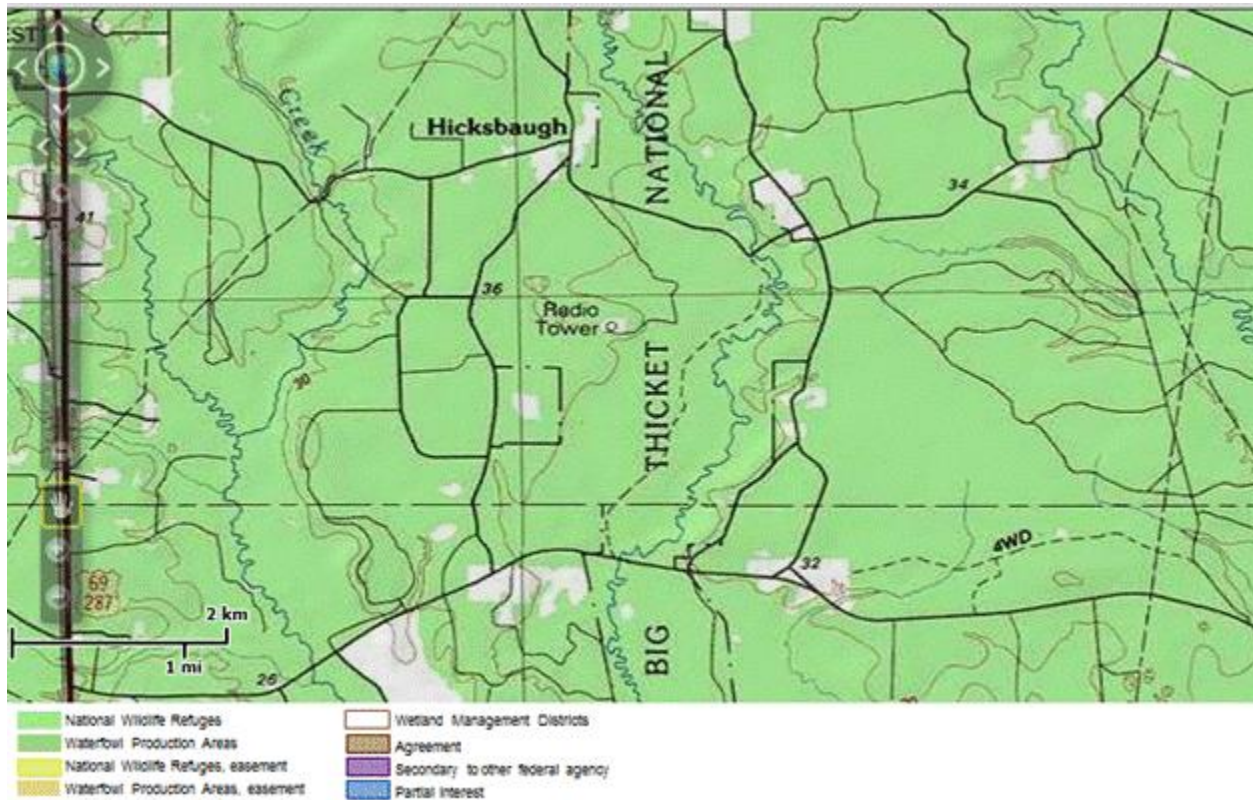


Figure 2 Location of Big Thicket isoprene monitoring site, 30.5446N, 94.3465W



Figure 3 Site is 34 miles NNW of Beaumont, a few miles (on unimproved roads) from the NPS HQ

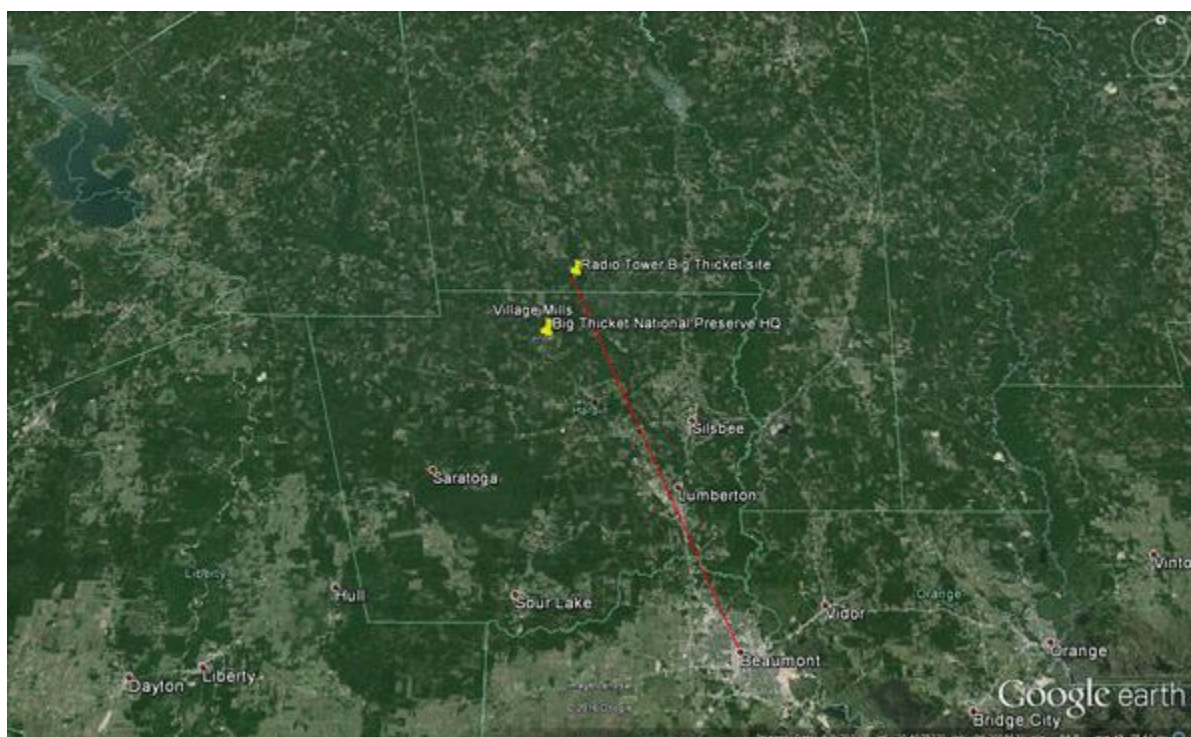


Figure 4 Big Thicket Radio Tower isoprene monitoring station and pad site



2. Summary of Major Activities

Table 2 summarizes major activities in the project and their associated deliverables to be sent to the TCEQ.

Table 2 Project deliverables and schedule

Deliverable	Deliverable Due Date
Grant Activities Description (GAD) (Task 1) Deliverable 1.1: TCEQ approved GAD Deliverable 1.2: TCEQ approved Quality Assurance Project Plan (QAPP)	July 24, 2015 July 24, 2015
Monitoring site evaluation (Task 2) Deliverable 2.1: Monitoring Site Proposal Report	September 1, 2015.
Isoprene and Meteorological Monitoring (Task 3) Deliverable 3.1: Monitoring Operations Report and Preliminary Data.	By the 15 th of each month (or the following workday if on weekend or holiday).starting October 2015 Monitoring March 15, 2016 – October 15, 2016, and March 15, 2017 – October 15, 2017
Data Validation (Task 4) Deliverable 4.1: Validated data	Within 60 days of the end of monitoring from Task 3
Final Report (Task 5) Deliverable 5.1: Draft Final Report Deliverable 5.2: Final Report	Draft January 25, 2018 Final February 8, 2018

Two additional sub-tasks had been added for 2017. During the summer of 2017, project operations was interrupted so the isoprene instrument could be moved to be collocated with a TCEQ monitoring station with an auto-GC that measures hourly isoprene concentrations along with 45 other hydrocarbon species. This intercomparison is part of the quality assurance for the instrument. Secondly, a permit request was made to do a tree survey in the area around the Big Thicket Radio Tower site during December 2017 and January 2018.

3. Scientific Approach

3.1 Experimental design

The project, at its beginning, was divided into five tasks:

Task 1: UT will compose the Grant Activities Description and Quality Assurance Project Plan.

Task 2: UT will evaluate TCEQ's network of CAMS sites in eastern Texas (east of 99° West Longitude) to determine if an existing CAMS location is sited where elevated biogenic isoprene concentrations are expected. In particular, UT will study data from 34 currently active automated gas chromatographs (auto-GCs) that measure hourly isoprene concentrations. An example of the method for evaluating existing sites is shown in Table 3. Table 3 shows the mean concentration of isoprene in parts per billion-carbon (ppbC) units from the TCEQ's Danciger site (Brazoria County, 29.149 N, 95.765 W) averaged over a 10 year period (2005 – 2015) and summarized by month and hour (Central Standard Time (CST)). By comparing all sites in this manner, the suitability of existing sites may be judged. Figure 5 shows a graph of the Table 3 data that provides another means to compare data from existing sites.

In addition, UT will use existing forest, land use, land cover, and biome data sources as well as biogenic emission modeling output to choose potential monitoring sites. An example of modeling output is shown in Figure 6. Information from various other studies of biogenic emissions will also be considered. Several research papers that are being reviewed are listed in the Reference section report.

Access to the site via developed roads; the availability of utilities, including internet; space for the monitoring trailer; and prevailing wind conditions will be considered. A proposal detailing at least three potential monitoring locations (including site photographs, utility connections, biogenic modeling isoprene emission estimates, forest type, and surrounding anthropogenic emission sources) will be delivered to the TCEQ project manager by September 1, 2015. UT expects that the site location will be chosen by the TCEQ Project Manager by September 15, 2015.

