Final Report

Identifying and Apportioning Ozone Producing Volatile Organic Compounds
in Central Texas

AQRP Project #: 17-053

QA Requirements: Audits of Data Quality: 10% Required

Project Participants: Aerodyne Research, Inc.

Prepared by: Tara I. Yacovitch and Scott C. Herndon

November 6th, 2017

Executive Summary

A field measurement campaign was undertaken to collect data needed to identify and apportion the volatile organic compounds (VOCs) that contribute to ozone (O_3) production in Central Texas. Measurement data was collected at three primary sites from May 10th to May 31st, 2017. The sites were selected to emphasize sampling air in the San Antonio urban area, the Eagle Ford oil and gas producing shale and a site near the Gulf of Mexico in Corpus Christi State Park. The composition measurements include research and commercial grade instrumentation to quantify the following classes of compounds:

1. ozone and the oxides of nitrogen
2. light hydrocarbon photoproducts such as formaldehyde, acetone and hydrogen peroxide
3. air mass tracer species such as carbon monoxide (CO), hydrogen cyanide (HCN, from biomass burning) and sulfur dioxide (SO_2, anthropogenic tracer)
4. oil and gas light alkanes such as propane, ethane and methane
5. biogenic emissions such as isoprene, terpenes and methanol
6. anthropogenic emissions such as benzene and toluene
7. particulate matter size and composition for both primary (e.g. black carbon, hydrocarbon like organic aerosol) and secondary (e.g. oxidized organic aerosol, sulfate) particulate matter
8. minor secondary photoproducts produced with ozone from a complex mixture of VOC species.

The complete composition dataset has been quality assured and is poised to identify VOC emission categories (e.g. oil & gas; biogenic; anthropogenic) and attribute the quantified production of ozone in central Texas. This project identified ozone production under different chemical regimes. Continued analysis beyond that provided in this report could use this understanding of chemical regimes to inform ozone mitigation strategies. The goals of the State of Texas Air Quality Research Program (AQRP) are:

1. to support scientific research related to Texas air quality, in the areas of emissions inventory development, atmospheric chemistry, meteorology and air quality modeling,
2. to integrate AQRP research with the work of other organizations, and
3. to communicate the results of AQRP research to air quality decision-makers and stakeholders.

Of the ten research priorities identified in the AQRP Strategic Research Plan FY 16-17, this project addresses two. They are 1) Improving the understanding of ozone and particulate matter formation (in central Texas), and 2) Quantifying the local ozone production that impacts the design value (DV) monitors that exceed the national ambient air quality standards (NAAQS) in central Texas. The continued analysis of the datasets collected in our project could be used to conclusively address the above research priorities.

Preliminary Findings

This project focused on collecting the measurement dataset and performing the in-depth quality assurance. The analysis using the resulting dataset is just beginning at the time of this writing. Some preliminary findings are warranted from the in-field analysis (Note that the $p(O_3)$ studies were performed in collaboration with Ezra Wood, AQRP Project 17-032):

- The quantification of low-yield nitrogen containing species involved in isoprene oxidation suggests that **biogenic VOCs play a significant role in net ozone production in San Antonio**.
- The mixing ratio enhancements of oil and gas VOCs (e.g. ethane, propane) suggest local impact in Floresville, however it is unclear that these VOCs fuel local ozone production.
- **A credible fractional attribution of the production rate of ozone ($p(O_3)$) to oil and gas VOC emissions will require additional analysis** because the nitrogen-containing oxidation products are not yet well characterized.
- When $p(O_3)$ was between $5 - 15$ ppb hr^{-1}, the chemical regime was NOx-limited.
- When $p(O_3)$, was less than 5 ppb hr^{-1} and the radical pool (e.g. HOx) was lower, either chemical regime was possible (NOx-limited or NOx-saturated).

Recommendations for Future Work

This section describes the collected research threads that follow on from the analysis of the May 2017 dataset completed as part of this project. It is divided into two sections. The first section describes the advanced analysis tasks associated with the data sets and the second describes the applied research avenues. These recommendations are meant to archive the ideas

that continue the pursuit of the broad project goals as well as to describe other avenues of investigation inspired by the observed data and results.

Advanced Dataset Analysis Items

- Conduct positive matrix factorization (PMF) analysis of high-resolution proton transfer reaction mass spectrometry (PTR-MS) data. This would enable us to separate biogenic and anthropogenic emissions and first-generation oxidation products at high time resolution throughout the campaign. The resulting data would differentiate between changing masses of anthropogenic or naturally influenced air.

- PMF of the iodide chemical ionization mass spectrometry (I-CIMS) data to identify highly oxygenated products of oil and natural gas emissions. The signals isolated from this analysis could serve as tracers of aged oil and natural gas (O&NG) emissions.

- Basic laboratory experiments to oxidize simulant O&NG emissions in a flow reactor and measure the outflow with the I-CIMS. These experiments will enable us to directly identify potential O&NG tracers in the San Antonio field dataset.

- Follow on analysis of high-resolution PTR-ToF-MS data

- Propane was quantified using tunable infrared laser direct absorption spectrometry (TILDAS). This measurement principle is based upon tuning an infrared laser (near 3 μm) across the vibrational absorption of propane. The propane spectrum is broad and ill-defined. During the project, to retrieve a useful propane concentration, a simple line model was used. To improve the quantitative accuracy a computationally expensive baseline decomposition will be coupled to the full line list. This will result in an improved 1 second propane dataset.

Applied Analysis Items

- We will employ the Dynamically Simple Model for Atmospheric Chemical Complexity (DSMACC) package that uses the Master Chemical Mechanism (MCM) to calculate OH reactivity in various ways. The rich array of VOC measurements and the model running in a semi-constrained mode should be able to calculate and apportion k[OH] to defined VOC families. We will use the versions of the MCM that include detailed isoprene oxidation chemistry.

- The project was active for three weeks in May of 2017. In this task, we will evaluate the extent to which the weather, transport and associated ozone production are representative of historical data in the region. This will help inform how broadly the apportionment of ozone producing VOCs can be interpreted.

- The presence of biomass burning markers (e.g. HCN, CH_3CN) in the observational data as slowly rising enhancements above background appear to be due to transported air. A cursory examination of the preliminary back trajectory calculations (**Figure 1**) suggests that fire emissions from the Yucatan Peninsula represent a quantifiable portion of the air sampled at Floresville. The analysis effort described in this task will involve trying to pinpoint the source of the fire emissions and model their potential atmospheric chemistry to understand the import of O_3 to central Texas.
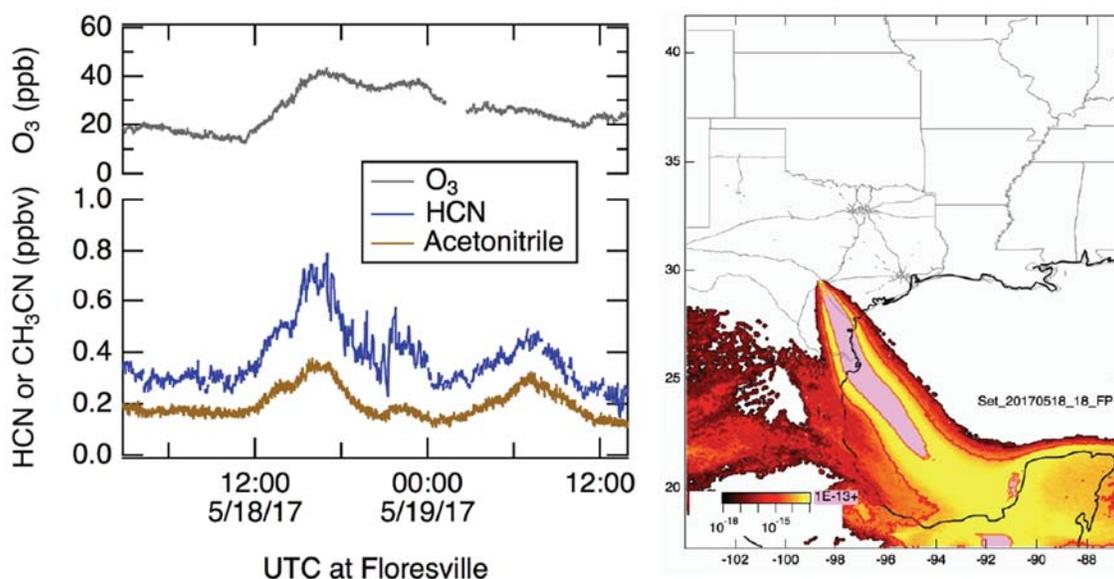
Figure 1. Fire Emission Impact. The left-hand panel shows a time series of ozone (grey), hydrogen cyanide (blue) and acetonitrile (brown). The right-hand panel indicates a HYSPLIT calculated sampling footprint. Taken together, these suggest that the observed enhancements of the biomass burning tracers (HCN and CH_3CN) are due to fires from the Yucatan.

- Sulfur dioxide (SO_2) was observed several times at the UTSA and Traveler's World Sites. As a criteria pollutant, SO_2 emissions are part of reported inventory tabulations. This research task dovetails with the other point source inventory analysis tasks described elsewhere to investigate whether the transport and dilution model framework and inventory agree with the spatial, temporal and magnitude of reported emissions. There are multiple

known SO_2 emission sources in San Antonio, however the majority of known emissions appear in the inventory as:

- o electricity generation
- o cement manufacturing
- o bulk mineral handling

- During the early morning hours of 5/11, 5/13, and 5/14, significant enhancements above background were observed for chlorine gas (Cl_2). This analysis task will examine the potential transport of industrial Cl_2 from industrial point sources in the region.

- Two distinct periods of unusually high particulate sulfate were observed. The observation was qualitatively corroborated by the Rice University AMS as well. Preliminary results indicate that the airmass was influenced by imported sulfate aerosol from the Gulf of Mexico. This research task will be to identify the source of this sulfate.

- The Eagle Ford Shale is an oil and gas producing region that is frequently upwind of San Antonio. The mixing ratios of various oil and gas associated VOCs observed in Floresville suggests local emissions (**Figure 2**). In this task, we will use detailed emission inventories together with the methane, ethane and propane data and transport data to interrogate the observation of a bimodal character to the ethane/methane ratio (3-4 or 7-8%). The premise is that the inventory data will spatially describe the distribution of the propane/ethane/methane ratios. The transport model and time series will be used first to potentially explain the bimodal observations and ultimately inform the accuracy of the emission magnitude.
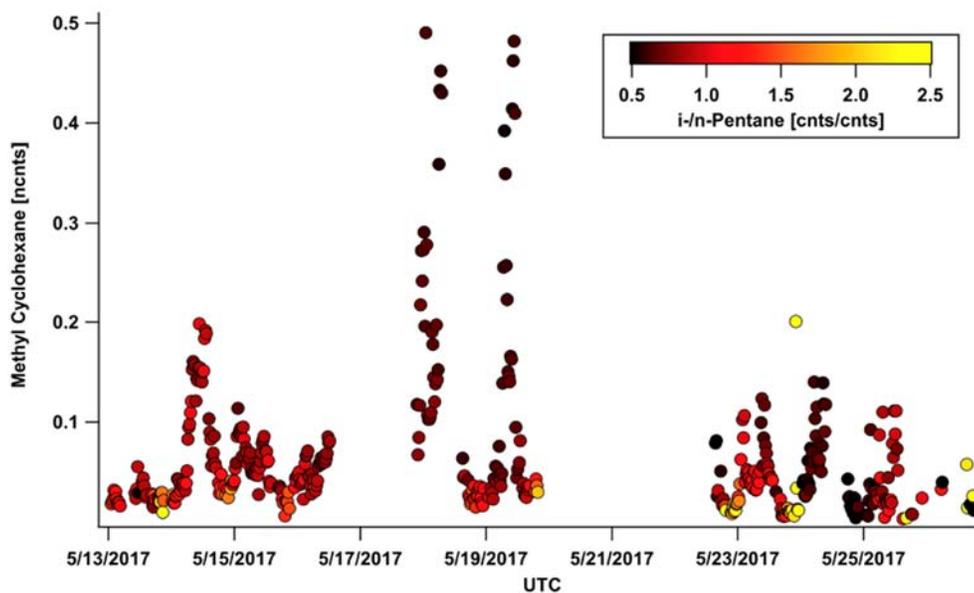
Figure 2. Methyl cyclohexane time series colored by ratio of iso- to normal- pentane. The dark colored circles 5/18-5/20 were collected at Floresville and the 5/24 dark colored points were collected at Corpus Christi State Park with transport from the north.

