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**	Jan 8, 2019
REPORTING PERIOD	**From:** Dec 1, 2018 **To:** Dec 31, 2018	**REPORT #**	3

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

A productive mini-meeting was held to discuss results from the EC-PTR PMF analysis. This meeting resulted in several action items for continued PMF exploration and HR fitting analysis. Much of the progress this month focused on those specific analysis pathways identified in this mini-meeting and during the last whole-project meeting.

Task 1: High-Resolution (HR) Analysis

Mass-calibrations are the first step in performing a high-quality HR fit. The final instrument to be mass-calibrated is the I-CIMS dataset. Progress has been made on this front, and preliminary results are presented in the section "Preliminary Analysis"

Examination of the PTR-ToF dataset has been done by B. Knighton and has identified several new key masses that vary diurnally or with addition of zero air. Some additional important masses due to fragmentation of a parent ion have also been pinpointed, which enhance the number of potential species detected by this instrument. Occasionally, a peak has been identified only by its chemical formula, without a specific known chemical structure. The identity of these species can be further refined by looking at their behavior in PMF analysis, and also by comparison to the masses present in the other instruments, notably the I-CIMS, which uses different ionization chemistry.

Task 2: PMF Analysis

PMF analysis continued on the PTR-ToF dataset. A mini-meeting was held to discuss the initial PMF results, and resulted in several new analysis ideas, notably the suggestion to include additional low-mass ions due to fragmentation from larger species including alkyl nitrates.

A new PMF exploration of organic particulate matter measurements is underway using data from the Aerosol Mass Spectrometer (AMS). This action item was identified in the last project-wide meeting after discussion of PTR-ToF results. The goal of this analysis is to identify if there are

differences in the oxidation state of particulate matter that coincide with other temporal features in the dataset.

Task 3: 0D Box Model

0D box model software is installed and ready for testing. Work has begun to understand how input files must be prepared for correct processing by the model. A rough plan has been devised to write some simple code allowing a given time-period of data (in Igor Pro format) to be easily output in a format appropriate for the model (simple text files with specific formatting requirements).

Task 4: Back-Trajectory Footprint Analysis

Testing of the back-trajectory model continued, focusing on release and receptor heights. A time period while the mobile laboratory was stationed at UTSA was selected. In this test the results of heights 10, 30, 70 meters are compared to look for discrepancies in the location of the main contour ridge of the footprint. A preliminary version of the release height comparison is described in the "Preliminary Analysis" section below.

Preliminary Analysis

Mass calibrations of I-CIMS. The iodide chemical ionization mass spectrometer (I-CIMS) is sensitive to a wide variety of VOCs by soft ionization (either by direct ionization of a VOC, or by complexing with the iodide anion) followed by detection using a high-resolution time-of-flight mass spectrometer. In order to extract meaningful concentration information from the mass spectrum, it must first be calibrated along the mass scale, as the position of individual peaks may drift substantially over the course of minutes or hours. During this period of analysis for the SAFS project I-CIMS mass spectra were calibrated.

While there will be further refinement of calibration as analysis continues, the initial calibration results look promising. In order to calibrate, peaks must first be identified in the mass spectrum that are associated with a known ions, that will serve as "yardsticks" against which the rest of the spectrum will calibrated. In principle, the arrival time of a certain ion will depend upon its mass by the equation:

$$t_{arr} = p_1 \times \sqrt{m} + p_2, \quad (1)$$

where p_1 and p_2 are fit parameters based upon a fit using the calibrant mass peaks. In practice, the actual arrival time of an ion deviates slightly from this equation depending upon factors such as external fields, instrument cleanliness and spectrometer tuning. To accommodate this, the arrival time is modified to:

$$t_{arr} = p_1 \times m^{p_3} + p_2, \quad (2)$$

where p_3 would collapse to 0.5 in an ideal scenario.

Shown below are mass calibration fits from the first 12 days of measurement of SAFS. The top three traces are file and identifiers. The p1, p2, and p3 values are the fit results from equation (2). Notably the value of p3 is very near 0.5, indicating that the fit is close to ideal scenario of equation (1).