Table 3 Mean isoprene ppbC from Danciger, 2005 – 2015, by month and hour

CST	Jan.	Feb.	Mar.	Apr.	May	Jun.	Jul.	Aug.	Sep.	Oct.	Nov.	Dec.
0	0.02	0.03	0.04	0.12	0.22	0.66	0.52	0.57	0.40	0.25	0.10	0.04
1	0.02	0.03	0.04	0.12	0.20	0.53	0.45	0.39	0.36	0.22	0.08	0.04
2	0.03	0.02	0.04	0.14	0.22	0.36	0.35	0.49	0.31	0.20	0.09	0.04
3	0.03	0.02	0.04	0.13	0.21	0.35	0.33	0.46	0.22	0.18	0.09	0.04
4	0.02	0.03	0.04	0.12	0.20	0.35	0.38	0.39	0.23	0.16	0.08	0.04
5	0.02	0.03	0.05	0.12	0.19	0.38	0.40	0.39	0.21	0.14	0.08	0.04
6	0.02	0.03	0.05	0.22	1.04	3.38	2.68	1.38	0.42	0.16	0.07	0.04
7	0.02	0.03	0.08	0.71	2.52	6.75	6.91	7.04	3.62	1.20	0.16	0.05
8	0.03	0.05	0.13	0.97	2.66	5.24	5.57	6.43	4.93	2.58	0.52	0.08
9	0.05	0.05	0.16	1.10	3.07	5.19	4.72	5.01	4.31	2.19	0.60	0.11
10	0.05	0.06	0.24	1.47	3.76	5.72	5.23	5.58	4.28	2.03	0.52	0.11
11	0.05	0.06	0.35	1.81	4.34	6.59	6.45	6.19	4.54	2.19	0.55	0.11
12	0.06	0.08	0.45	2.08	4.66	6.91	6.88	6.77	4.95	2.27	0.59	0.12
13	0.06	0.09	0.52	2.14	4.74	7.64	7.53	7.48	5.17	2.37	0.61	0.13
14	0.06	0.09	0.50	2.04	4.78	8.02	7.60	8.15	5.23	2.40	0.59	0.13
15	0.05	0.08	0.44	1.80	4.54	7.97	8.18	8.24	5.29	2.33	0.52	0.11
16	0.04	0.07	0.36	1.52	4.17	7.82	8.46	8.48	5.05	2.40	0.48	0.10
17	0.04	0.06	0.26	1.27	3.44	7.28	7.88	8.54	5.24	2.80	0.59	0.11
18	0.03	0.04	0.17	1.09	2.73	6.53	7.13	8.18	4.15	1.87	0.37	0.09
19	0.03	0.03	0.09	0.66	1.51	4.09	4.63	4.58	2.20	1.11	0.25	0.06
20	0.03	0.02	0.06	0.44	0.81	2.11	2.23	2.42	1.24	0.76	0.19	0.05
21	0.02	0.02	0.05	0.29	0.54	1.28	1.24	1.41	0.80	0.53	0.14	0.04
22	0.02	0.02	0.05	0.20	0.41	0.88	0.82	0.94	0.60	0.43	0.12	0.04
23	0.02	0.02	0.04	0.16	0.33	0.67	0.64	0.70	0.48	0.33	0.11	0.04

Figure 5 Mean isoprene ppbC from Danciger, 2005 – 2015, by month and hour

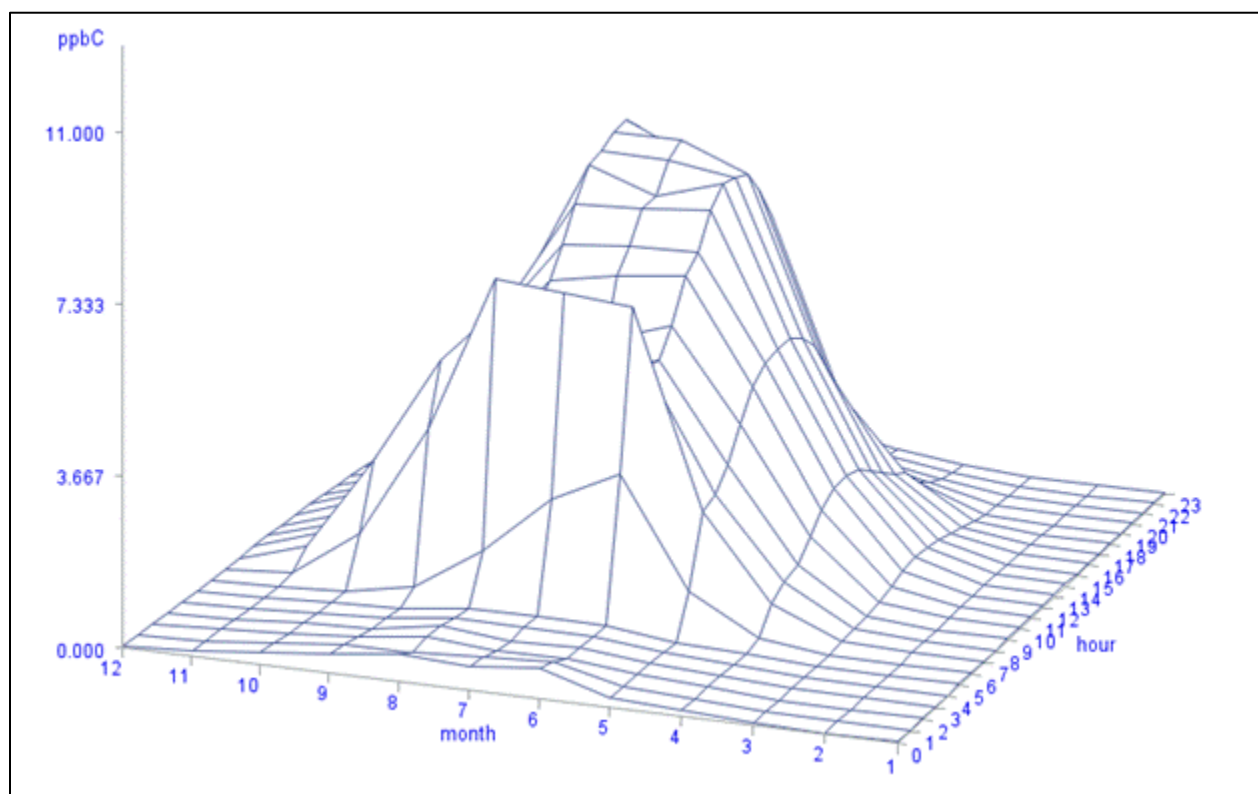
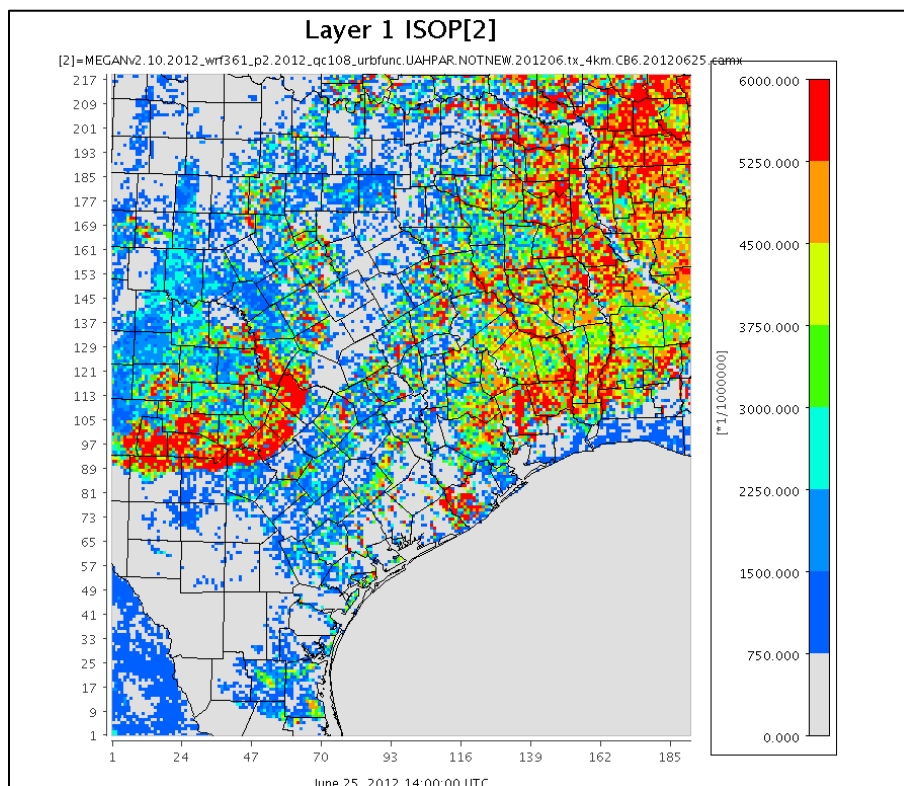


Figure 6 An example of isoprene modeling output from June 2012



Task 3: If the site selected is not a current TCEQ monitoring site, the UT will prepare a new site to accommodate the trailer and monitor. In the event of either a new site or additions to an existing site, fencing and other necessary measures will secure the site, and if necessary, utilities will be connected to the site. UT will install, calibrate, and operate the Peak Performer 1 Reducing Compound Photometer (RCP) isoprene instrument, photosynthetically active radiation (PAR) instrument, and standard meteorological instrumentation (wind direction, wind speed, temperature) for a period of one calendar year. All instruments will collect data at an hourly or higher frequency. UT will be responsible for operating and maintaining the entire site according to the current TCEQ QAPP for Ambient Air Monitoring in Texas for SLAMS/Border, PM_{2.5}, and PAMS Programs and the Photochemical Assessment Monitoring Stations (PAMS) Network QAPP for Ambient Air Monitoring in Texas. When an issue is noted by UT or TCEQ, including issues with the instruments, data, or monitoring trailer, UT or UT's contractor will be on site no later than 24 hours after the concern (for example, a broken instrument or extraordinarily elevated sampled data) is realized to assess the issue. The UT will work with instrument manufacturers to troubleshoot and repair instrument malfunctions, which may include returning the equipment to the factory or installing a replacement part. All site preparation and instrument installation/ calibration/ operation activities will be summarized in a monthly monitoring operations report. The previous month's preliminary collected data and monitoring operations report will be delivered to the TCEQ Project Manager in an agreed upon electronic format by the 15th of every month or the following workday if on a weekend or holiday, starting no later than October 15, 2015. The monitoring will occur April 15, 2016 to October 15, 2016 and April 15, 2017 to October 15, 2017.