Table of Contents

List of Figures

List of Tables

Acronyms and Abbreviations

AQRP: Air Quality Research Program.

AutoGC: automated gas chromatograph

C_2H_6: ethane

C_3H_8: propane

CAMS: continuous ambient monitoring station

CH_4: methane

CIMS: chemical ionization mass spectrometry

DV: design value

ECHAMP: Ethane CHemical AMPlifier

FY: fiscal year

HCN: hydrogen cyanide, a product of biomass burning

HOx: the sum of the concentrations of the radicals OH and HO_2

HYSPLIT: Hybrid Single-Particle Lagrangian Integrated Trajectory

I-CIMS: Iodide chemical ionization mass spectrometry: CIMS using the iodide reagent ion, I^-.

jNO_2: production rate of NO_2

NAAQS: national ambient air quality standards

NaN: not a number

NO: nitrogen oxide, a component of NOx

NO_2: nitrogen dioxide, a component of NOx

NOx-limited: chemical regime in which ozone production is limited by the concentration of the oxides of nitrogen

NOx-saturated: chemical regime in which ozone production is not limited by the concentrations of the oxides of nitrogen, but instead by the availability of volatile organic hydrocarbons. This regime is also called VOC-limited.

NOx: the oxides of nitrogen, NO and NO_2

O&NG: Oil and natural gas, also sometimes written O&G.

O_3: Ozone

OVOC: oxidized volatile organic hydrocarbon.

$p(O_3)$: the production rate of ozone

PM: particulate matter

PMF: positive matrix factorization. This is an analysis technique used on the raw data from mass-spectrometer-based instruments.

ppb: parts per billion, 10^{-9}. A unit of concentration

ppt: parts per trillion, 10^{-12}. A unit of concentration

PTR-MS: proton transfer reaction mass spectrometry

PTR: proton transfer reaction

QA: quality assurance

QC: quality control

$RONO_2$: alkyl nitrates, where R symbolizes an alkane group

SO_2: sulfur dioxide

SP-AMS: Soot particle aerosol mass spectrometer

TCEQ: Texas Commission on Environmental Quality

TIDLAS: tunable infrared laser direct absorption spectroscopy

ToF-MS: time of flight mass spectrometry

UTSA: The University of Texas at San Antonio

VOC-limited: chemical regime in which ozone production is not limited by the concentrations of the oxides of nitrogen, but instead by the availability of volatile organic hydrocarbons. This regime is also called NOx saturated

VOC: Volatile organic hydrocarbon. In this document VOC can include small hydrocarbons like ethane and propane as well as larger carbon-containing species like isoprene.

μm: micron, a unit used in describing the frequency of laser light.

Introduction

Ozone in San Antonio

The Environmental Protection Agency (EPA) designates ozone as a criteria pollutant, with National Ambient Air Quality Standards (NAAQS). The 2015 value is set at 70 ppb, but not yet adopted. Thus, the 2008 value (75 ppb) is still in effect for determining ozone attainment. The 3-year average of the annual 4th maximum 8-hour daily maximum is used for the designation. The ozone monitor network in San Antonio indicates that the city is on the verge of being out of compliance for federal standards. The EPA monitor at Camp Bullis (CAMS 058), shows 14 maximum daily 8-hour averages exceeding 70 ppb, since 2015, on track to exceed future ozone standards. As of August 2017, three year average value for the Camp Bullis site is 73 ppbv O_3, which is dangerously close to the current non-attainment level. The mitigation strategy could involve curtailing emissions of ozone-producing volatile organic compounds (VOCs) emitted either in the city (for those VOCs that are oxidized rapidly) or further upwind in regions such as the Eagle Ford or in the refineries at Corpus Christi.
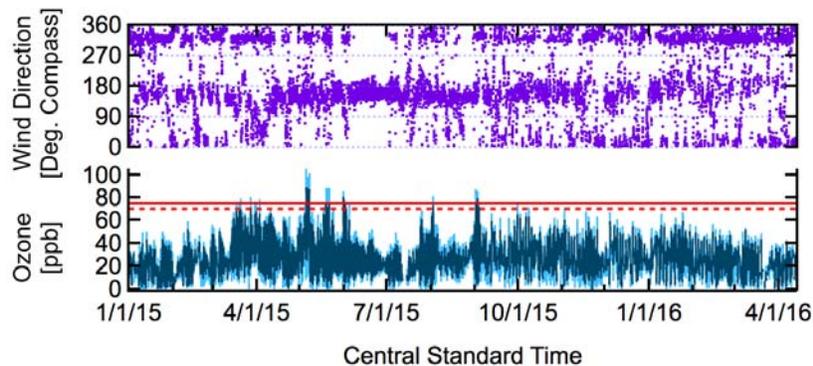
Figure 3. 1-hour ozone measurements from the Camp Bullis (CAMS 058) monitoring station are shown (pale blue) alongside 8-hour averages (dark blue) and wind direction (purple). EPA ozone limits (red) are shown at 75 ppb (solid, current standard) 70 ppb (dotted, 2015 standard, yet to be enforced).

Ozone is produced from sunlight, NOx and VOCs. VOCs are emitted from many different sources. They can be biogenic in origin, like isoprene and other terpenes; they can be oil and gas associated such as propane or various aromatic compounds. Numerous other anthropogenic compounds participate in ozone production chemistry. VOC intermediates can associate with NOx and leave signature compounds that still retain information about the source. Although

parent VOC measurements are very useful, they do not directly indicate the history of ozone formation or its sensitivity to NOx and VOC emissions. Quantification of unique markers of oxidation, such as speciated oxygenated VOCs and alkyl nitrates is an intriguing way to apportion ozone formation since they are created at the same time as the ozone. Additionally, these measurements can be used to ascertain the production rate of ozone, $p(O_3)$, and determine whether it is VOC-limited or NOx-limited, which provides scientific underpinnings to possible abatement strategies.

Project Goals

A field measurement campaign was undertaken to collect data needed to identify and apportion the VOCs that contribute to ozone production in central Texas. We deployed two mobile laboratories and a tall-mast as a portable super site, set up at three locations. The sites were chosen to meet the science objectives. The common air flow pattern around San Antonio is southeasterly; two of the sites are upwind of San Antonio and one is on the downwind edge of San Antonio. The decision to move the portable supersite to the next location was based on the forecast meteorology, facilitated by daily calls with TCEQ and the larger project team. Notionally, the project characterized the incoming air from the Gulf of Mexico, through the Corpus Christi complex, as it passes through the Eagle Ford, into, and out of San Antonio. The mobile laboratories were outfitted with the capability to address the science questions via this sampling strategy.

This project addresses the following goals of the AQRP Strategic Research Plan FY 16-17:

1. Improving the understanding of ozone and particulate matter formation (in central Texas)
2. Quantifying the local ozone production that impacts the design value (DV) monitors that exceed the national ambient air quality standards (NAAQS) in central Texas.

In order to gain insight into the classes of VOCs that affect O_3 in central Texas, the following steps/goals and milestones were met:

1. Design experiment program to sample central Texan air in various stages (e.g. "clean", fresh emissions, transported emissions mixed with urban NOx, aged air)
2. Design measurement payload to inform the strategic research plan goals

3. Execute project with logistic flexibility (e.g. geography and forecast meteorology)

4. Thoroughly quality assure dataset and make available to TCEQ and other researchers

The dataset awaits additional analysis to more conclusively identify VOC emission categories (e.g. oil & gas; biogenic; anthropogenic). Future analysis should attribute the observed production of ozone in central Texas to the identified VOC categories and identify the chemical regime (e.g. "NOx-limited" vs "VOC-limited"). This knowledge will inform mitigation strategies.

Methods

Measurement Sites Chosen

To meet the science objectives of the project, we conducted measurements at three different sites. The timing of the moves was done in coordination with the TCEQ weather forecasting resources. A map, depicting the locations of this monitoring is below.
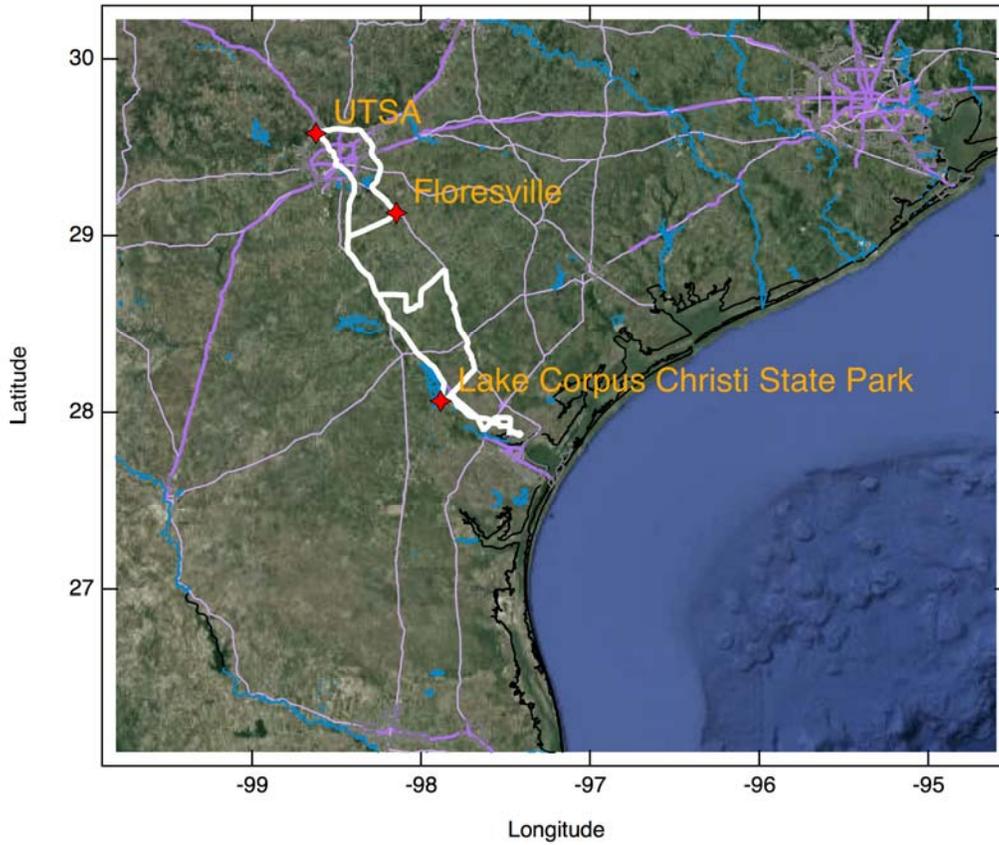
Figure 4. Measurement Locations for Project 17-053. The red diamond symbols indicate the locations where the mobile labs were stationed. The white line indicates the route of the two mobile labs where a limited set of tandem mobile data was collected.

The **University of Texas at San Antonio (UTSA)** was selected as a core measurement site. It was also the location of the Baylor University measurements and the vertical wind profiling project. Additionally, during the last few days of the project, the Aerodyne and University of Houston mobile labs sampled contemporaneously, and performed extensive cross-calibrations. The mobile laboratories were onsite at UTSA on the following May 2017 dates: 5/10/2017 – 5/16/2017 and 5/27/2017 – 5/31/2017. A limited set of instruments began logging data on 5/8/2017, during set-up.

