AQRP Monthly Technical Report

PROJECT TITLE	Apporting the Sources of Ozone Production during the San Antonio Field Study	**PROJECT #**	19-025
PROJECT PARTICIPANTS	Aerodyne Research, Inc.	**DATE SUBMITTED**	May 8, 2019
REPORTING PERIOD	**From:** April 1, 2019 **To:** April 30, 2019	**REPORT #**	7

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

High-resolution analysis has been completed for both the I-CIMS dataset, and these results have been incorporated into subsequent tasks like PMF analysis. Preliminary examination of the hundreds of ion signals identified in the I-CIMS data show that the original 2017 SAFS dataset will be supplemented as part of this project, both with improved time coverage due to improved fits, and with additional chemical species. Minor problems in the HR fitting procedure have been identified (including glitches in the fit results, and inconsistent error estimates) and will be corrected in the coming weeks.

Task 2: PMF Analysis

Preliminary PMF analysis of the I-CIMS dataset has been executed. This analysis looks at hourly data, excluding the impact of zero-air additions and other invalid data. It reveals a number of distinct factors, including factors with clear diurnal character. These PMF analyses are preliminary and subject to revision. The initial results are reported in the "Preliminary Analysis" section below. Future PMF investigations will look at higher-resolution data in order to identify those ions that respond to additions of zero-air.

Task 3: 0D Box Model

The 0D Box Model is based on the dynamically simple model for atmospheric chemical complexity (DSMACC) [Emmerson et al, 2009]. With assistance from Barron Henderson, the master chemical mechanism (MCM) version 3.3 has been incorporated into the code base. The quantified $j(NO_2)$ data has been injected as well, supplanting the native clear sky photolysis rates. The challenge we encountered lay in the intermediate species. We found that as the model ran to steady state, the mixing ratios of unmeasured (or unconstrained) compounds increased in an unrealistic manner. We have adopted the methods described in Edwards et al., 2013 to mitigate the model artifact. Essentially, this works by introducing a depositional loss term that is a catch all value with 1/*k* time constant of 24 hrs for inert species and 10 hrs for compounds known to have additional true depositional losses. We are pursuing two paths for progress. The first involves running a simple set of constrained species to fine tune the model work-flow. The current method of operation involves stopping the model every half hour and reasserting the constrained species. The model stop/starts are introducing bottlenecks that are being addresses with more optimized code.

The second progress path involves expansion of the suite of volatile organic carbon compounds. We have identified additional data input needs of the model (e.g. concentrations of certain alkanes). Depending on the identity of the desired input species, there may be data gaps during the campaign. One solution that has been developed is to determine ratios of species of interest versus certain common denominator species that have complete data coverage during the campaign. Such denominator species include ethane and carbon monoxide. Identifying representative ratios and their typical ranges will allow us to give the model reasonable input concentrations, even during periods where data coverage was poor.

The GC-ToF dataset has been mined to produce select ratios of chemical tracers. These ratios will be used in the 0D model to ensure realistic defaults get used in the simulations.

Task 4: Back-Trajectory Footprint Analysis

A more complete Hysplit footprint dataset (with better spatial resolution and covering the entire SAFS timespan) has been used in a footprint overlap analysis with different Texas land use types. Categories of land use were also modified versus the preliminary analysis in order to separate vegetation types including oak (a strong isoprene emitter), and to include the impact of all oil and gas plays in the measurement domain (including, for example, the Barnett shale play).

Preliminary Analysis

Preliminary PMF investigations were conducted on the high-resolution dataset from the I-CIMS instrument. This analysis is ongoing and these results are subject to revision. A strict quality-assurance procedure was done on the raw dataset to remove the influence of zero-air additions, fit failures, and any other periods of data deemed unsatisfactory in the original 2017 project dataset. Note that final data produced from these high-resolution fits will be able to cover additional time periods.