Task 4: UT will validate the collected isoprene and meteorological data according to the TCEQ Monitoring Division Standard Operating Procedure (SOP) DQRP-016 for meteorology with appropriate modifications for vertical wind measurements and with isoprene data. Additional instructions will be created using the Peak Performer 1 RCP Isoprene Analyzer Operations Manual that is specific to this project. Accuracy and precision metrics for all collected parameters will be calculated. The collected data will be flagged according to the quality-assured level of the data; including times of calibration, in-operation, and/or lost data. The validated data will be delivered to the TCEQ Project Manager in an agreed upon electronic format within 60 days of end of monitoring.

In validating, analyzing, and summarizing data, UT will use SAS¹ software 9.4, MS Excel, NOAA HYSPLIT, Golden Software Surfer 13, Google Earth Pro, or other software application approved by TCEQ, provided UT and TCEQ hold existing licensing rights to such software application.

Task 5: UT will write a Final Report which will provide a comprehensive overview of activities undertaken and data collected and analyzed during the contract period. It will highlight major activities and key findings, provide pertinent analysis, describe encountered problems and associated corrective actions, and detail relevant statistics including parameter accuracy and precision. The report will include the data sources and raw data (provided on CD, flash memory drive, or FTP site). A draft of the final report will be submitted by January 25, 2018. The final report will be submitted by February 8, 2018.

4. Data Analyses

4.1 Ambient Isoprene Data

Figure 7 shows a time series graph of the one-hour time scale isoprene measurements taken at The Big Thicket site from March 2016 through October 2017, including the planned interruption over the 2016-2017 winter, outages owing to bad weather, and period of operation at other locations. The site recorded a maximum short term (5-minute) isoprene concentration on August 11, 2016 at 17:35 of 243 ppbC with a corresponding one-hour average of 227.6 ppbC for the hour starting at 17:00 CST. Figure 8 shows time series graphs for one-hour averaged isoprene, pyranometer (solar radiation), photosynthetic active radiation, humidity, and temperature, March 2016 to October 2016 and March 2017 to October 2017. Figure 8 is only intended to illustrate the time range of measurements and the range of values for each parameter.

The diurnal patterns for isoprene concentrations by month, with afternoon peak concentrations, and nighttime near-zero concentrations appears in Figures 9 and 10 for 2016 and in Figure 11 for 2017. In 2016, measurements were made from March well into October; graphs for these eight months are shown Figure 9. However, in 2017, insufficient data were taken at Big Thicket in July and August, so the six months March – June, September & October only are shown in Figure 10. Thus, Figure 10 is directly comparable with the six months in 2017 in Figure 11, from which can be drawn a conclusion that mean concentrations were generally lower in 2017

¹ SAS is not an abbreviation. SAS Institute has developed an extensive suite of software for statistical analyses for which TCEQ and UT hold separate and individual existing licensing rights.

compared to 2016. A similar finding was made in comparing the same six months in 2016 and 2017 at the TCEQ's Nederland High School CAMS 1035 auto-GC, although no significant difference was observed with TCEQ's Downtown Beaumont, which had similar mean concentrations between the two years.

Figure 7 Time series of Big Thicket 1-hour averaged isoprene initially coded “okay” and “ambient”, March 2016 – October 2016 and – March 2017 - October 2017

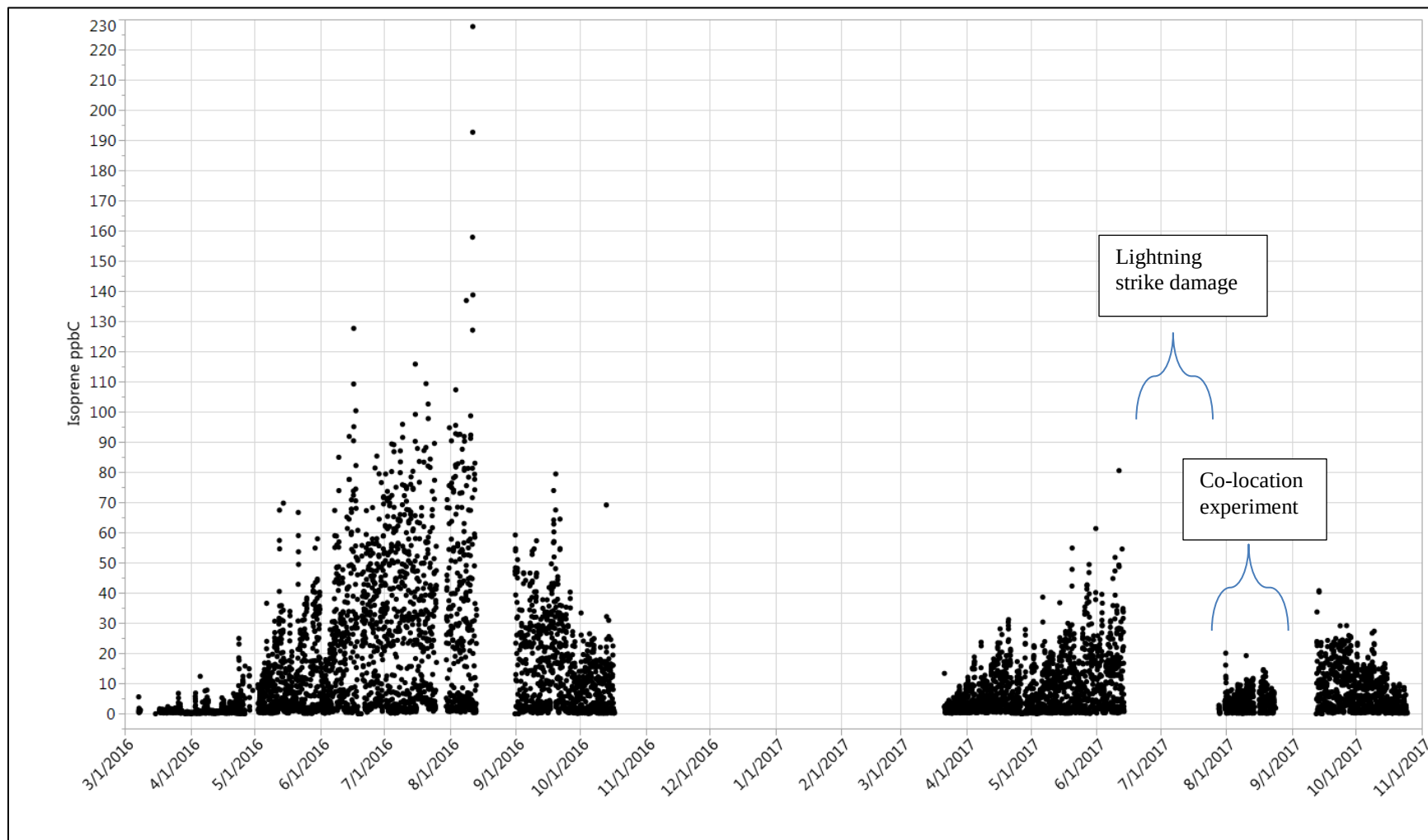


Figure 8 Time series of Big Thicket 1-hour averaged isoprene, pyranometer, photosynthetic active radiation, humidity, and temperature, March 2016 – October 2016 and – March 2017 - October 2017