The **Floresville** station was selected because it is an approved TCEQ location for conducting measurements and has a lengthy time series of monitoring data in the vicinity of the Eagle Ford oil and gas production region. The site was secure and power was installed at relatively low cost to the project. The mobile laboratories were onsite at Floresville on the following May 2017 dates: 5/16/2017 – 5/21/2017.

19

The **Corpus Christi State Park** served two purposes: the first was to sample gulf air before it was exposed to inland biogenic and oil and gas emissions. Under the right circumstances, it would also be a vantage from which to sample industrial emissions and initial photochemistry from the refineries in Corpus Christi. The mobile laboratories were onsite at Corpus Christi State Park on the following May 2017 dates: 5/21/2017 – 5/26/2017.

University of Texas, San Antonio   Floresville TCEQ Monitoring Site   Corpus Christi State Park

Figure 5. Site Details for the Three Measurement Locations for Project 17-053.

Data Acquired

The Aerodyne Mobile Laboratory (AML) is a well-tested and extremely suitable measurement platform for the goals of the proposed study. Previous deployments have included measurements in urban polluted areas such as Mexico City during the 2006 MaxMEX/MILAGRO campaign [*Herndon et al.*, 2008; *Wood et al.*, 2009], the 2009 Queens, NY, study [*Massoli et al.*, 2012], or for more specific sources such an aircraft emissions [*Santoni et al.*, 2011] or oil and gas extraction [*Yacovitch et al.*, 2015]. Research and commercial instruments are installed into the AML to collect data while in motion for plume characterization, area mapping or portable deployment for photochemistry and transport experiments. Real-time monitoring of both gas-phase and particulate species is the key feature of the AML.

Most instruments proposed for this ozone study, including the TILDAS [*McManus et al.*, 2008; *McManus et al.*, 2015; *Nelson et al.*, 2006] and the SP-AMS [*Onasch et al.*, 2012], have been successfully deployed by ARI researchers and others in numerous field campaigns. Further descriptions of the most novel (I-CIMS-HRTOF and GC-EI-TOF-MS, **Table 1**) and new additions to the analytical payload are described below. The instrument manifest includes all of the combustion tracers (CO_2, CO, NO, NO_2, SO_2) the light alkanes (CH_4, C_2H_6, C_3H_8) and alkenes (C_2H_4, C_3H_6), oxygenated and aromatic VOCs.

Composition data

The mobile laboratories measured a number of trace gases, volatile organic hydrocarbons (VOCs) and particulate matter (PM) properties.

Table 1. Gas species and particulate matter composition measurements.

Measurement Species or Class	Instrument	Citation
Ozone, O_3	2B Tech, 205	
Carbon monoxide, CO	TILDAS	[*Zahniser et al.*, 1995]
Carbon dioxide, CO_2	Licor 6262	
Nitric oxide, NO	Thermo 42c	
Nitrogen dioxide, NO_2	ARI CAPS-NO2	[*Kebabian et al.*, 2007]
Sulfur dioxide, SO_2	Thermo 41	
Formaldehyde, HCHO	TILDAS	[*Herndon et al.*, 2007]
Hydrogen peroxide, H_2O_2	TILDAS	
Hydrogen cyanide, HCN	TILDAS	
Ethyne, C_2H_2	TILDAS	
Methane, CH_4	TILDAS	[*Yacovitch et al.*, 2014]
Ethane, C_2H_6	TIDAS	[*Yacovitch et al.*, 2014]
Propane	TILDAS	[*Roscioli et al.*, 2017]
Various VOCs	I-CIMS-HRTOF	[*Lee et al.*, 2016]
Various VOCs	PTR-ToF	[*de Gouw and Warneke*, 2007]

Measurement Species or Class	Instrument	Citation
Various VOCs	GC-EI-TOF-MS	
PM 1.5 size and composition	SP-AMS	[*Fortner et al.*, 2012]
$HO_2 + RO_2$ radicals	ECHAMP	[*Wood et al.*, 2017]

Meteorological data

The mobile laboratory measured a number of meteorological, position and status parameters at the measurement site.

Table 2. Meteorological, position and status parameters collected during the measurement campaign. The measurements are classified by parameter type.

Parameter Type	Parameter Name	Description	Instrument
Wind	True Wind: speed direction X, Y and Z	Wind measurement atop the tall-tower. This measurement includes vertical wind. It has been corrected for tower orientation.	RMYoung 3D anemometer
Wind	3m True Wind: speed direction X and Y	Wind measurement atop the mobile laboratory (at a height of approximately 3 meters). This measurement does not include vertical wind and has been corrected for truck orientation.	RMYoung 2D anemometer
Position	Latitude Longitude Speed	Measurement position. A high-precision GPS measured latitude longitude, truck speed (stationary for most of the time) as well as bearing that was used to calculate true wind.	HemiRover V100 GPS compass
Status	Site Name Site Color	The three separate measurement location names were saved as a function of time in a text file. A numeric site index called "site color" was also produced for graphing purposes.	N/A
Status	Tower State	Mask wave indicating whether the tall tower was up (1) or down/disconnected (NaN).	N/A
Status	Strict Background Mask	Mask wave (1 or NaN) meant to indicate periods of regional background sampling (1) versus periods of potential local source contamination (NaN). This wave was calculated based on CO concentrations.	Calculation Product

Parameter Type	Parameter Name	Description	Instrument
Other met	SEA	Solar elevation angle. This data helps visualize time-of-day.	Calculation Product
Other met	Temperature	Ambient outdoor temperature	RMYoung 3D anemometer

In addition to the wind measurements performed aboard the mobile laboratory, measured wind at the three closest TCEQ sites (Continuous Ambient Monitoring Stations or "CAMS" sites) and 6 other weather stations from Wunderground.com were also downloaded and output on the same one-minute time base as the measured AML wind. These files generally have slower frequency wind measurements (several minutes to 1-hour) than the AML, but can be used to supplement or compare with local AML wind data. In some cases, these auxiliary data provide complimentary measurements to fill in gaps in the instrument suite. For example, ambient pressure at these stations allows for the conversion between relative humidity and water concentration, two AML-measured quantities. The table below lists the weather stations that have been downloaded.

Table 3. Auxiliary Weather Station Data. The station name, description, and location for each station is listed.

Station Name	Description	Latitude	Longitude
CAMS058	TCEQ Camp Bullis site, CAMS 58, nearest CAMS site to University of Texas San Antonio	29.632	-98.564
CAMS1038	TCEQ Floresville site, CAMS 1038	29.130	-98.148
CAMS685	TCEQ Ingleside site, CAMS 1038, nearest CAMS site to Corpus Christi State Park	27.902	-97.249
FLORE3	Wunderground weather station KTXFLORE3	29.214	-98.231
FLORE15	Wunderground weather station KTXFLORE15	29.135	-98.282
KSAT	KSAT San Antonio Airport	29.53	-98.47
MATHI11	Wunderground weather station KTXMATHI11	28.26	-97.944
SANAN455	Wunderground weather station KTXSANAN455	29.591	-98.64
SANAN493	Wunderground weather station KTXSANAN493	29.583	-98.618

HYSPLIT calculations

HYSPLIT is an air parcel trajectory model developed and maintained by the Air Resources Laboratory at NOAA. The model calculation can be run in multiple modes, but in this project,

we focus on two types. The first is simple back trajectory (centroid) computation, while the second attempts to capture the relative dispersion of multiple air parcels. The simple back trajectories were calculated in near real time while the more computationally expensive model products were computed after the campaign. Movie files of these calculation results are delivered along with this project's data set.

Audits of Data Quality

After the campaign, every data trace acquired was analyzed by the scientist responsible for the instrument. Each instrument's data was quality assured and output onto a 1-minute time base (file names pre-pended with MM_). Invalid data has been set to "not a number" or NaN so as not to interfere with future analysis. The following routine data quality tasks have been done:

1. calibrations have been applied and the calibration time periods excised,
2. clean air additions (zero air) have been used to correct offsets if needed, and the data excised,
3. time periods of invalid data noted by experimenters during the campaign have been excised.

Furthermore, the data quality officer, Dr. Tara Yacovitch, has performed a **data quality audit** of 114 of the 114 available data files (100%). As part of the audit, a minor mismatch in number of data points was found and corrected in 21% of files. 5 out of 114 (4%) of the data files had problems that still needed to be corrected. However, for each of these 5 files, problems were limited to small (<1 hr) portions of the time. New versions of these files were produced before submission of the final data set.

This audit was done by loading and graphing final 1-minute data files from each scientist (or start-stop files for the gas chromatograph). A sub-sample of traces that passed this audit are shown in **Figure 6**.
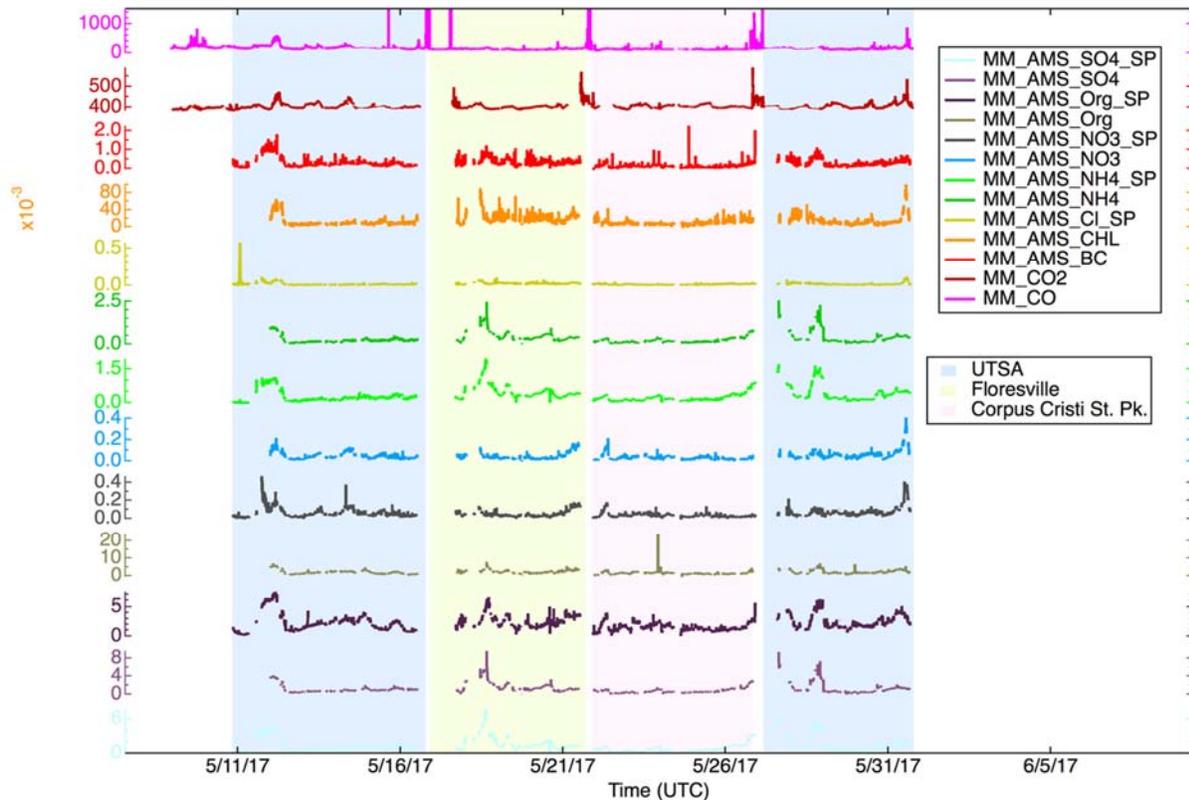
Figure 6. Sub-sample of traces from the data quality audit. These traces show Aerosol Mass Spectrometer (AMS) data taken in normal or soot particle (SP) mode. Gas phase CO and CO_2 are also shown for comparison. The three separate measurement sites are colored in pastel.

