AQRP Monthly Technical Report

PROJECT TITLE	Apportioning the Sources of Ozone Production during the San Antonio Field Study	PROJECT #	19-025
PROJECT PARTICIPANTS	Aerodyne Research, Inc.	DATE SUBMITTED	August 8, 2019
REPORTING PERIOD	From: July 1, 2019 To: July 31, 2019	REPORT #	10

A Financial Status Report (FSR) and Invoice will be submitted separately from each of the Project Participants reflecting charges for this Reporting Period. I understand that the FSR and Invoice are due to the AQRP by the 15th of the month following the reporting period shown above.

Detailed Accomplishments by Task

Task 1: High-Resolution (HR) Analysis

A finalized high-resolution dataset for the PTR-ToF instrument has been produced, with calibrations and sensitivity factors applied. Ions have been assigned chemical names, where possible, using chemical intuition and literature. Analysis of the GC-ToF dataset has also been completed, including production of time series from the second half of the campaign. This second half was measured using a replacement GC column that was not well characterized, and so results are largely uncalibrated. High-resolution analysis has been completed for the I-CIMS dataset, and progress on calibration and zero removal is underway. A software glitch has been identified that is complicating the output of a 2-day period in Floresville. The software engineers who wrote the program have been contacted, and parallel efforts are underway to get a fix or a work-around.

Task 2: PMF Analysis

Additional analysis of the I-CIMS PMF results is underway, in order to identify whether factors can be correlated with known photochemical processes such as isoprene oxidation. The mass spectra are dominated by intermediate oxidation products, which means that they may original from numerous source categories.

In addition to PMF analysis, traditional correlation analysis between tracers has been undertaken. The analysis shown below examines Floresville CAMS data for tracers of condensate tank vs traffic emissions.

Task 3: 0D Box Model

Progress has been made implementing a software wrapper to speed up and run the 0D Box Model. This wrapper helps load and constrain mixing ratios to their measured values.

Task 4: Back-Trajectory Footprint Analysis

The completed footprint analysis has been used in combination with PMF time series to help with interpretation of various factors.

Preliminary Analysis

The mobile lab was stationed at the Floresville AutoGC site from May 17 – May 22, 2017. Floresville due its proximity to the Eagle Ford oil and gas fields is expected to be impacted by the emissions from this activity. This is readily apparent in the GC data reported by from the Floresville AutoGC facility, where there are numerous episodes where large enhancements in major alkane species are observed. Analysis of the AutoGC data set for the month of May 2017 shows that most of measured species are highly correlated to ethane when its concentration exceeds 20 ppb, as shown in Figure 1.
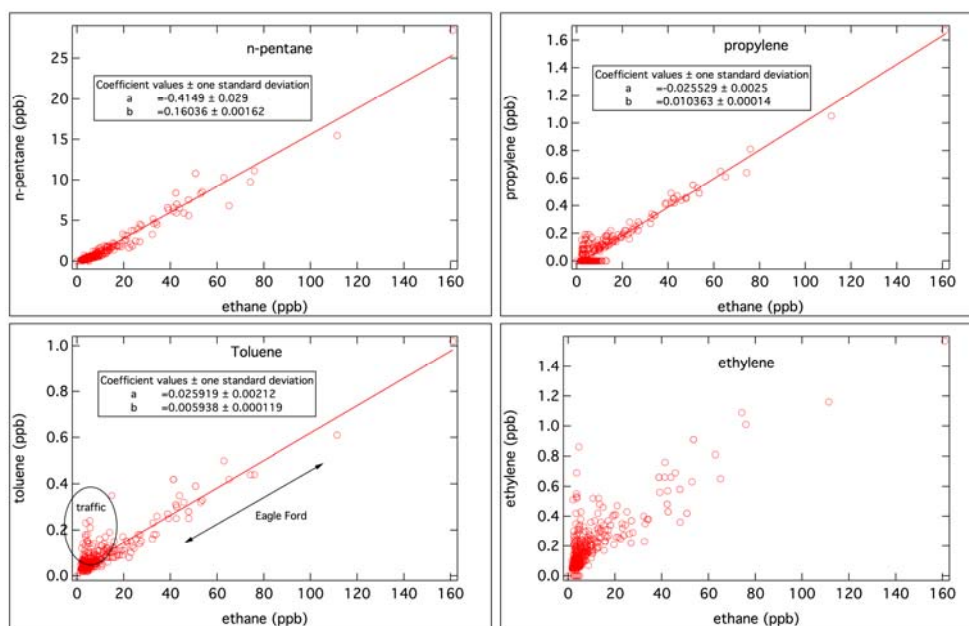

Figure 1. Correlation plots of selected hydrocarbons versus ethane. Data from the Floresville AutoGC.