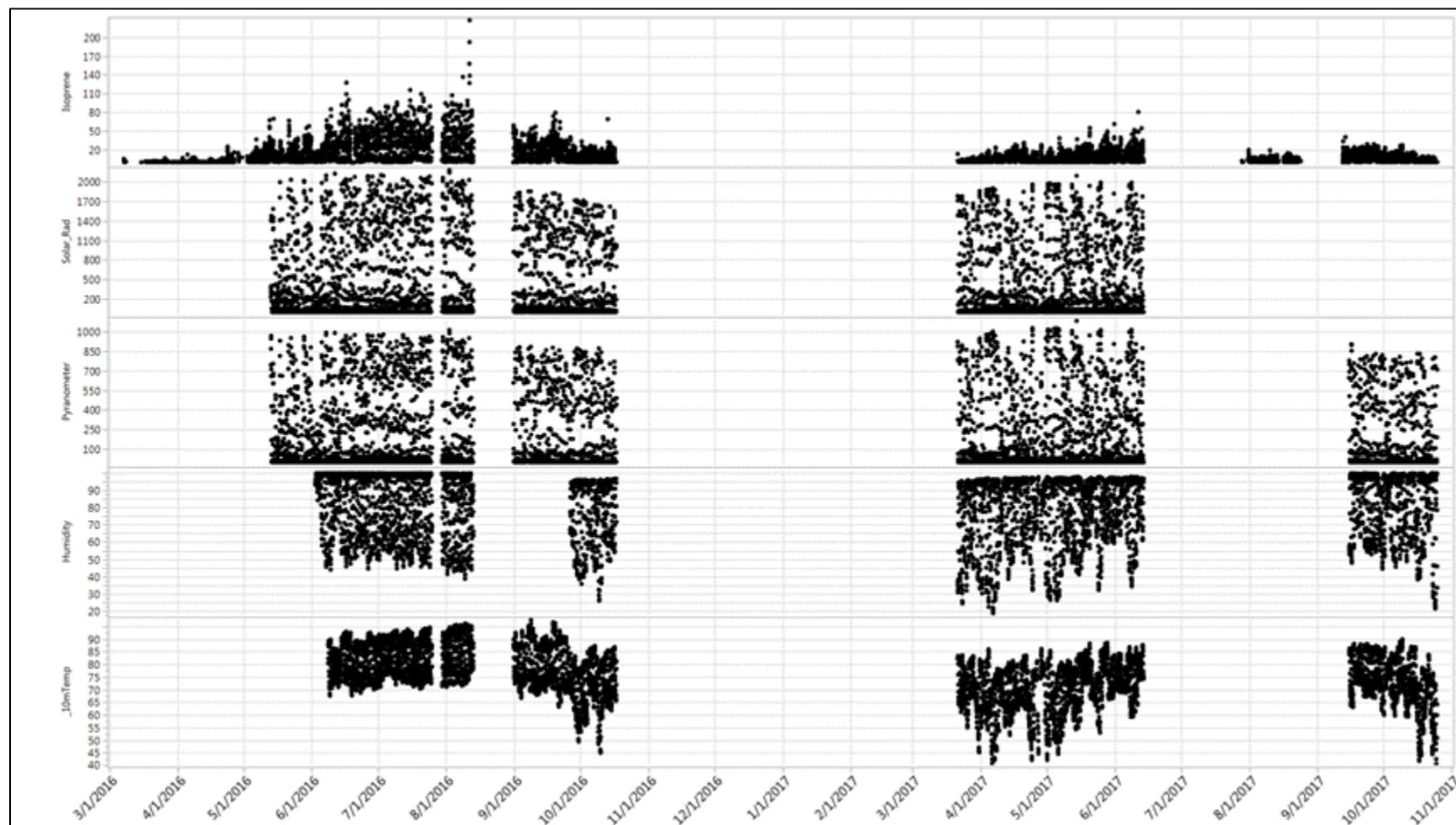


Figure 9 Diurnal patterns for isoprene at Big Thicket in 2016 by month

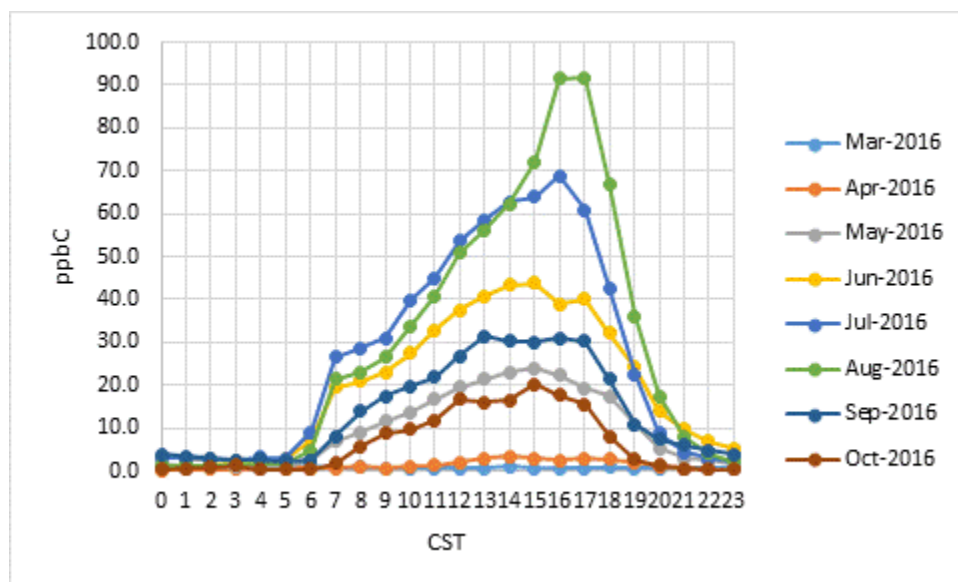


Figure 10 Diurnal patterns for isoprene at Big Thicket in 2016 by month excluding July & August

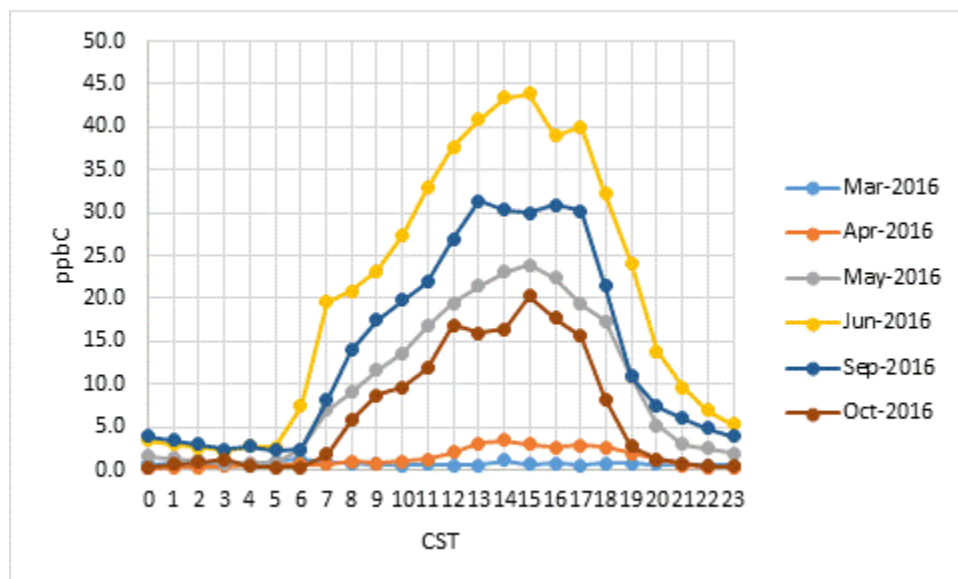
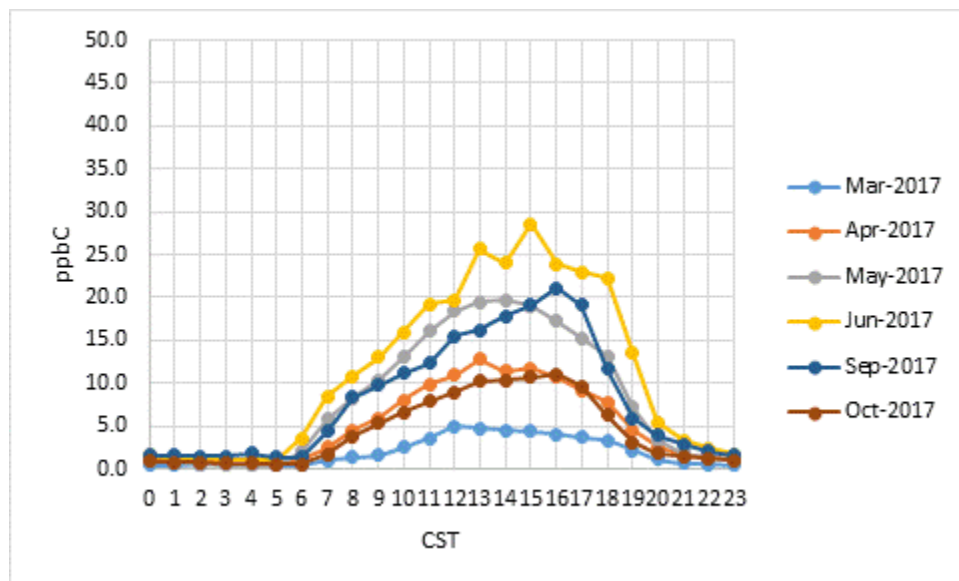


Figure 11 Diurnal patterns for isoprene at Big Thicket in 2017 by month



4.2 Colocation experiment

The Peak isoprene instrument and support gases were installed in late July 2017 at the TCEQ's CAMS 1035 Nederland High School in Beaumont in order to compare measurements from the Peak instrument to isoprene measurements among the suite of 46 hydrocarbon species measured by the automated gas chromatograph (auto-GC) at the Nederland High station. The equipment ran at CAMS 1035 from July 31 to August 14, 2017 and was disconnected and moved to CAMS 1016 Lake Jackson (TCEQ) in Brazoria County for a similar Peak to auto-GC comparison. At Lake Jackson the instrument ran from August 16 to August 23, 2017. Figures 12 and 13 show the aerial images of the two colocation experiment sites with a circle of radius 1.0 mile drawn around each site. Photos to the Nederland High School site are at <https://tinyurl.com/yc355gt9> and photos of the Lake Jackson site are at <https://tinyurl.com/y8ggamcr>.

On Thursday August 24, 2017, in advance of the approaching Hurricane Harvey, the Lake Jackson site was shut down. After the weather improved and conditions were safe, the Peak instrument was removed and reinstalled at the Big Thicket site on September 12, 2017.