Figure 7 shows one of the time periods where data failed the audit. Two minor problems remain in three data files: MM_C3H8, MM_CH4, MM_HCHO (see **Figure 7**).

1. Large negative numbers, or unphysical zero concentrations, sometimes seen after bad spectral backgrounds on laser instruments,
2. Straight interpolated lines across segments of missing data instead of NaN data.

These problems were **corrected before final data delivery**.
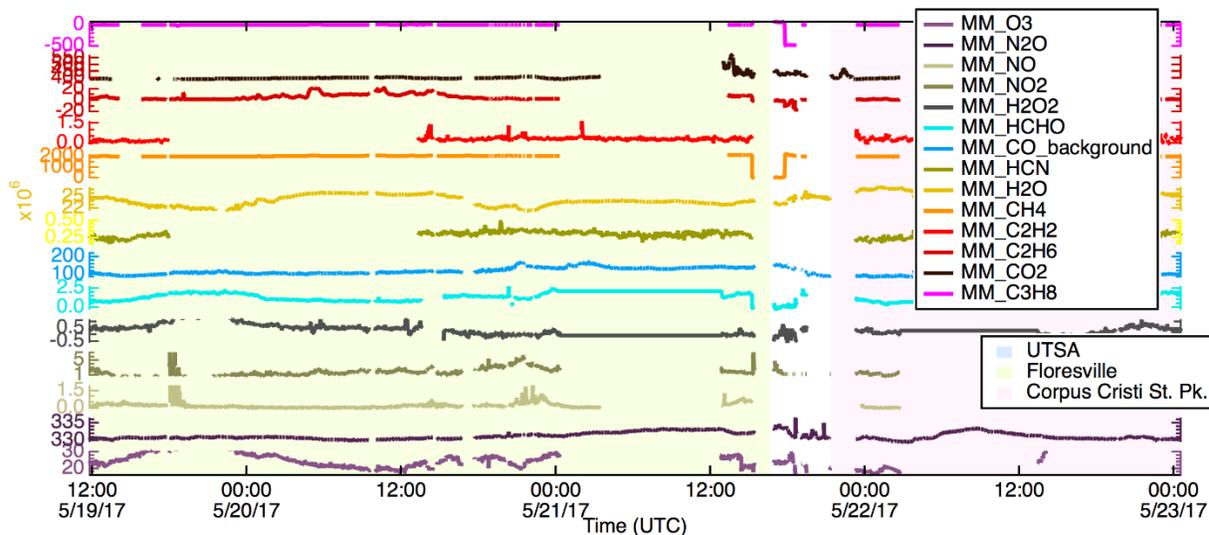
Figure 7. Example of data quality problems. Three of the 14 displayed data files have remaining problems. Gas phase mixing ratios are plotted versus time. Two different types of data glitches are observed: an incorrect interpolation in MM_HCHO at 5/21/17 06:00 and false negative or zero values for MM_C3H8 and MM_CH4 at 5/21/17 15:00.

Finally, as part of each individual scientist's data analysis, a **Quality Assurance Document** has been produced and kept updated. This document has been delivered and archived along with the data files. It describes each of the files produced and includes information like:

- calibration factors applied,
- noise performance
- limit of detection
- reasons for missing data,
- possible interferences,
- description of known data quality problems
- quick intercomparisons between the data in question and other instruments.
- Further analysis to be done as part of future projects

Dataset Format and Sharing

Two time-bases have been produced: 1-minute data (prefixed with MM_, in oneMinuteBase files) and GC start-stop times (see **Figure 8**).

The dataset has been delivered in its entirety. Files are in *.txt and *.xlxs formats. Files are also available in the *.ibw (Igor binary wave) format for ease of use with the primary analysis software at Aerodyne, Igor Pro. The current 1-minute data file includes 92 individual columns and is approximately 18 MB in size. The gas chromatographic data file contains 18 columns and is approximately 56 KB in size. A third file reports data from outside sources at approximately 13 MB.

Figure 8. Example file structure showing delivered datasets.

HYSPLIT results (back-trajectories and footprint calculations) are delivered as movie files (.mov), showing the progression of the calculations as a function of time.

Preliminary Results

This section describes findings consistent with the initial data analyses outlined in the scope of work. First, the science questions that form the basis of this project will be reviewed. Several observations that do not directly answer these questions but are useful to understand the nature of the dataset are also presented as initial findings.

Science Question One: Individual VOC emission sources (for example, oil production vs biogenic emissions) all participate in ozone production in central Texas. Can examination of the oxidation products and radical termination species (e.g. butanone and alkyl nitrates) that still retain specific parent VOC information be used to apportion the VOC component of regional ozone production?

Quantification of speciated VOCs is an important tool for tracing and identifying which VOCs contribute the most to ozone formation [*Gilman et al.*, 2013], but mainly reflects the local

ozone production at the measurement site and not necessarily the ozone formation integrated over the last day of the air mass' history. Alkyl nitrates ($RONO_2$) are formed by very similar reactions as those that form ozone from alkane oxidation, and therefore contain information about which VOCs contributed to ozone formation during the life of the air mass.

Using alkyl-nitrates to attribute VOC emissions and ozone production has been demonstrated before [*Gilman et al.*, 2013; *Yarwood et al.*, 2015]. In this work, we have a strong, quality assured dataset at locations spanning Corpus Christi, Floresville and San Antonio. Two chemical ionization species, iodide (I^-) and hydronium (H_3O^+) were used to overlap and capture a wide variety of VOC chemical classes. Those instruments are buttressed by the electron impact gas chromatogram data.

The quantification of low-yield nitrogen containing species involved in isoprene oxidation suggests that biogenic VOCs play a significant role in net ozone production in San Antonio. A credible fractional attribution of the production rate of ozone ($p(O_3)$) to oil and gas VOC emissions will require additional analysis because the nitrogen-containing oxidation products are not yet well characterized.

The future analysis section describes the next steps to fully exploit the data content and inform Science Question 1.

Science Question Two: What is the instantaneous rate of ozone production in central Texas and is it occurring under NOx-limited or VOC-limited conditions? Coupled with question one, how does this answer inform potential mitigation strategies?

The Drexel University peroxy radical measurements (ECHAMP) quantified the ozone production rate $p(O_3)$ by coupling the measured HO_2 and RO_2 radicals with the NO mixing ratio. The knowledge of $p(O_3)$, coupled with radical initiation rates and VOC reactivities, can reveal which NOx regime dominates ozone chemistry (VOC-limited vs NOx-limited).

In this study, the production rate of ozone revealed two possibilities. A clear NOx-limited chemical regime was observed when ozone production rates were higher ($p(O_3)$ between $5 - 15$ ppb hr^{-1}). On the other hand, when $p(O_3)$ was less than 5 ppb hr^{-1} and the radical pool (e.g. HOx) was lower, either chemical regime was possible (NOx-limited or VOC-limited).
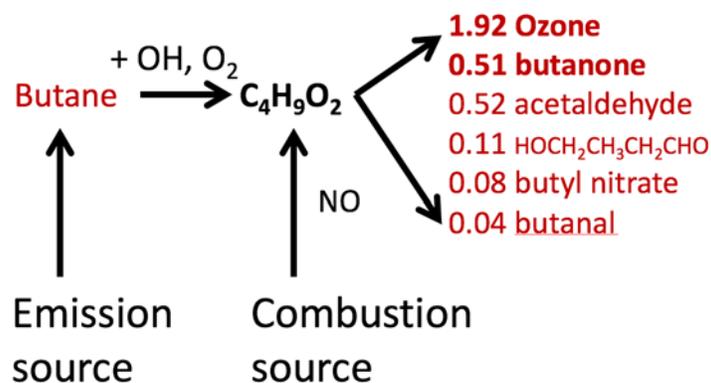
Figure 9. Apportionment of historical ozone production to responsible VOCs using indicator species. In this example, in the presence of plentiful NOx, each molecule of butane oxidized will produce 1.92 molecules of ozone and 0.51 molecules of butanone. One ppb of butanone quantified by PTR-MS therefore indicates that 3.8 ppb of O_3 observed was from butane oxidation.

Science Question Three: Can improved characterization of specific industry sector emissions offer insight into the ozone and air quality impact? Do medium-large process flares represent an emission source not well represented in emission inventories?

Following discussions with TCEQ and AQRP project managers, the emphasis on this question was shifted away from doing emissions measurements near individual sources and instead towards evaluating the contribution of any large site emissions at the chosen sampling sites. In this way, the data collection required to fulfill questions one and two was maximized. One example of an emission source contributing to local air quality was the SO_2 and sulfate aerosol enhancements observed at the San Antonio site early in the campaign. The VOC emission profile from the Floresville measurements has been examined. These results show a clear influence of O&NG sources on the Floresville air mass, but the impact of these sources on local ozone production was unclear.

A small amount of mobile data was collected without impacting the core measurements: during the final transit leg of the campaign, instruments and data collection were left on while driving a lazy route from the Corpus Christi State Park site back up to UTSA. This meant that we collected some data in an area that was downwind from the industrial emissions due to the Corpus Christi refineries. The quality assurance for this mobile data will be challenging since the emission plumes from other automobiles needed to be identified and removed. This auxiliary

dataset is beyond the scope of this project but has been archived by Aerodyne for use in future projects.

Diurnal Ozone

In **Figure 10**, the diurnal character of odd oxygen (O_X, O_3 + NO_2) is shown for the three study sites. Due to the more limited time at two of the sites, direct comparisons may not be warranted, however some comparisons of odd oxygen with O_3 are interesting. Overall, we observed little difference between odd oxygen and ozone. This suggests that the quality assurance has acceptably filtered out any strong direct emissions of O_3. The remaining influence of O_3 emissions is visible in the difference between the solid and dotted lines in **Figure 10**. It is greatest in the most urban location (UTSA), modest in Floresville and minimized in the cleanest location, Corpus Christi State Park.
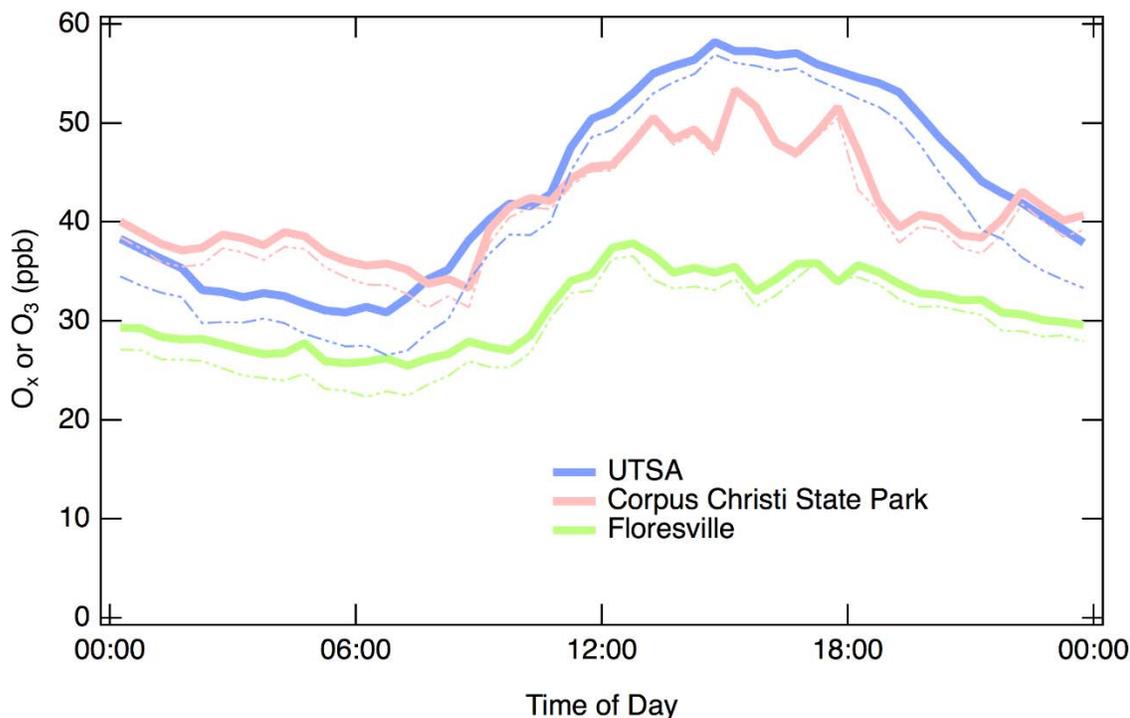

Figure 10. Site-based diurnal Ox. The three diurnal Ox traces (solid lines) for UTSA, Corpus Christi State Park and Floresville have been computed using the sum of quality assured O_3 and NO_2 in 30 minute bins. The same computation for O_3 is depicted by the dashed lines.