The calibrant peaks in this case were $I^-(H_2O)$ at mass 144.916 amu, $I^-(HNO_3)$ at 189.901 amu, ,I_3^- at 380.714 amu, CO_3^- at 59.985 amu, HCO_3^- at 60.993 amu and Lactic acid at 216.937 amu. The "ppm" traces are the difference between the arrival times of each of these calibrant mass and the

expected arrival times based upon the mass, multiplies by 10^6. Importantly, these values are <5 ppm over most of this period. On 5/16/2017 and 5/20/2017 the I-CIMS was re-tuned, resulting in dramatic improvements in the ppm levels for all peaks.

Future work for this data set will include further refinement of this mass calibration, peak identification, and development of time series for species of interest.

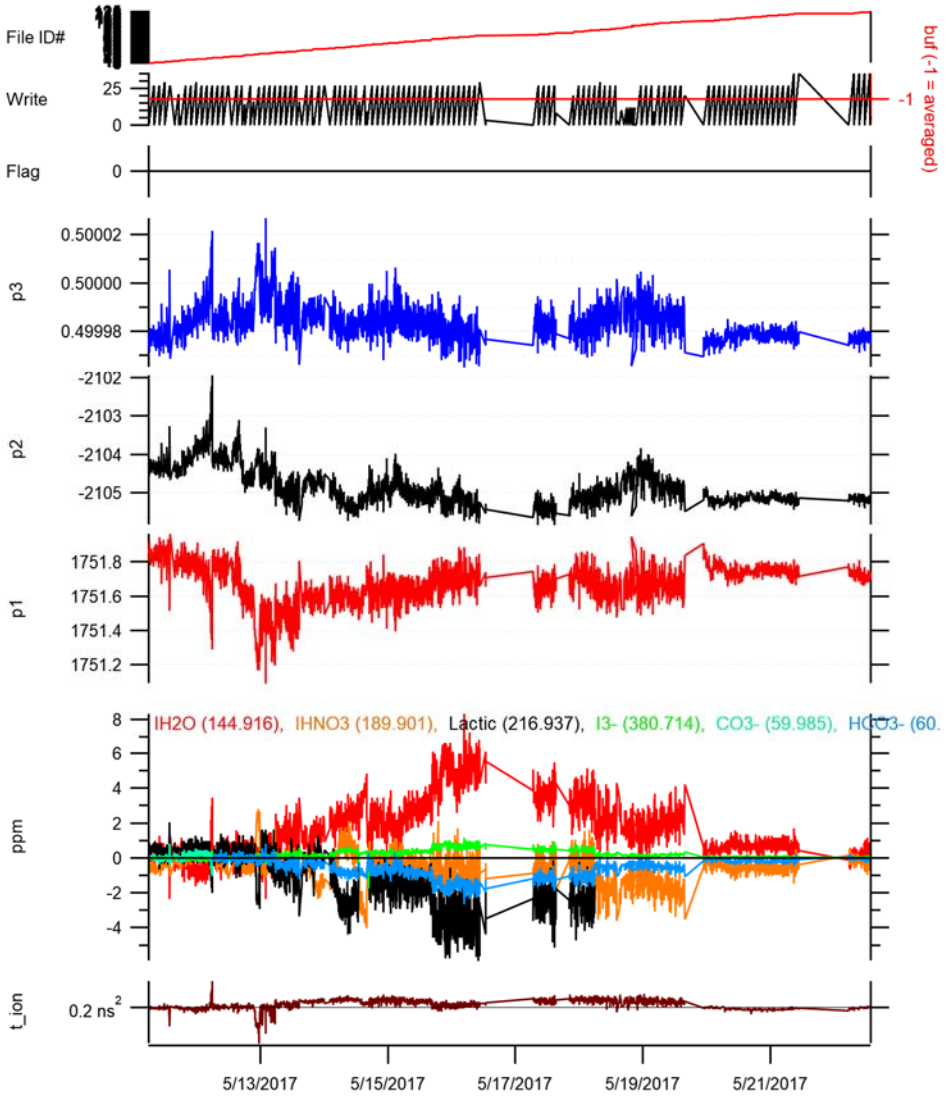

Figure 1. Mass calibration result for the I-CIMS instrument.