Figure 14 shows the comparison hourly time series for the Peak instrument and the coincident Nederland auto-GC. Because the auto-GC takes a 40-minute sample, only the first 8 five-minute Peak measurements were used each hour to calculate the mean for that hour. Figure 15 shows the Nederland and Peak isoprene comparison on August 7, 2017, in which the two match well in terms of the increases and decreases in concentration, but the Peak concentrations were all greater than the auto-GC concentrations. Figure 16 shows the linear regression for the Nederland isoprene against the Peak isoprene 40 min averages, in which the correlation is excellent but the Peak instrument concentrations were systematically higher than the coincident auto-GC concentrations.

Figure 17 shows the comparison hourly time series for the Peak instrument and the coincident Lake Jackson auto-GC, and Figure 18 shows the linear regression comparison. Again, the

correlation is excellent but the Peak instrument concentrations were systematically higher than the coincident auto-GC concentrations, but the slope being closer to 1.0, the comparison was better than at Nederland. The comparison was carried out for only 8 days, owing to the imminent threat posed by Hurricane Harvey. The Lake Jackson site was shut down and secured on August 24.

UT asked Orsat to comment on the observed differences between the Peak instrument and the TCEQ auto-GCs. Their response follows:

The differences between the Peak and AutoGC absolute concentrations can possibly be attributed to several factors. The data I have on AutoGC recoveries for isoprene are all at concentrations of approximately 30 ppbC and at this level the recoveries are 90-95%. However, we have seen that losses in these systems due to adsorption result in reduced recoveries as the concentration goes down. That is, if the system loses 5% at 30 ppbC to adsorption on steel and sorbents then it is possible that the percent recovery will go down as the loss remains constant but becomes a larger percentage of the expected as the concentration goes down. The Peak instrument also does not use any type of sample drier as the AutoGC does which could also account for some losses at low levels.

In addition, no attempt was made to correlate possible differences in standards between the two systems although we did analyze both the isoprene standard from this year and last year against a propane standard we use in the lab to assure that they were within the certification spec supplied by the manufacturer. The blend tolerance for these standards is +/- 5%.

Figure 12 Nederland High School (TCEQ) in Jefferson County

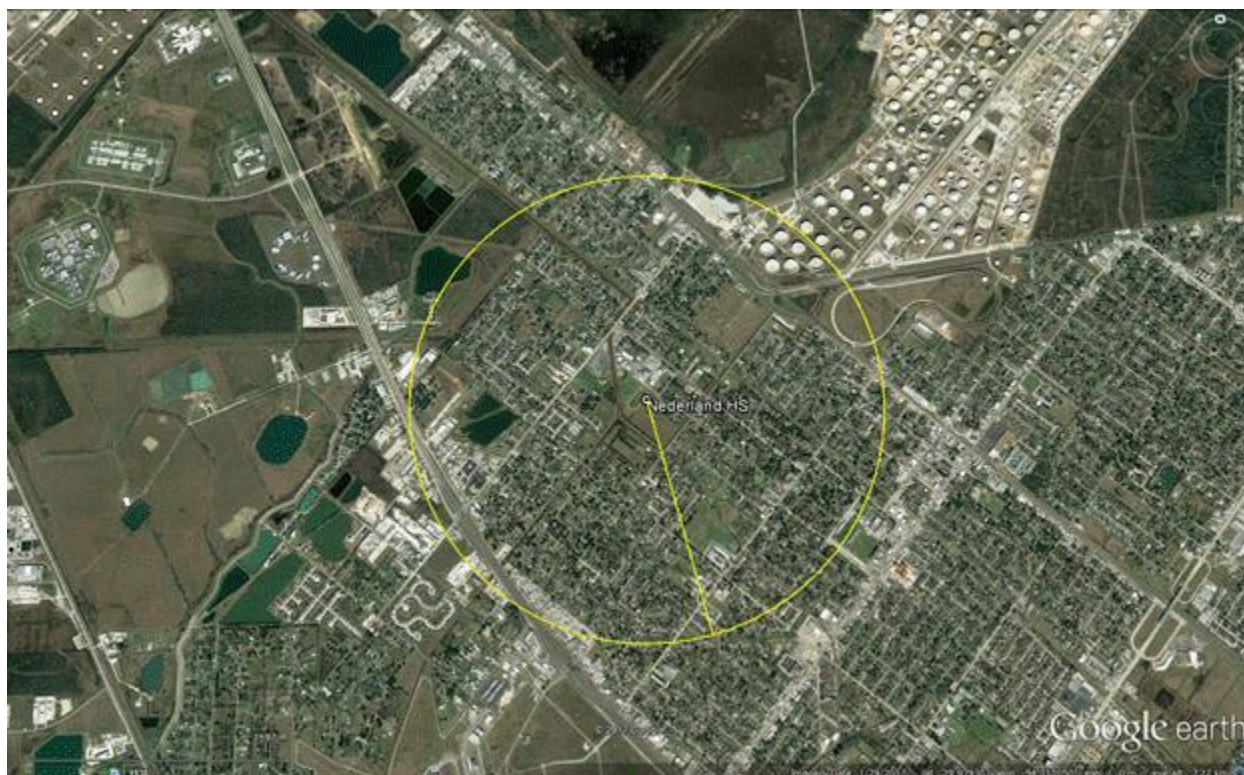


Figure 13 Lake Jackson (TCEQ) in Brazoria County



Figure 14 Nederland High School isoprene vs Peak isoprene 40 min averages time series