Evidence of Photochemical Reactants and Products

Evidence of volatile organic hydrocarbon (VOC) oxidation was observed in the dataset. In one example shown below, measurements taken at Corpus Christi State Park on 05/27/2017 are analyzed. Data from several instruments (PTR-MS, ECHAMP and two separate TILDAS chassis, see Methods section) are combined, and their ratios show clear differences between reactants and products of atmospheric oxidation.

Figure 11 shows correlation plots of xylene and acetone mixing ratios as a function of benzene mixing ratios. RO_X radical data from our collaborator Ezra Wood (Drexel) colors the plots, with low values in black (as seen at night) and higher values in yellow (as seen in the day). Here, benzene concentration is used as a dilution tracer because of its relatively low reactivity.
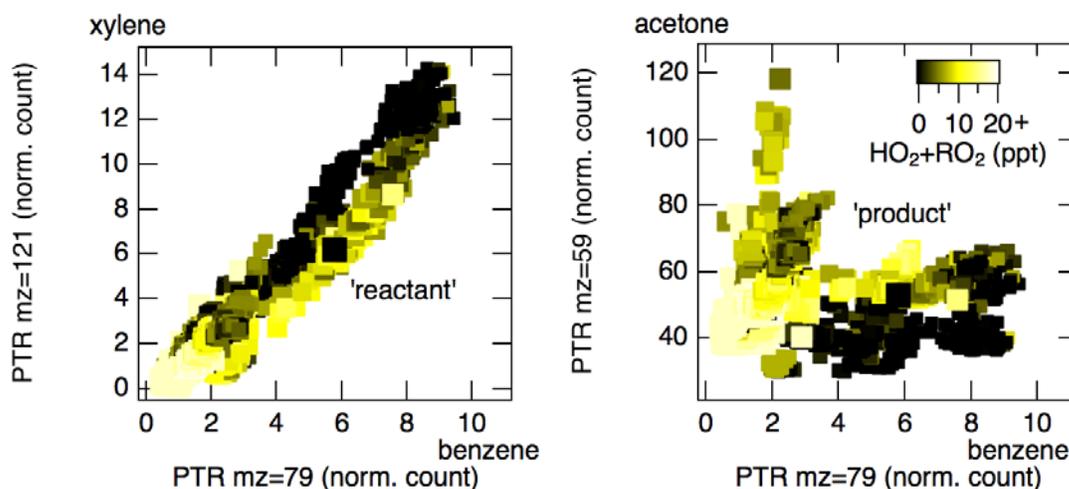
Figure 11. Example of VOC photochemistry observed at Corpus Christi State Park (near Mathis, TX) on 05/24/2017. On the left-hand side, the xylene signal is plotted vs benzene. On the right-hand side, acetone is similarly depicted. In each plot, benzene is being used as a general VOC dilution tracer. The coloring uses the RO_X signal, $RO_X = HO_2 + RO_2$.

Since xylene reacts more quickly with OH radical than benzene, we see that when RO_X increases the xylene/benzene ratio is slightly lower than when the sun is down (**Figure 11**, left, yellow points are lower than black points). Xylene is acting more like a photo-reactant, relative to benzene. Acetone, another VOC, can be produced by several different channels which are activated in sunlight. In **Figure 11**, right, we see that acetone concentrations are higher when the oxidation potential of the atmosphere is higher (yellow points are higher than black points). Here, acetone is a photo-product relative to benzene, the general VOC dilution tracer.

An analogous picture emerges looking at other species in the atmosphere, for example formaldehyde (HCHO). Instead of benzene, we can use carbon monoxide as a dilution tracer for combustion. **Figure 12** shows a plot very similar to the acetone result in **Figure 11**. We see that the ratio of formaldehyde to CO is much higher when RO_X is high (yellow points have a higher slope than black points); HCHO is a photo-product.
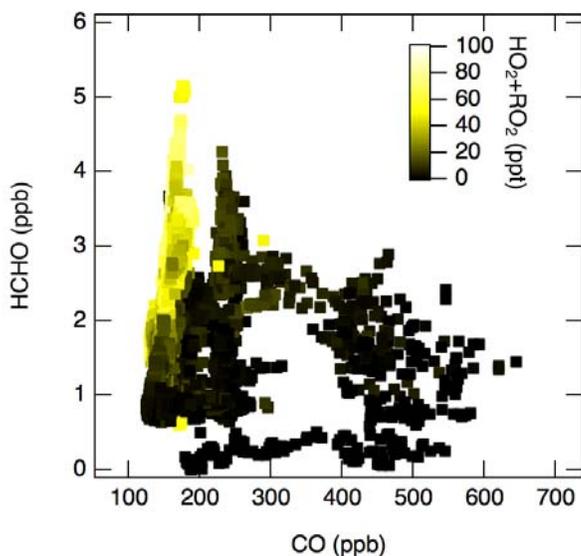
Figure 12. Example of formaldehyde photochemistry observed at Corpus Christi State Park (near Mathis, TX) on 05/24/2017. Formaldehyde (HCHO) mixing ratios are plotted against carbon monoxide (CO), which is being used as a general dilution tracer for combustion. The coloring uses the RO_X signal, $RO_X = HO_2 + RO_2$.

Strong Isoprene Photochemistry Observed at UTSA site

Isoprene, a commonly occurring organic compound emitted from many species of trees, has been studied extensively due to its ubiquity in the atmosphere. In this example, we show how isoprene chemistry at the UTSA site was more prominent than at the Floresville site.

Like most time-of-flight (ToF) mass spectrometry-based instruments, including the PTR-ToF and the GC-ToF, the chemical ionization mass spectrometer (CIMS) relies upon a detailed knowledge of each measured product's precise mass. Isoprene and its photoproducts (including IEPOX, ISOPOOH, ISOPN), having been studied extensively,[*Lee et al.*, 2016] were thus possible to extract quickly from the very large number of masses present in the CIMS data. Less-studied photoproducts including alkyl nitrates from anthropogenic VOCs are also of major interest in these campaign results, and are discussed in the "Future Analysis" section.

Figure 13 shows results for the first two weeks of data. The first half of this dataset (left, pre-5/17/2016) was taken at UTSA; the second half at the Floresville site. Isoprene and its photoproducts from the CIMS and the PTR instruments are shown as a function of time. Overlaid on all the data is jNO_2, a proxy for the oxidation potential of the atmosphere. Though jNO_2 is of comparable magnitude from week-to-week, we see abundant isoprene and associated products at the UTSA site, and a significant decrease once the measurement site was Floresville. The isoprene products at UTSA appear to be dominated by organic nitrates, which are OH-oxidation products formed in the presence of NO. Although the chemistry is a continuum, this observation suggests the isoprene oxidation was not particularly "NO-limited". This is consistent with the relatively higher NO expected at the UTSA site (downwind of San Antonio city-center) versus the Floresville site (upwind of San Antonio). Indeed, the low-NO products (blue) are low and relatively constant through both sites.
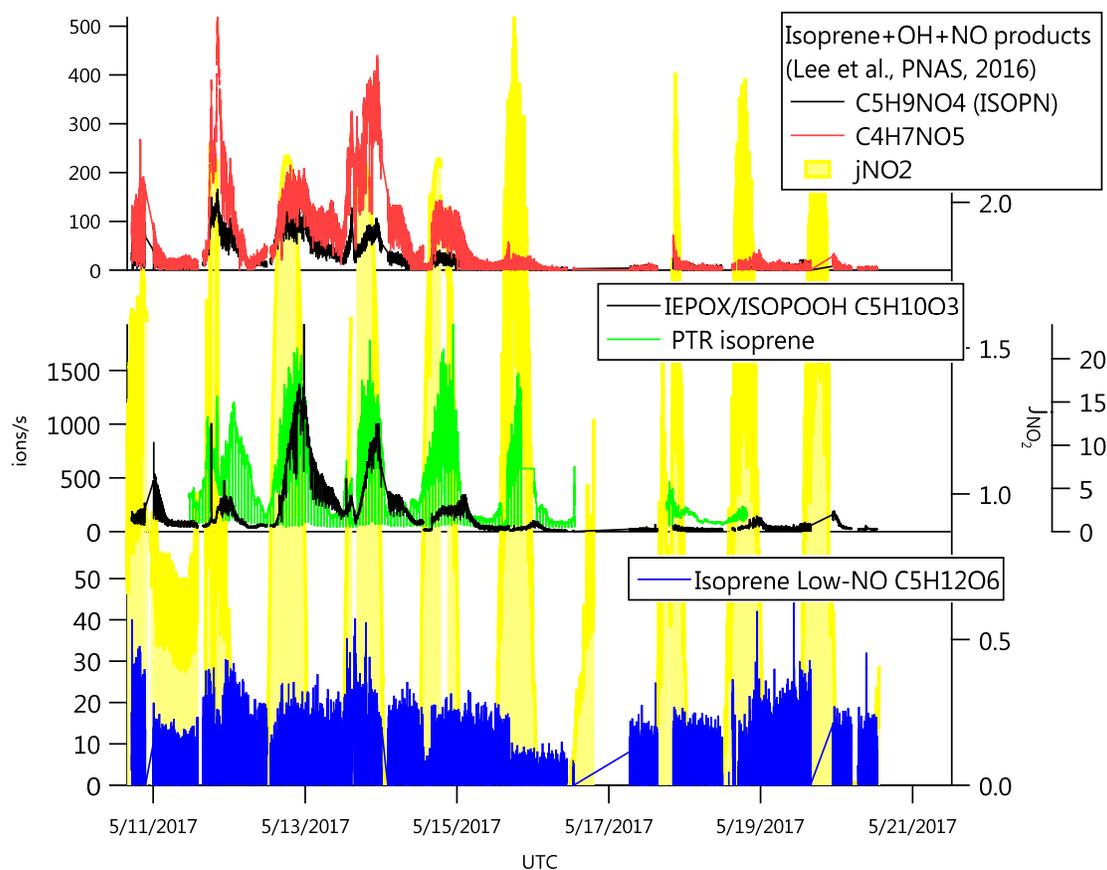
Figure 13. Example of isoprene photochemistry at the UTSA site (left) diminishing after moving to the Floresville site (right). The move from UTSA to Floresville occurred around 19:00 UTC, 5/16/2017. These data are shown as raw ion counts. The left side of the graph shows higher intensities of isoprene (green), IEPOX or ISOPOOH (black, middle), ISOPN (black, top) and C4H7NO5 (red). Low-NO products (blue) are constant throughout.

Oil and Gas Footprint Analysis

In order to understand the measurements done at each field site, it is be important to understand the source of the air masses that are being sampled. Large scale changes in atmospheric transport directions can often be visualized in the data. In the example shown here, we observe a shift from air originating from a combined agricultural and oil and gas source region to air more dominated by oil and gas sources.