It is instructive to examine whether other reactive alkene species, beyond those monitored by the AutoGC (C2-C4 alkenes) are associated with the alkane and aromatic enhancements from the Eagle Ford. PTR-ToF data is examined. While H_3O^+ reacts will all of the alkenes except ethylene, these species typically undergo a significant of fragmentation and produce ions predominately at m/z 43, 57, 71 and 85 depending on the number of carbons in the original molecule. The presence of additional alkenes would to lead to enhanced signals in these masses above what is anticipated from AutoGC data for the C3 and C4-alkenes. Figure 2 provides time series for the aforementioned species along with ethane and CO measurements recorded by Aerodyne. As might be expected, there are no significant enhancements for the alkene components. The signal containing the propylene response ($C_3H_7^+$) is general agreement (~ 1% of ethane).
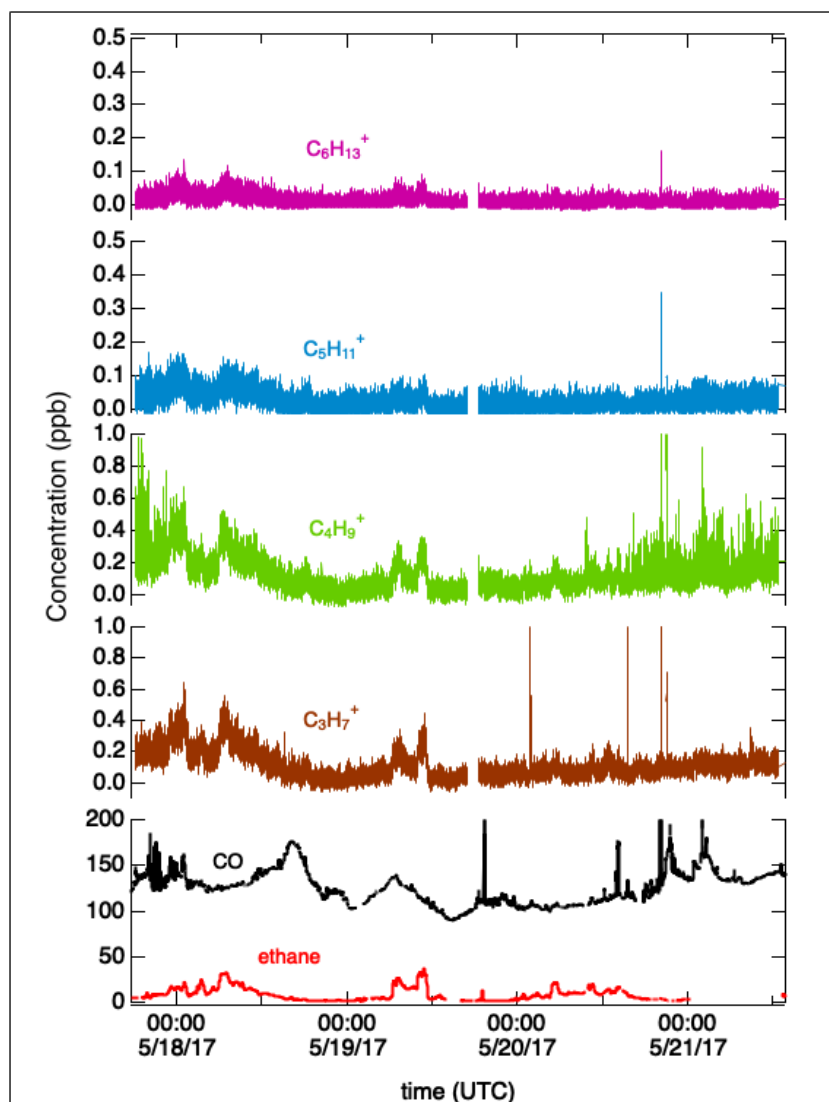
Figure 2. PTR-ToF-MS measurements from Floresville of ions produced from alkenes. Enhancements correlate with ethane and are in general agreement with what is anticipated from AutoGC measurements.

Data Collected

No data will be collected as part of this project. However, HR datasets are partway complete using final results from Task 1, HR Analysis.

Identify Problems or Issues Encountered and Proposed Solutions or Adjustments

The main challenge of this time in the project is in managing time spent on the analysis and writing given unforeseen demands of an extremely busy fieldwork season.

In late July, we asked for a no-cost extension to help complete the final analysis and reporting. With approval from all required parties, the **due date for the draft report has been extended to September 1st, 2019**.

We aim to have final results and conclusions completed before this date, however, in time to present at the August 22nd in-person meeting in August.

Goals and Anticipated Issues for the Succeeding Reporting Period

In the next reporting period, there are several goals:

- Task 1: Fix glitch in I-CIMS dataset, and apply zeroes and calibrations.
- Task 2: Analyze PMF results in the context of the draft final report outline.
- Tasks 1 and 2: Continue with peak identification efforts on PTR-ToF and I-CIMS data using results from Task 2. Include other existing SAFS data to help in identification (e.g. isoprene). Write results for draft report.
- Task 3: Apportion OH reactivity using box model
- All Tasks: Continue writing draft final report and preparing datasets for delivery.

Detailed Analysis of the Progress of the Task Order to Date

Dr. Yacovitch, original project PI, has returned from leave, and will resume work on this project. She is taking on much of the day-to-day project management and reporting responsibilities, while Dr. Roscioli maintains official project manager status through this final month.

Progress on Task 1 is complete, except for the 2-day Floresville glitch in the I-CIMS data. Task 4 is also complete. 0D modeling progress is slower than expected due to challenges in running the model itself and a busy fieldwork season. The main efforts on the project at this point are being directed towards 0D modeling (Task 3), outputting finalized data deliverables, and writing a cohesive final report.

Do you have any publications related to this project currently under development? If so, please provide a working title, and the journals you plan to submit to.

___Yes   _X_No

Do you have any publications related to this project currently under review by a journal? If so, what is the working title and the journal name? Have you sent a copy of the article to your AQRP Project Manager and your TCEQ Liaison?

___Yes   _X_No

Do you have any bibliographic publications related to this project that have been published? If so, please list the reference information. List all items for the lifetime of the project.

___Yes   _X_No

Do you have any presentations related to this project currently under development? If so, please provide working title, and the conference you plan to present it (this does not include presentations for the AQRP Workshop).

___Yes   _X_No

Do you have any presentations related to this project that have been published? If so, please list reference information. List all items for the lifetime of the project.

___Yes   _X_No

Submitted to AQRP by   Dr. Tara Yacovitch

On behalf of

Dr. Rob Roscioli

Principal Investigator