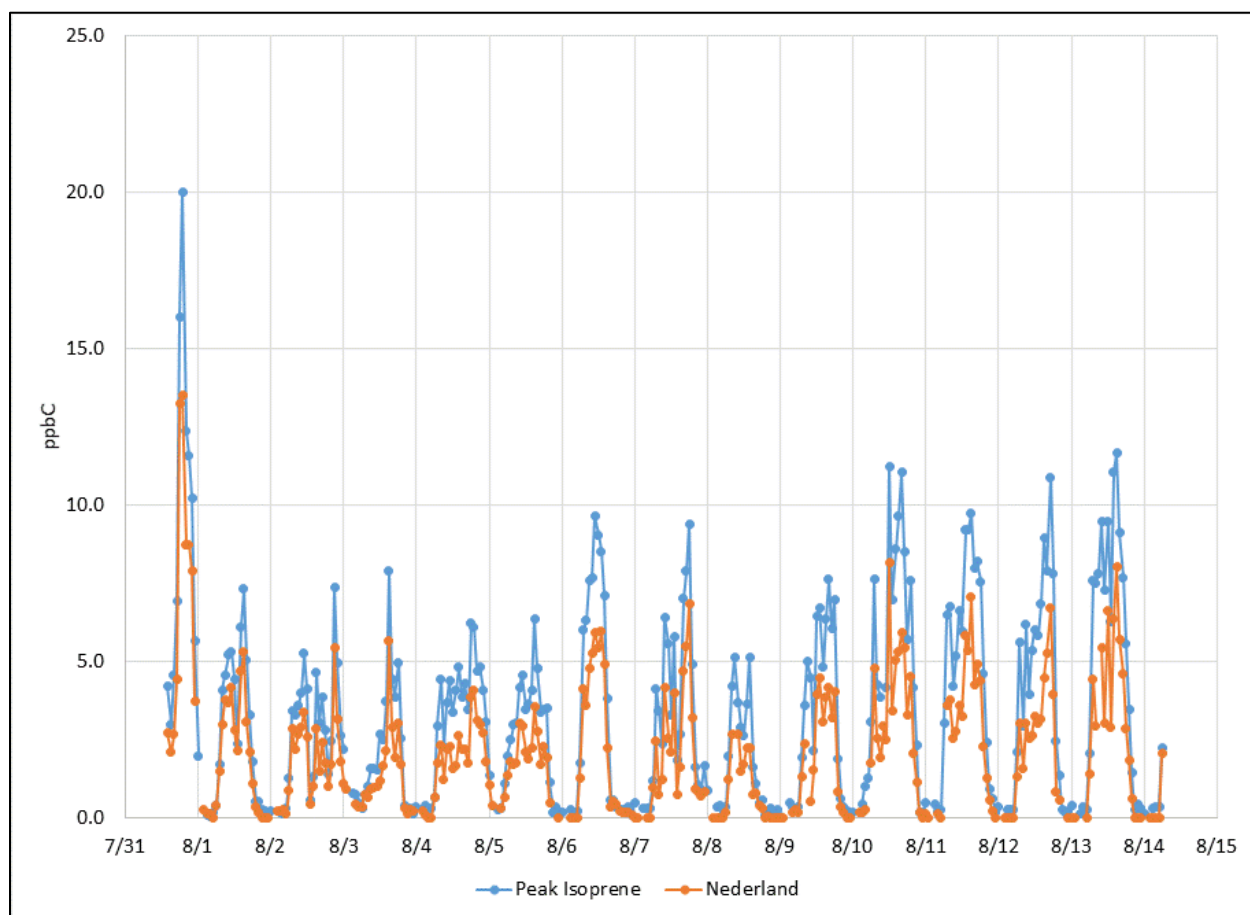


Figure 15 Nederland and Peak isoprene comparison on August 7, 2017

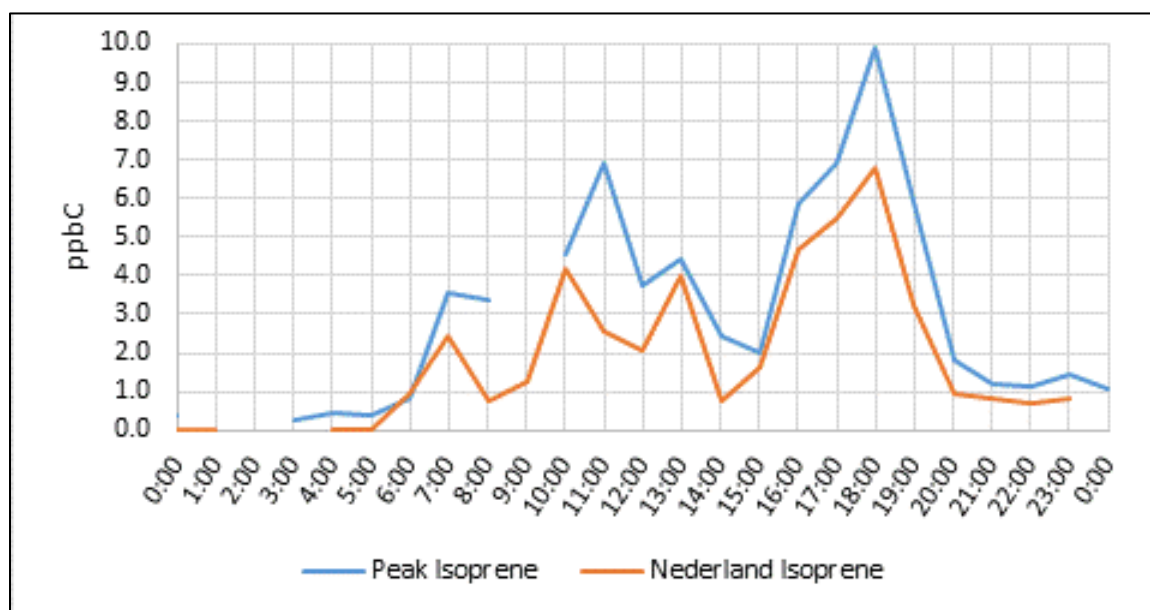


Figure 16 Nederland High School isoprene vs Peak isoprene 40 min averages scatterplot/regression

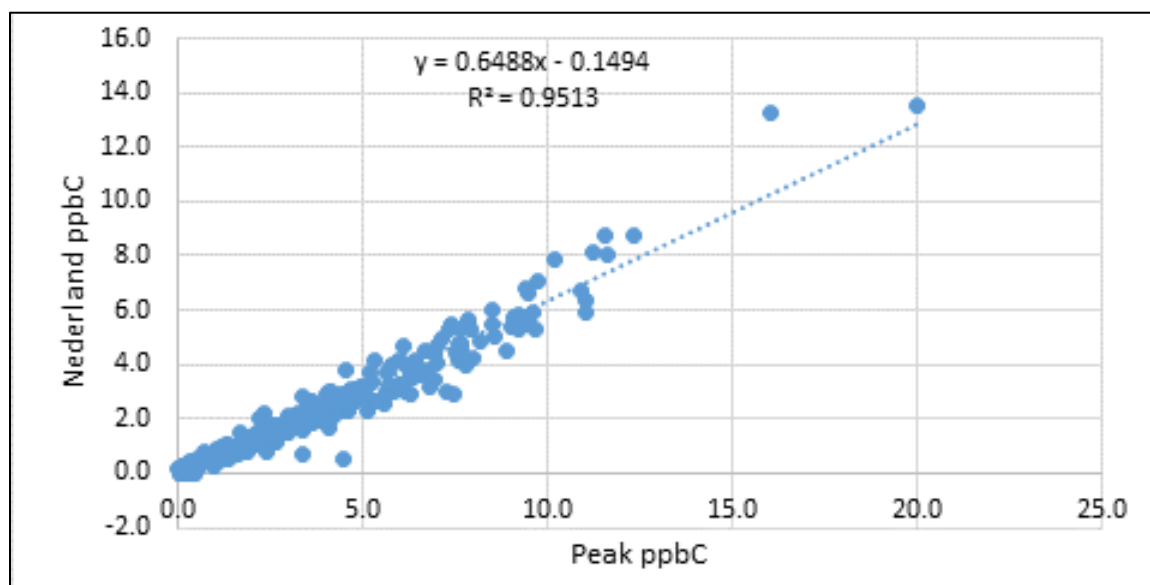


Figure 17 Lake Jackson isoprene vs Peak isoprene 40 min averages time series

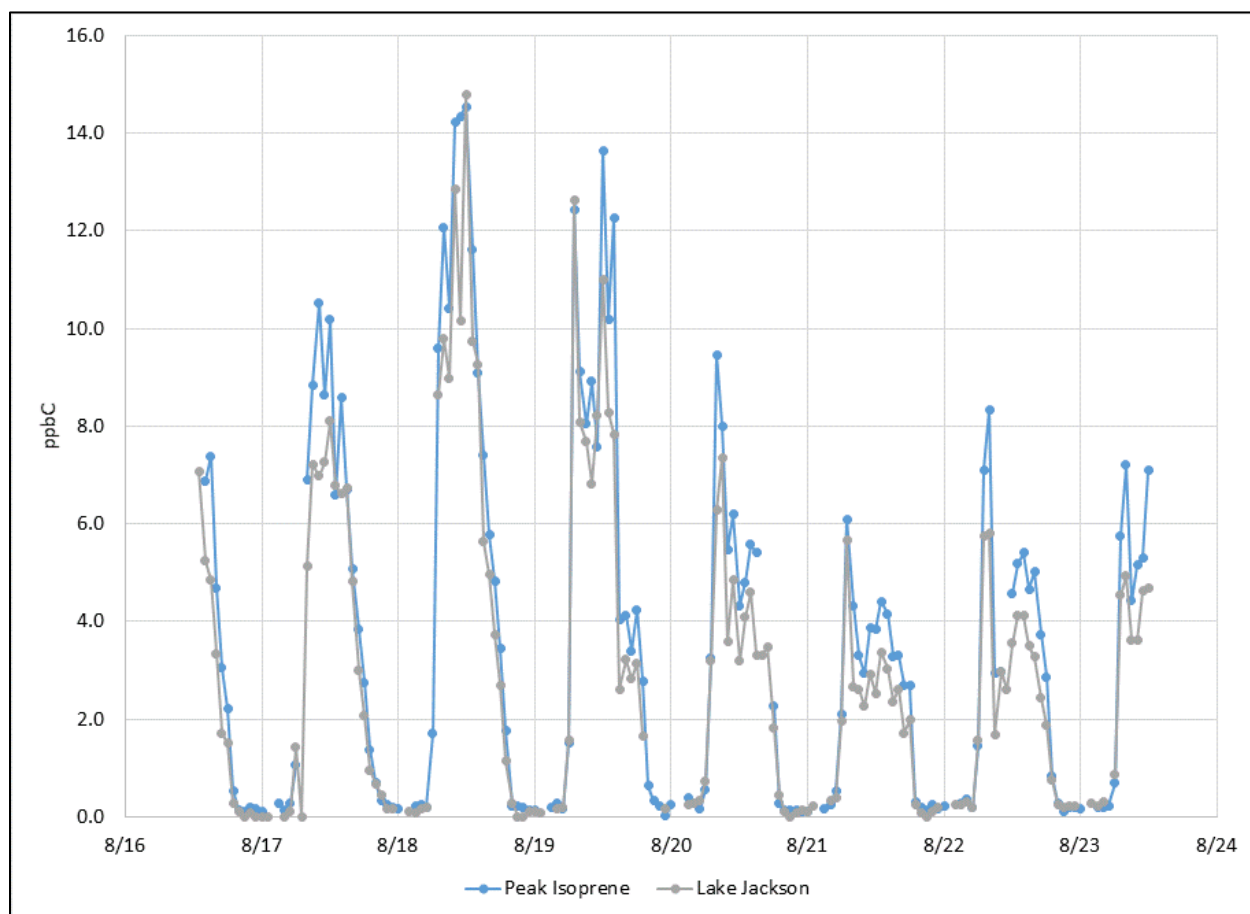
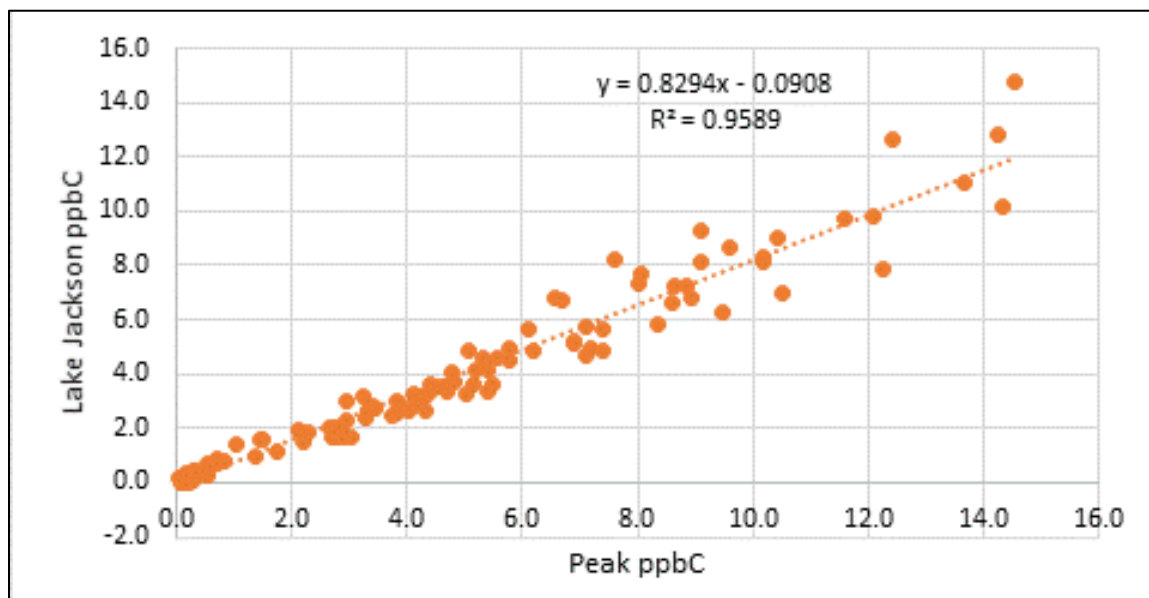