Simple atmospheric tracers with long photochemical lifetimes are good tracers of different source regions. **Figure 14** shows carbon monoxide (CO), ethane (C_2H_6) and methane (CH_4) over an 18 hour measurement period at Corpus Christi State Park on 5/25/2017. In the beginning of this time period, we observe fluctuations in methane mixing ratios with relatively low ethane

fluctuations. This first time period has an average ethane/methane ratio of 0.035, or 3.5%. Carbon monoxide, a combustion tracer, is also elevated. Just after 6:00 UTC, we observe a drastic change in the relative amount of ethane being measured. Carbon monoxide also decreases. This higher-ethane period has an ethane/methane ratio of 0.08 (8%) which is characteristic of a natural gas field moderately high in higher hydrocarbons. Indeed, when back-trajectories are done for this dataset, the first part of the dataset shows air parcels originating just south of San Antonio, where they may be impacted by vehicles (CO), agriculture (CH_4) and some oil and gas ($CH_4 + C_2H_6$). After the change, air parcels originate from a region with significant oil and gas activity (C_2H_6 and CH_4).
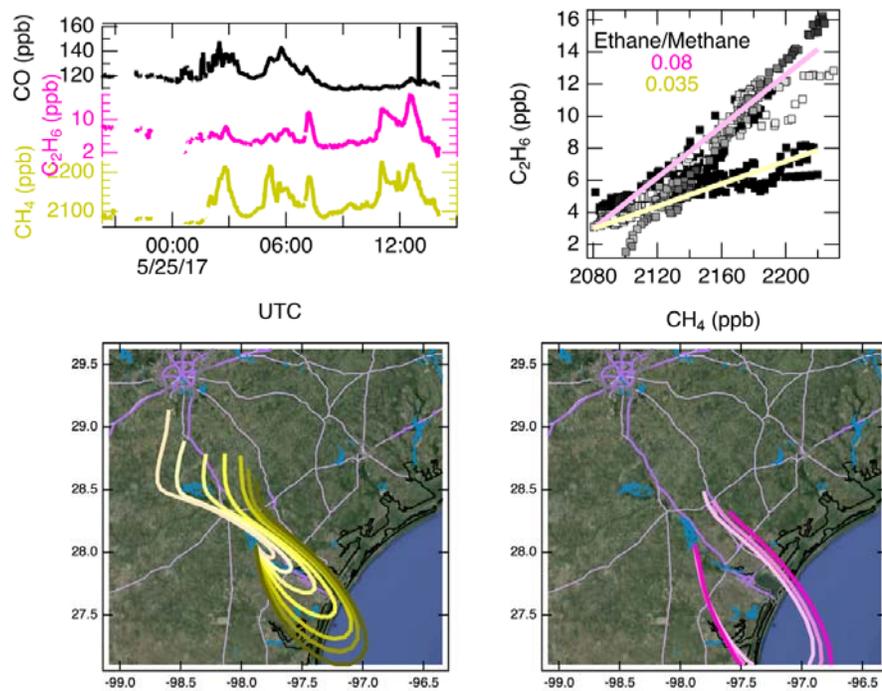
Figure 14. Ethane and methane mixing ratios give a simple idea of the oil and gas character of an airmass that can be verified with HYSPLIT back-trajectories. Carbon monoxide (CO, black), ethane (C_2H_6, pink) and methane (CH_4, gold) mixing ratios for 18 hours of measurement time are shown (top left). The ratio of ethane to methane is determined with a correlation plot (top right) showing two distinct ratios for this data. Two back trajectories show the air parcel source during the low-ethane time (bottom left, yellow trajectories) versus the higher-ethane times (bottom right, pink trajectories).

Intercomparison of VOC measurements

This campaign was the first field deployment of a fast and portable gas chromatograph system coupled to a time of flight mass spectrometer. This Aerodyne Research Inc. instrument is called the ARI GC-EI-ToF-MS: gas chromatography electron impact time of flight mass spectrometer, or GC-ToF for short. At 20-minute cycles, it is much faster than most GC systems: samples were collected for 5 minutes, followed by 15 minutes of analysis and instrument preparation for the next sample. The GC-ToF complements and extends the number of VOCs detectable by other instruments including PTR-ToF and CIMS. Some overlapping species (e.g. benzene, **Figure 15**) allow for an intercomparison of measurement technologies and a diagnosis of any instrument problems.

First results for this new instrument are compared with other available data in **Figure 15**. The GC-ToF agrees well with the PTR-ToF that sampled from the same inlet, showing spikes in benzene concentrations at the same times and magnitudes. The Floresville site was also home to CAMS 1038, a TCEQ monitoring station operating an Automated Gas Chromatograph (AutoGC). Here we see some discrepancies that seem to be associated with a somewhat higher limit of detection (LOD) for the AutoGC data. When benzene concentrations are low, this results in data points set to exactly 0.
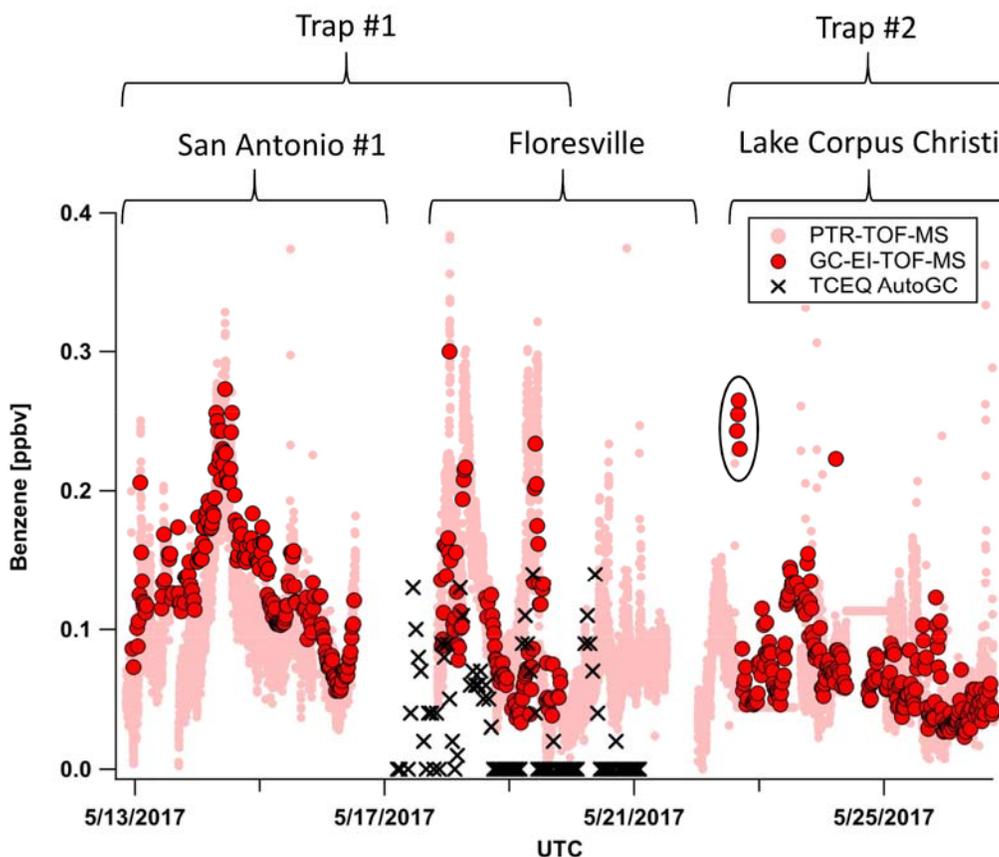
Figure 15. Intercomparison of benzene measurements between instruments. Data from a proton transfer time of flight mass spectrometer (PTR-ToF-MS, pink) and a gas chromatograph electron impact time of flight mass spectrometer (GC-EI-ToF-MS, red) were both aboard the mini Aerodyne mobile lab for the duration of the field campaign. Data from the CAMS 1038 site at Floresville (TCEQ AutoGC) is also shown for comparison. Circled points are likely outliers. The pre-concentration trap for this system was changed in Floresville (Trap #1 and Trap #2).

Figure 15 also highlights some remaining data issues warranting further investigation, including benzene background signals ~30 pptv at the beginning of the campaign, decreasing to ~2 pptv, near the limit of detection, by the end of the campaign. The GC-ToF instrument precision for benzene was typically less than 5% for the campaign, and total uncertainty was ~7% based largely upon the accuracy of calibration standards (not shown). The instrument limit of detection for benzene during the campaign was 1 pptv (at 1-sigma). Overall, **Figure 15** demonstrates a successful first deployment of the ARI GC-ToF.

Future Analysis

Overview

Aerodyne Research, Inc. built a dataset using a mobile laboratory as a portable photochemistry super site. The goal of this study is to understand ozone production and the emission sources that ultimately impact air quality in central Texas. The suite of instrumentation was selected to quantify key oxygenated volatile organic carbon species (OVOC) and nitrogen-containing species (e.g. alkyl nitrates) to pinpoint and apportion ozone due to broad categories of VOC emission sectors. The dataset has been rigorously quality assured, however additional analysis will be required to fully unlock the potential in this dataset.

The individual research priorities identified by TCEQ and the AQRP will be further addressed with the continued analysis described in this section. **The preliminary observations support the theory that ozone production in San Antonio is NOx-limited.** The early evidence suggests that oil and gas VOC compounds, while elevated, **were not** competitive with ample biogenic VOCs when considering net $p(O_3)$. In order to conclusively support this early finding though, more attention to the analytical quantification of trace compounds will need to expended.

A critical component of this project involves identifying and quantifying VOCs that have undergone oxidation but still retain fingerprint information about the source. This has been accomplished for the biogenic source VOCs from prior work, guiding where to look in the iodide CIMS and PTR-ToF. This has not yet been achieved for oil and gas specific VOCs with this instrument tandem. The analysis of these datasets with positive matrix factorization methods can help reveal other secondary products. A subtopic describing these goals is presented below.

I-CIMS and PTR-MS data sets

- Conduct positive matrix factorization (PMF) analysis of high-resolution proton transfer reaction mass spectrometry (PTR-MS) data. This would enable us to separate biogenic and anthropogenic emissions and first-generation oxidation products at high time resolution throughout the campaign. The resulting data would differentiate between changing masses of anthropogenic or naturally influenced air.
- PMF of the Iodide-CIMS (I-CIMS) data to identify highly oxygenated products of oil and natural gas emissions. The signals isolated from this analysis could serve as tracers of aged oil and natural gas (O&NG) emissions.

- Basic laboratory experiments to oxidize simulant O&NG emissions in a flow reactor and measure the outflow with the I-CIMS. These experiments will enable us to directly identify potential O&NG tracers in the San Antonio field dataset.