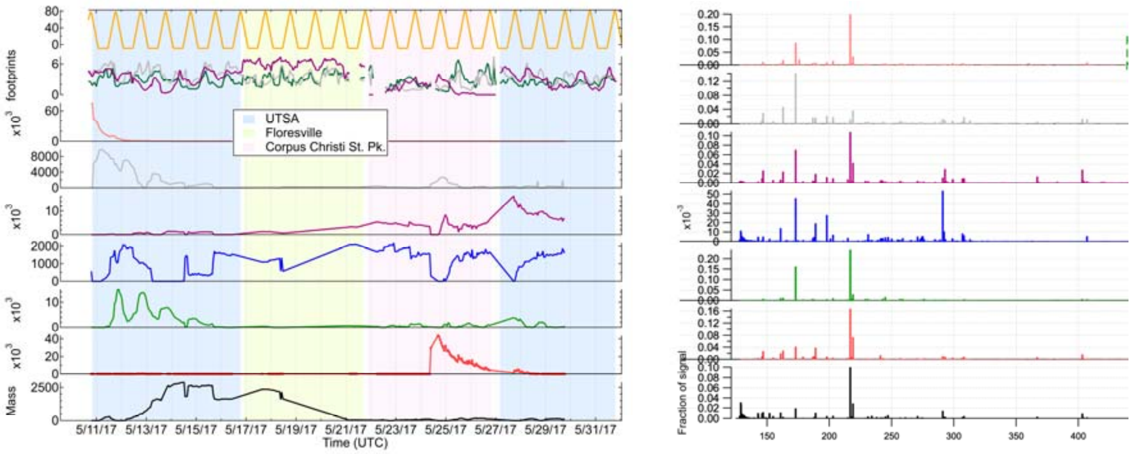

Figure 1. Time traces for preliminary I-CIMS PMF analysis (left) and mass spectra (right). PMF factors (bottom 7 traces, black through pink) are shown. The time trace graph also shows solar elevation angle (gold) and Hysplit overlap footprints with oil and gas (purple), oak (green) and urban (grey) landcover. Times are shaded according to measurement location.

Two interesting factors are identified in the data that have opposite behavior relative to sunlight (Figure 2). The green factor peaks at mid-day while the grey factor peaks at night. Such observations will be combined with a detailed investigation of the mass spectra in order to identify potentially new ions of scientific interest, and, more importantly, to understand their sources.

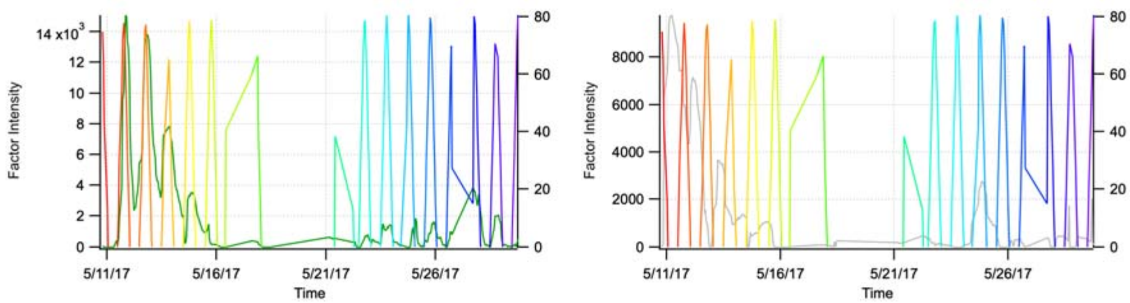

Figure 2. Time traces showing I-CIMS PMF factors (green, left, and grey, right) compared to solar elevation angle (rainbow).

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 issues have come up in the most recent reporting period.

Goals and Anticipated Issues for the Succeeding Reporting Period

In the next reporting period, there are several goals:

- Task 1: Identify species of most interest in integrated high-resolution I-CIMS dataset.
- Task 2: Run PMF on I-CIMS dataset looking for ions that respond to zero air addition.
- 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). This task will be ongoing through the next few reporting periods.

- Task 3: Incorporate additional real measurement data and/or ratios of tracers into the 0D model.
- All Tasks: Tailor work towards answering main project goals and filling in the final report outline

No issues are anticipated.

Detailed Analysis of the Progress of the Task Order to Date

Management of the project, including reporting responsibilities, has been transitioned over to Dr. Roscioli as Dr. Yacovitch takes leave. This was done following the procedures laid out in the contract, and with full approval of AQRP management.

Progress continues on all tasks. Tasks 1 and 2 have seen major progress as the high-resolution fit results from the I-CIMS instrument have been analyzed.

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. Rob Roscioli

Principal Investigator

References

Emmerson, KM; Evans, MJ (2009) Comparison of tropospheric gas-phase chemistry schemes for use within global models, *ATMOS CHEM PHYS*, **9(5)**, pp1831-1845 doi: 10.5194/acp-9-1831-2009 .

P. M. Edwards, M. J. Evans, K. L. Furneaux, J. Hopkins, T. Ingham, C. Jones, J. D. Lee, A. C. Lewis, S. J. Moller, D. Stone, L. K. Whalley and D. E. Heard, "OH reactivity in a South East Asian tropical rainforest during the Oxidant and Particle Photochemical Processes (OP3) project", Atmos. Chem. Phys., 13, 9497–9514, 2013, doi:10.5194/acp-13-9497-2013