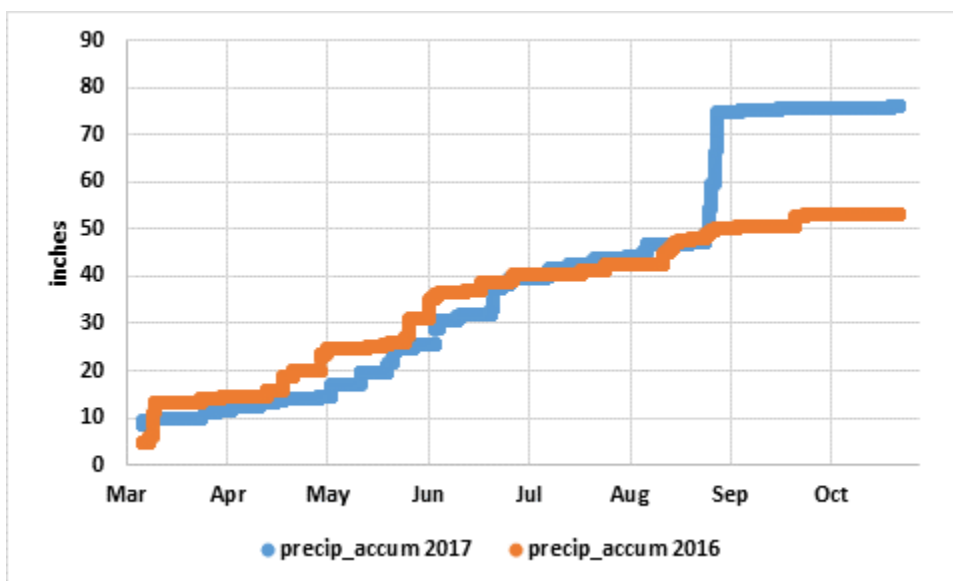
Figure 18 Lake Jackson isoprene vs Peak isoprene 40 min averages scatterplot/regression



4.3 Meteorological Data Collection

Figure 19 compares 2016 and 2017 rainfall at the Big Thicket as measured by the National Weather Service WRRT2 site located a few meters from the UT trailer. From early March through July, somewhat more rain fell in 2016 as opposed to 2017, but for most of the period from July through October, 2017 was wetter. In particular, Figure 19 shows the large increase in rainfall in 2017 from Hurricane Harvey in late-August 2017.

Figure 19 Rainfall to date each year, 2016 and 2017 at Big Thicket

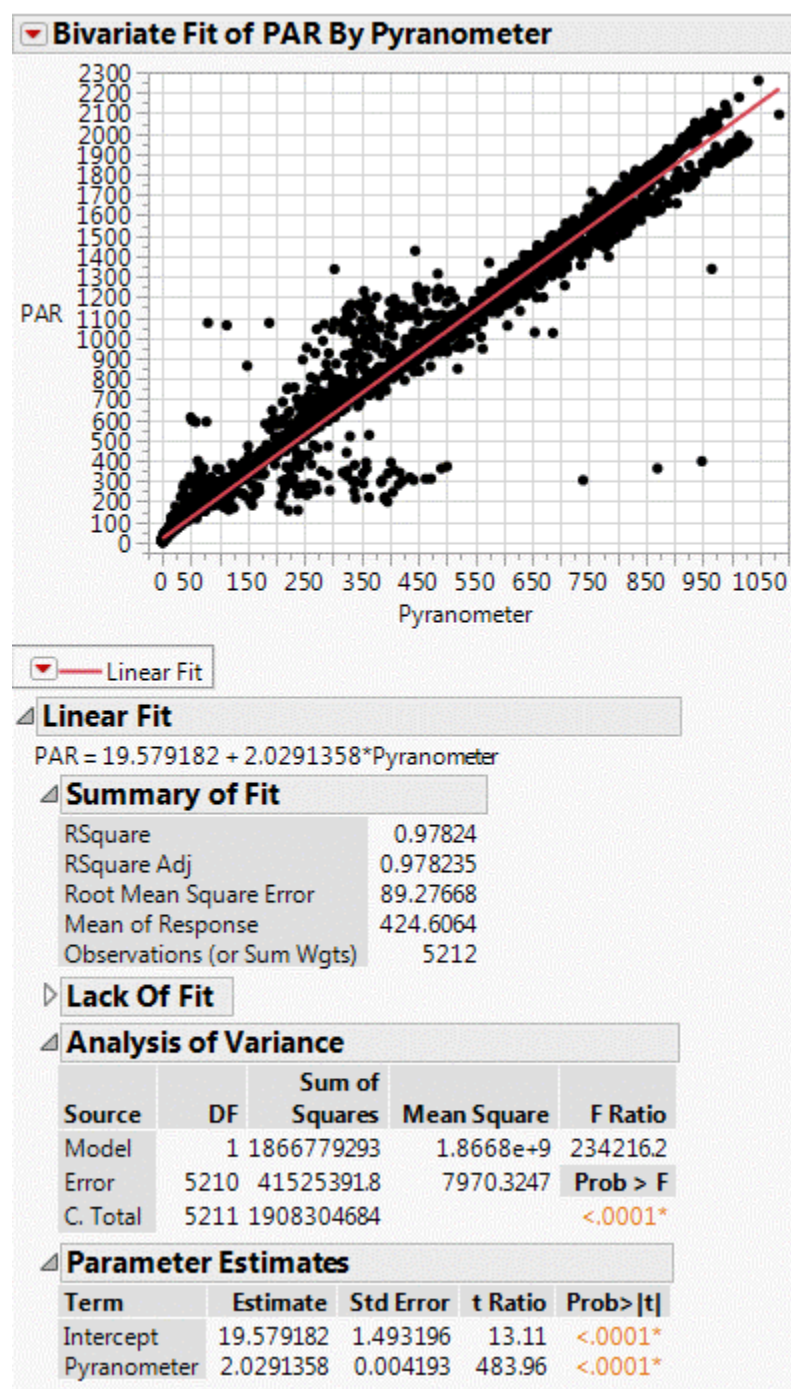


Work is ongoing in examining the photosynthetically active radiation (PAR) measurements, the solar radiation measurements, and the WRRT2 solar radiation measurements. Measurement of

PAR at UT's Big Thicket site was made with a sensor that measures light in the 400-700 nm waveband recorded in micromoles per square meter – second ($\mu\text{mol m}^{-2} \text{s}^{-1}$). These units are based on the number of photons in a certain waveband incident per unit time (s) on a unit area (m^2) divided by the Avogadro constant ($6.022 \times 10^{23} \text{mol}^{-1}$).

Figure 20 shows a regression of the PAR data to the solar radiation measurements at the UT site over the two years of measurements. Work is being done to isolate why there appears to be two different linear relationships in Figure 20 and the source of the seemingly random points in the figure.

Figure 20 PAR ($\mu\text{mol m}^{-2} \text{s}^{-1}$) vs solar radiation (Watts/m^2) at Big Thicket, all data



5. Isoprene Analysis in Ambient Air SOP (by Orsat LLC)

5.1 Description:

The Peak PP1 Analyzer monitors ambient air for isoprene. The PP1 is a chromatographic analyzer that uses dual Unibeads 1S columns in an isothermal oven connected to an RCP (reducing compound photometer) detector with Nitrogen carrier gas. The PP1 injects a 1cc sample onto the columns every 5 minutes. The columns are held at 115°C and sample is heart-cut to the detector which is at 265°C. The remaining sample is back flushed off the column to vent for 100 seconds to prepare the columns for the next injection. The system will run a daily calibration and blank to ensure the system is operating within specification. These quality controls are run between 1:00 and 2:00 am and controlled by the Sutron data logger. The analytical result from each cycle is sent via RS232 to the Sutron data logger along with wind speed, wind direction, temperature, humidity, solar radiation, and pyrometer readings from the meteorological equipment. The site is equipped with a broadband cellular modem to allow the automatic polling of the data logger. The analyzer is additionally connected to a computer which allows remote access and control of the analyzer and collects the chromatographic data.

The sample is collected from 3 meters above the ground using 1/8" SS Sulfinert® tubing attached to a 12" glass filter filled with glass wool for particulate filtration. The Sample line flow is controlled via a sample pump connected to the output of the sample manifold at 100mL/min. A sample at 50 mL/min is pulled from the manifold through the analyzer sample port and the residual 50mL/min flows by to vent. The dilution system is connected to the manifold with ~1ft 1/8" SS Sulfinert tubing and provides excess flow for calibration checks and blanks. Flow through the analyzer is controlled to 50mL using an MFC device. Excess flow on the manifold is controlled using a 1/8" adjustable rotameter.

Cautions: The PP1 uses a mercury bed which releases small amounts of mercury to vent. The mercury scrubber should be changed out every 6 months. The RCP detector uses an UV light source and caution should be exercised when handling/viewing source. Flow should be maintained on the detector whenever heat is applied to the mercury bed to prevent significant damage to the detector.

Safety: The PP1 has two headed zones and caution should be exercised when handling the oven and detector. The system utilizes several gas bottles and normal bottle handling practices should be used.