- Follow on analysis of high-resolution PTR-ToF-MS data

Positive Matrix Factorization (PMF) can be a valuable tool in de-convolving complex mass spectra. Due to limited time, the preliminary PMF analysis has been performed using "unit" mass spectra, which in the case of PTR data contains multiple peaks of differing levels of oxidation. For instance, at the nominal m/z 71, both the hydrocarbon $C_5H_{10}H^+$ and isoprene oxidation product $C_4H_6OH^+$ are detected. Similar overlap occurs at virtually every odd mass within the PTR-ToF mass spectrum. Because of the vast abundance of isoprene associated with oaks in Texas, the traditional PMF analysis correctly associates m/z 71 with the biogenic factor. For other ions where the distribution between the ion intensities is less dramatic, conducting the PMF analysis on the high-resolution data could help reveal important information about the sources and photochemical products in the South Texas atmosphere. To illustrate the advantage of using high-resolution data, the ions at m/z 99 are examined. The high-resolution mass spectrum of m/z 99 reveals that there are 3 major peaks detected at this mass as shown in **Figure 16**.
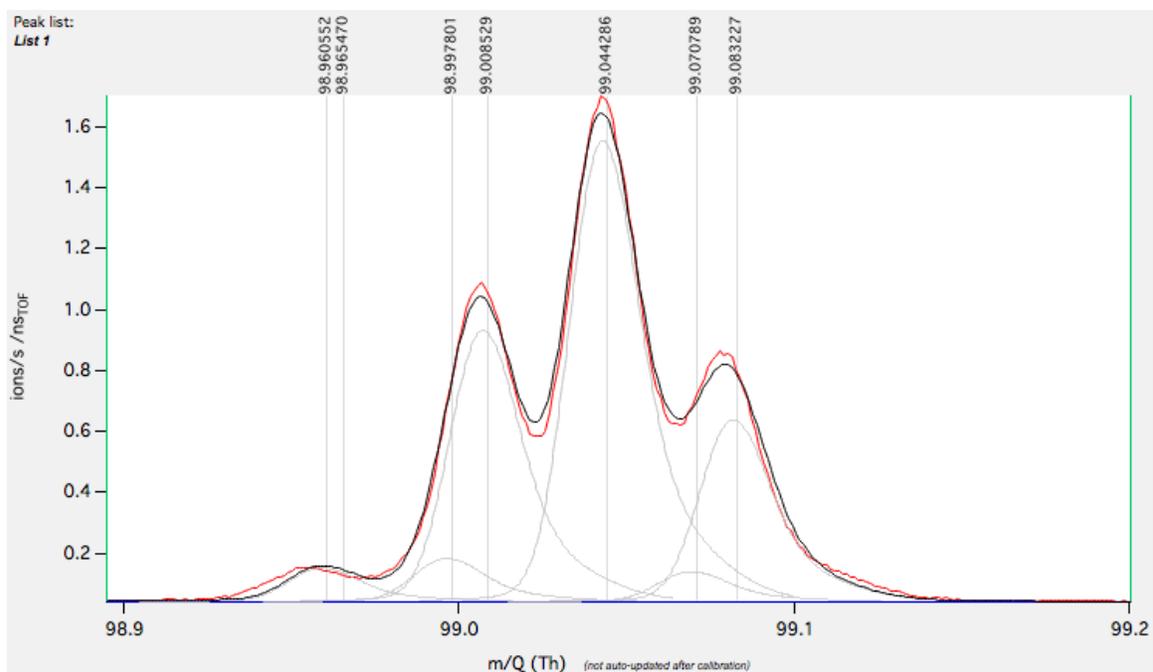
Figure 16. High-resolution Mass Spectrum. The mass spectrum measured at m/z=99 (red) has been deconvolved into different contributions from specific exact masses (grey). The black trace is the combined fit of the component exact masses.

Extracting the time series for these ions reveals that each one has a different temporal profile as is shown in **Figure 17**.

Figure 17. High-resolution fit results as time series. The exact masses for the ions C4H2O3H+(red), C5H6O2H+(green) and C6H10OH+(blue) have been fit and depicted as a time series with jNO2 (yellow) and CO (black).

The simple preliminary analysis illustrates the potential for a detailed analysis of the PTR-ToF-MS data to reveal informativ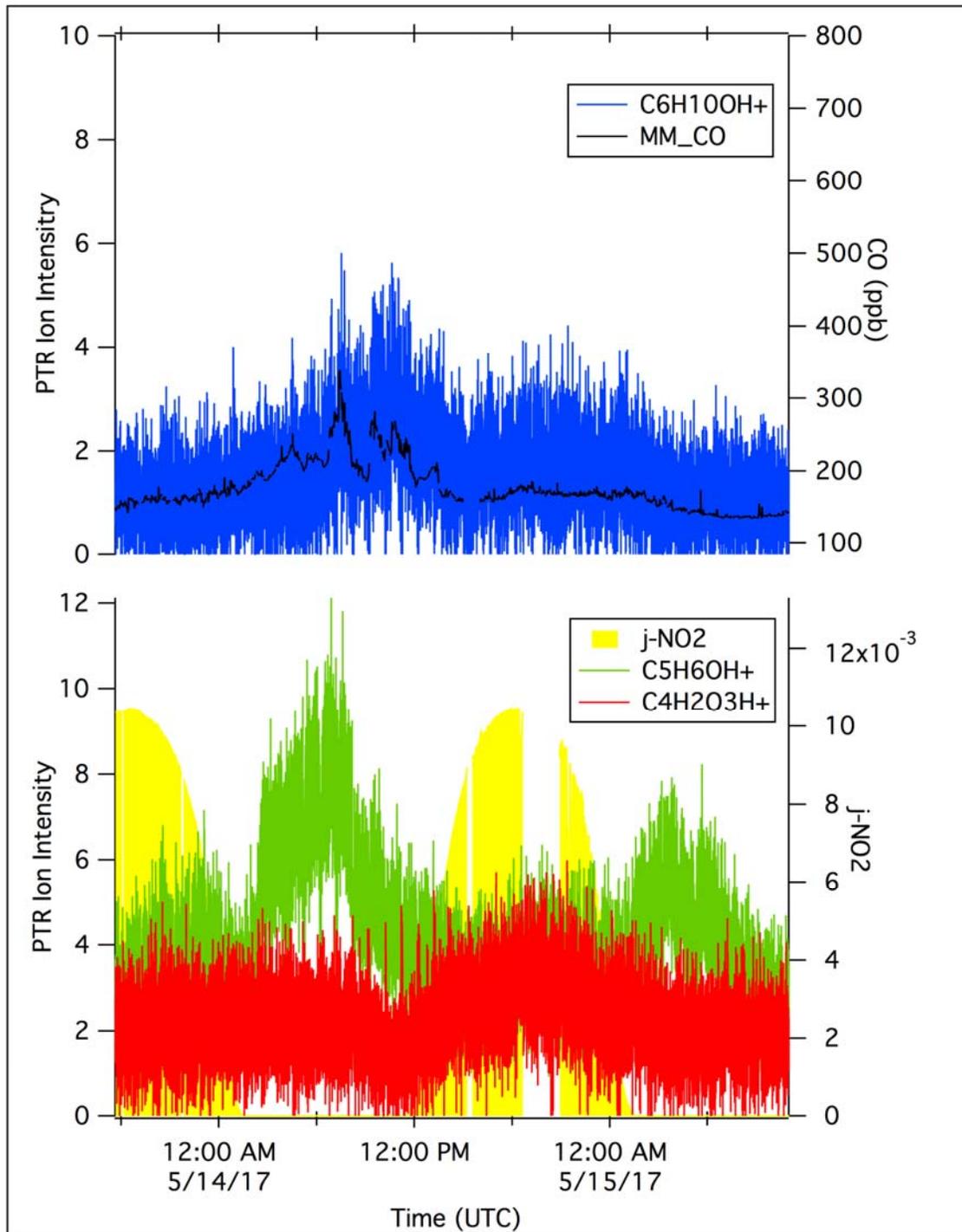e information about the South Texas atmosphere. To complete such analysis requires a careful fitting of the high-resolution data followed by extraction of the background zeros that are embedded in the data.

SP-AMS AQRP data

The SP-AMS 1 minute data has been analyzed and QA performed. The canonical organic, black carbon, nitrate, sulfate, chloride and ammonia mass loadings have been quantified. The dataset contains additional information, however, and would benefit from further analysis. Two main areas to be explored are the analysis of particle time of flight (PToF) and the application of positive matrix factorization (PMF) to the time series already developed.

The size mode for each species is determined using PToF and this should be examined in more detail both as a whole and more specifically focusing on time periods of interest. There were time periods during this campaign where elevated sulfate was observed and the size evolution of this sulfate should be examined more closely. This task will also couple to the back-trajectory research that is proposed.

The subtle variations in the mass spectral signature can be detected using PMF analysis of a time series. The resulting factors are based on similarities in that mass spectral signature. It is useful for pulling out sources or aerosol types associated with certain wind directions or time of day. It would be useful to apply this to time periods with the high sulfate to see what other species are present with the sulfate.

Back-trajectory research

One avenue of future research is to investigate the calculated back-trajectories in combination with the measured data. Examples of such investigations are discussed below.

Simple trajectory

A rapidly moving storm front abruptly switched the source of air coming to the UTSA site on 5/29/17 at 00:20 UTC. This was the product of large storm system that developed in the northern portion of central Texas that late afternoon (e.g. 5/28 16:00 – 18:00 local time). **Figure**

18 shows the satellite image of the developing storm and the abrupt change in CO with wind direction. In the center portion of the figure, a simple HYSPLIT back-trajectory during the hour of the switch is depicted. All of the in-field back-trajectories were calculated using the Eta Data Assimilation System (EDAS40), 40 km square 3 hourly meteorology data from the re-analysis processed produce. The in-field back-trajectories were initialized at the latitude and longitude of the site at a height of 10 meter and run backward for 24 hours. The result in **Figure 18** indicates that the centroid of air was still advected from the south of the state.
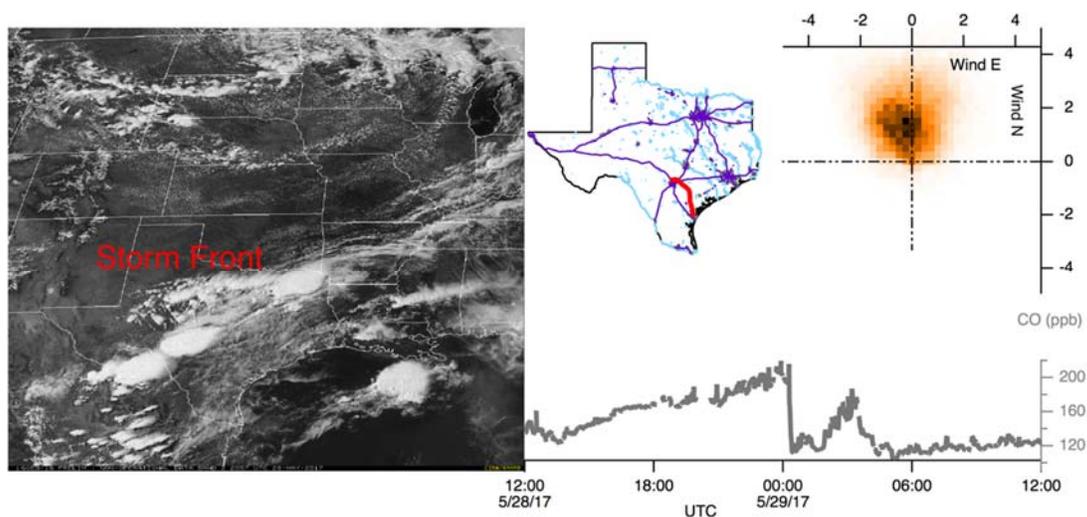

Figure 18. Storm Front Ventilation. The left hand panel is a photo from the Regional and Mesoscale Meteorology Branch satellite data website taken at 2017/05/28 20:57:22 UTC. It shows an abrupt storm front forming and propagating southward. At 5/29 00:20 the front abruptly switched the wind direction incident at the UTSA site (upper right panel) and dropped the CO mixing ratio from ~ 200 to ~120 ppbv (lower right panel).