HYSPLIT Release Height Investigation. The results of a preliminary test of the release height are depicted in Figure 2. The figure suggests that the long-range transport contours are not strongly coupled to the choice of release height. In the case of the measurements, the air was sampled at ~10m. The convention within the back-trajectory calculation community, 10 meters is considered too low to the ground for the model to accurately calculate a footprint. This figure suggests that for long-range interpretation of airmass sources, the choice of release height (within the bounds explored here) may not matter. Note that the next steps will be to compare the actual magnitude of the footprint. In this analysis, owing to the use of a log scale, some numerical differences due to the simulated release height will not be discerned. This release height insensitivity lends confidence, however, to the planned use of these results in this research

project: figures such as those below will be used in a qualitative way to look at the geographic area sampled for better understanding of the potential emission sources.

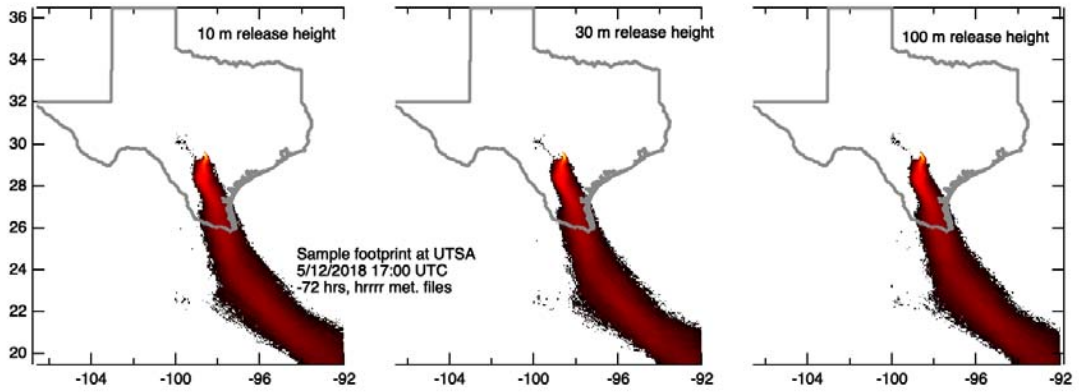

Figure 2. Sensitivity of the model release height. The three panels (from left the right) are the result of the HYSPLIT model calculation of airmass 'footprint' at 10, 30, 100 meters respectively. The color scale is a logarithmic representation of likely surface sources during the prior three days.

Data Collected

No data will be collected as part of this project. However, data will be generated after completion of Task 1, HR analysis.

Identify Problems or Issues Encountered and Proposed Solutions or Adjustments

No specific problems or issues have come up during this reporting period. We will continue with regular project meetings to assess progress and challenges for each task.

Goals and Anticipated Issues for the Succeeding Reporting Period

In the next reporting period, there are several goals:

- Task 1: Finalize the I-CIMS mass calibration and begin generation of a pseudo-HR dataset.
- Tasks 1 and 2: Continue with peak identification efforts on PTR-ToF data using results from Task 2
- Task 2: Hold two mini-meetings on the GC-ToF dataset: one working meeting to discuss PMF analysis methodology specific to this instrument, and one to review overall progress on data analysis for this instrument.
- Task 2: Continue PMF analysis of the PTR-ToF dataset based on action items from the last mini-meeting.
- Task 3: Test the 0D box model with the provided test case. Write simple code to output SAFS data in a format that is easily ingested by the box model.
- Task 4: Complete testing of HYSPLIT model.

No issues are anticipated.

Detailed Analysis of the Progress of the Task Order to Date

A decent amount of progress has been completed in this past reporting period, despite a lull due to the holidays and a scientific conference.

Significant progress has been made on Task 1, HR fitting, with the final mass-based instrument, the I-CIMS, undergoing mass-calibration.

Task 4, HYSPLIT back-trajectories, is nearing completion. This task is mostly independent of the other tasks, and as a result could be begun earlier than planned.

Significant progress is also continuing on Task 2, PMF analysis, spurred along by a mini-meeting specific to the PTR-ToF instrument.

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

Principal Investigator