5.2 Equipment:

- Peak Laboratories PP1 Analyzer Model 910-32
- Merlin MicroScience Dilution system Model MMSD-VOC
- Computer
- Sutron Xpert 2 Data logger
- Sampling pump
- SS sample line
- Standard (1 ppmV) in summa canister

Consumables:

- Nitrogen gas (PP1 carrier)
- Air (valve actuator)
- N₂ or Air (dilution system)
- 1ppm Isoprene standard

5.3 System Settings:

- Support Gases: All bottle gas output can be set between 70-80 psig. Nitrogen carrier bottles can be ganged together so bottles can be changed out without disrupting system operation.
- PP1 settings: The PP1 oven temperature should be set to 115°C while the detector is held constant at 265°C. The PP1 lamp signal should be between 1200 and 2200mV. Valve timing on PP1 is set to inject sample at 1 second, the detector signal is zeroed at 50 seconds, and the injection valve returned to back-flush at 80 seconds. The PP1 run ends at 300 seconds and immediately begins the next run. All results were reported as ppbC.

5.4 Quality Control:

Calibration curves are run at the initial start of sampling and at the end. Additionally calibrations are performed if any significant maintenance is performed. Quality Control samples are used to ensure that the data produced from the analyzer are of a known quality, and consistent throughout the analytical process. Nightly quality control checks along with analytical blanks are run to insure that the response of the instrument remains consistent and does not vary. Quality control limits are listed in Table 4.

Table 4 Quality Controls

Quality Control Sample	Limits
Nightly Check Standard	±25%
Analytical Blank	< 2 ppbC
Calibration Curve	< 10% RSD

5.5 Operator Responsibilities:

The site operator is responsible for monitoring and inspecting all parameters in order to maintain system operation and data collection.

Routine site checks:

- Daily remote checks- Operator will review calibrations daily. Spot checking the chromatograms to ensure no interferences and proper integration is recommended. File sorting should be done as needed to keep data storage areas free of clutter.
- Weekly onsite checks- Operator will visit the site once a week and check gas bottles for pressure. Standard canister pressure and dilution system pressures should be checked to

verify calibration levels. Pad site should be checked for plant growth and safety issues.

Additional site visits may be required depending on the results of routine site checks and quality control sample results. The site operator is required to investigate and correct problems which result in a failure of quality control data to meet the quality objectives and correct problems with communications when necessary.

5.6 System Maintenance:

Operator will change out UV light source once signal has dropped below 1200mv. Mercury bed and mercury scrubber should be changed out every 24 months. Standard canister should be refilled before canister pressure drops below 16 psig to ensure dilutor has proper supply pressure. Gas bottles should be changed out before bottle reaches 250 psig.

5.7 System Calibration:

The dilution system will supply a daily calibration check level of nominally 50 ppb used to check the 3 point calibration response factor. The 3 point calibration is run at 13 ppbC, 99 ppbC, and 168 ppbC and is run anytime major changes to the instrument are made as well as at startup and shutdown. Figure 21 shows the dilution system set-points used for this calibration curve and the resulting calculation of response factor used in the PP1 analytical system. Figure 22 shows the chromatograms for the three point curve. Figure 23 shows the nightly check standard, blank and a typical ambient chromatogram. Appendix A includes the certificate of analysis for the isoprene stock standard used for this testing.

5.8 References:

Peak PP1 RCP manual

Figure 21 Dilution System Calibration Curve

Calibration Curve Response Factors				Big Thicket	Date:	10/13/2016
Level	Zero psig	Span psig	Blend Ratio			
1	70.0	5.0	0.0028			
2	50.0	20.0	0.0198			
3	30.0	20.0	0.0337			
Standard Concentration ppbv	Level	File Name	Theoretic al Concentr	Response Factor	Average Response Factor	
Isoprene	1	1145	13.79	270089	13581	
	2	1050	93.18	2142661	21603	20879
	3	1000	168.79	3621297	21454	4.4 %RSD
						<10%
RED TEXT requires user input Caution! Shaded fields may be linked to other pages Caution! Shaded fields may be calculated						

Figure 22 Calibration Curve Chromatograms - High, Mid and Low points

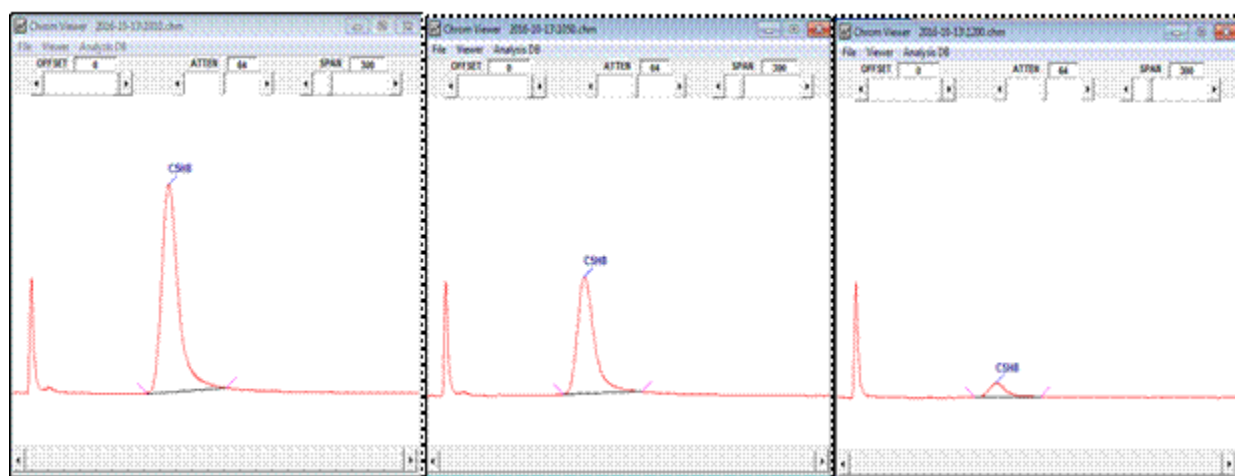
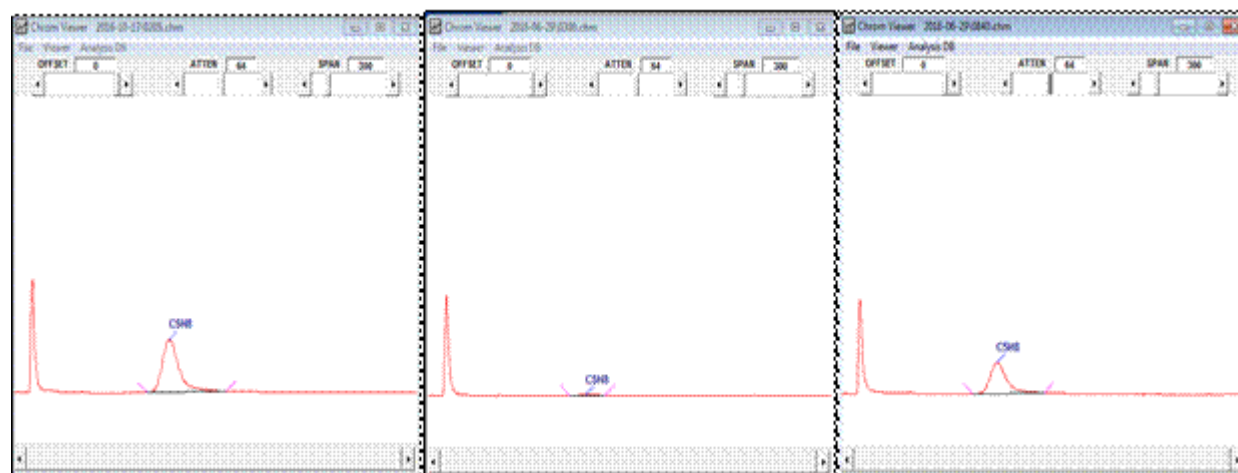


Figure 23 Nightly check standard (48 ppbC), blank (0.8 ppbC) and typical ambient sample (32.5 ppbC)



**Airgas USA, LLC**

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CERTIFICATE OF ANALYSIS**Grade of Product: CERTIFIED HYDROCARBON**

Customer: CONSOLIDATED SCIENCES (EQP ONLY) - LAPORTE, TX
Part: X02NI99C15A0133

Reference Number: 126-400621948-1

Number:
Cylinder: CC68952

Cylinder Volume: 144.3 CF

Number:
Laboratory: ASG - LaPorte Mix (SAP) - TX
Analysis: Nov 11, 2015

Cylinder Pressure: 2015 PSIG
Valve Outlet: 350

Date:
Lot Number: 126-400621948-1

Expiration Date: Nov 11, 2016

Traceability Statement: Hydrocarbon Process standards are NIST traceable either directly by weight or by comparison to Airgas laboratory standards that are directly NIST traceable by weight.

CERTIFIED CONCENTRATIONS

Component	Requested Concentration	Reported Mole %	Accuracy
ISOPRENE	1.000 PPM	1.002 PPM	+/- 5%
NITROGEN	Balance	Balance	

Notes:
PO# 15193



Approved for Release

6. Conclusions and Recommendations

Overall finding from this study to date are as follows:

- Higher isoprene concentrations have been measured at the Big Thicket site than at other sites in the State of Texas at auto-GC stations.
- Concentrations peak in the late afternoon, as predicted by models and shown by other monitors.
- Concentrations are higher under bright sunlight, as predicted by models and shown by other monitors.
- In colocation comparisons with two TCEQ monitoring stations, the agreement between the project Peak instrument and the TCEQ auto-GC were highly correlated, with higher concentrations recorded by the Peak instrument, which may be explained by its higher recovery for isoprene, which is a highly reactive gas.

If the NPS would identify specific questions to be answered through more data analysis, UT CEER would be happy to study them.