In **Figure 19**, the results of several in-field back-trajectories of the air coming to UTSA during this event are plotted. The pre-front arrival trajectories are colored in gray, the arrival of the front is approximately the red trajectory and the browns are post-front arrival. It appears the front did shift the incident air mass from coming over the western side of San Antonio to the northeastern edge, but this does not necessarily capture the switch in local wind direction. The simple in-field trajectories do contain a useful qualitative assessment of where the air is transported from, but we may wish to use a more complex representation of the footprint of potential contributions to the sample.
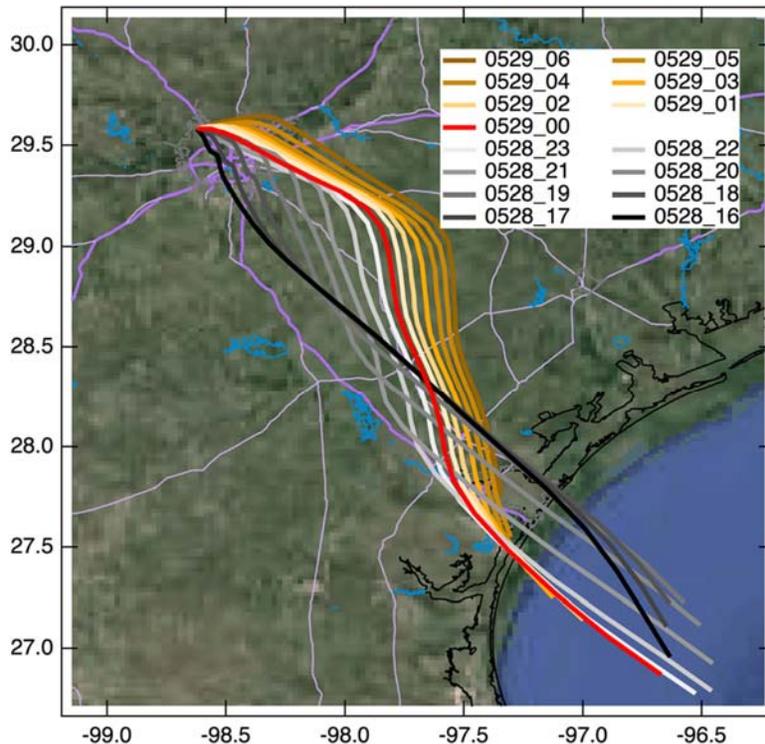
Figure 19. Trajectories Before and After Front Passage. The map depicts the back trajectories for several hours before and after the front system arrived at UTSA. The red line marks the switch in local wind.

Complex trajectory

Figure 19 shows a potential limitation of simple back-trajectory calculations. The model is also capable of running a more complex system that tracks multiple air parcels, running them forward or backward in time and tracking which geographic box they end up in. This is referred to as a **concentration** run and has direct applicability to performing dispersion analysis when run in the forward mode. It is challenging to deduce what has taken place upwind however. In the forward mode, one knows where and when a released gas will be mixed downwind. In the backward mode, the mixing has already taken place and one does not a priori know how old an airmass might be. **Figure 20** shows in the left-hand panel, the results of two HYSPLIT concentration simulations where 200,000 virtual massless particles were released at the UTSA site and run backward in time (-20 and -40 hours). The release point was at the latitude and longitude of the site at a height of 10 meters. To accommodate the longer run, the Global Data Assimilation System (GDAS) meteorological files are used outside the coverage of the EDAS40 input. The contour coloring shows where the preponderance of air masses are likely to have

been 20 and 40 hours respectively. When the resulting contours for the prior 72 hours are summed, the contour series depicted in the right-hand panel of **Figure 20**. Currently, we are thinking of this as the sampling "footprint".
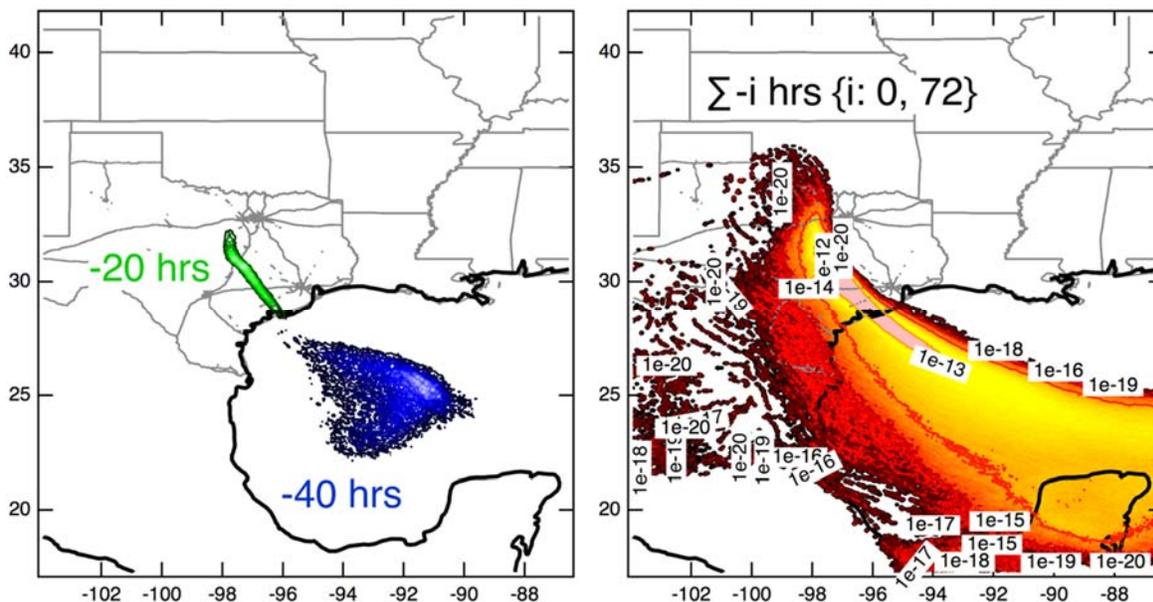

Figure 20. Development of the "footprint" for 2017/05/21 08:00. The left-hand panel shows two HYSPLIT runs at minus 20 and minus 40 hours (green field and blue field, respectively). The right-hand panel shows the result of geographically summing each of the HYSPLIT runs for the prior 72 hours.

The footprint calculations have been completed for the whole project dataset. This set of calculations would be useful for future investigations aiming to apportion observed enhancements in biomass burning tracers like HCN; in oil and gas tracers such as C_2H_6; or in C_2H_6/CH_4 ratios. The unusual observation of unattributed sulfate aerosol could also be considered in light of these calculations.

Acknowledgements

References

de Gouw, J. A., and C. Warneke (2007), Measurements of volatile organic compounds in the earth's atmosphere using proton‐transfer‐reaction mass spectrometry, *Mass Spectrom. Rev.*, *26*(2), 223-257.

Fortner, E. C., et al. (2012), Particulate Emissions Measured During the TCEQ Comprehensive Flare Emission Study, *Ind. Eng. Chem. Res.*, *51*(39), 12586-12592, doi:10.1021/ie202692y.

Gilman, J. B., B. M. Lerner, W. C. Kuster, and J. A. de Gouw (2013), Source Signature of Volatile Organic Compounds from Oil and Natural Gas Operations in Northeastern Colorado, *Environ. Sci. Technol.*, *47*(3), 1297-1305, doi:10.1021/es304119a.

Herndon, S. C., et al. (2008), Correlation of secondary organic aerosol with odd oxygen in Mexico City, *Geophys. Res. Lett.*, *35*(15), L15804, doi:10.1029/2008GL034058.

Herndon, S. C., M. S. Zahniser, D. D. Nelson, Jr., J. H. Shorter, J. B. McManus, R. Jimenez, C. Warneke, and J. A. de Gouw (2007), Airborne measurements of HCHO and HCOOH using a pulsed quantum cascade laser system, *J. Geophys. Res.*, *112*, D10S03, doi:10.1029/2006JD007600, doi:10.1029/2006JD007600.

Kebabian, P. L., W. A. Robinson, and A. Freedman (2007), Optical extinction monitor using cw cavity enhanced detection, *Rev. Sci. Instrum.*, *78*, 063102 (063109), doi:10.1063/1.2744223.

Lee, B. H., et al. (2016), Highly functionalized organic nitrates in the southeast United States: Contribution to secondary organic aerosol and reactive nitrogen budgets, *Proc. Nat. Acad. Sci.*, *113*(6), 1516-1521, doi:10.1073/pnas.1508108113.

Massoli, P., et al. (2012), Pollution Gradients and Chemical Characterization of Particulate Matter from Vehicular Traffic near Major Roadways: Results from the 2009 Queens College Air Quality Study in NYC, *Aerosol Sci. and Technol.*, *46*(11), 1201-1218, doi:DOI: 10.1080/02786826.2012.701784.

McManus, J. B., J. H. Shorter, D. D. Nelson, M. S. Zahniser, D. E. Glenn, and R. M. McGovern (2008), Pulsed quantum cascade laser instrument with compact design for rapid, high sensitivity measurements of trace gases in air, *Appl. Phys. B*, *92*(3), 387, doi:10.1007/s00340-008-3129-9.

McManus, J. B., M. S. Zahniser, D. D. Nelson, J. H. Shorter, S. C. Herndon, D. Jervis, M. Agnese, R. McGovern, T. I. Yacovitch, and J. R. Roscioli (2015), Recent progress in laser-based trace gas instruments: performance and noise analysis, *Appl. Phys. B*, *119*(1), 203-218, doi:10.1007/s00340-015-6033-0.

Nelson, D. D., J. B. McManus, S. C. Herndon, J. H. Shorter, M. S. Zahniser, S. Blaser, L. Hvozdara, A. Muller, M. Giovannini, and J. Faist (2006), Characterization of a near-room-temperature, continuous-wave quantum cascade laser for long-term, unattended monitoring of nitric oxide in the atmosphere, *Opt. Lett.*, *31*(13), 2012-2014, doi:10.1364/OL.31.002012.

Onasch, T. B., A. Trimborn, E. C. Fortner, J. T. Jayne, G. L. Kok, L. R. Williams, P. Davidovits, and D. Worsnop (2012), Soot Particle Aerosol Mass Spectrometer: Development, Validation, and Initial Application, *Aerosol Sci. and Technol.*, *46*(7), 804-817, doi:DOI:10.1080/02786826.2012.663948.

Roscioli, J. R., S. C. Herndon, T. I. Yacovitch, W. B. Knighton, D. Zavala-Araiza, M. R. Johnson, and D. R. Tyner (2017), Characterization of Methane Emissions from Cold Heavy Oil Production with Sands (CHOPS) Facilities, *J. Air Waste Manage. Assoc.*, *submitted*.

Santoni, G. W., B. H. Lee, E. C. Wood, S. C. Herndon, R. C. Miake-Lye, S. C. Wofsy, J. B. McManus, D. D. Nelson, and M. S. Zahniser (2011), Aircraft Emissions of Methane and Nitrous Oxide during the Alternative Aviation Fuel Experiment, *Environ. Sci. Technol.*, *45*(16), 7075-7082, doi:10.1021/es200897h.

Wood, E. C., B. L. Deming, and S. Kundu (2017), Ethane-Based Chemical Amplification Measurement Technique for Atmospheric Peroxy Radicals, *Environ. Sci. Technol. Lett.*, *4*(1), 15-19, doi:10.1021/acs.estlett.6b00438.

Wood, E. C., et al. (2009), A case study of ozone production, nitrogen oxides, and the radical budget in Mexico City, *Atmos. Chem. Phys.*, *9*(7), 2499-2516.

Yacovitch, T. I., S. C. Herndon, G. Pétron, J. Kofler, D. Lyon, M. S. Zahniser, and C. E. Kolb (2015), Mobile Laboratory Observations of Methane Emissions in the Barnett Shale Region, *Environ. Sci. Technol.*, *49*(13), 7889-7895, doi:10.1021/es506352j.

Yacovitch, T. I., et al. (2014), Demonstration of an Ethane Spectrometer for Methane Source Identification, *Environ. Sci. Technol.*, *48*(14), 8028-8034, doi:10.1021/es501475q.

Yarwood, G., P. Karamchandani, L. Parker, D. Parrish, and T. Ryerson (2015), Quantifying Ozone Production from Light Alkenes Using Novel Measurements of Hydroxynitrate Reaction Products in Houston during the NASA SEAC4RS, edited.

Zahniser, M. S., D. D. Nelson, J. B. McManus, P. L. Kebabian, and D. Lloyd (1995), Measurement of Trace Gas Fluxes Using Tunable Diode Laser Spectroscopy, *Philos. Trans. R. Soc., A*, *351*(1696), 371-382, doi:10.1098/rsta.1995.0040.