

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	June 10, 2019
REPORTING PERIOD	From: May 1, 2019 To: May 31, 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 the I-CIMS dataset, and these results have been incorporated into subsequent tasks like PMF analysis. A two-day period from Floresville is still being analyzed.

Task 2: PMF Analysis

The hourly ICIMS data has been analyzed using PMF to create time-dependent factors for comparison to other gas phase species as well as other data. A list of As described below there are clear correlations between certain PMF factors and other VOCs measured. These PMF analyses are preliminary and subject to revision. The initial results are reported in the “Preliminary Analysis” section below. A list of 34 ion masses that are most active in the PMF analysis have been compiled, and that list has been further refined to identify those that respond to zero air additions. These ions are currently being investigated to identify atmospherically relevant chemistry.

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. Gaps in the GC-ToF dataset will be addressed by using VOC-to-small-molecule ratios determine during periods with good overlap between GC-ToF and TILDAs, VOCUS, or I-CIMS datasets.

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

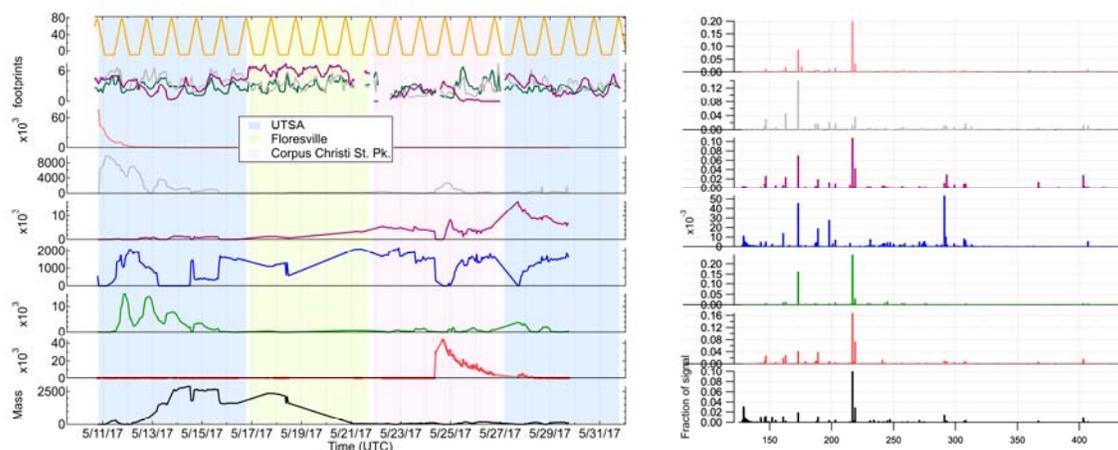


Figure 1. Time traces for preliminary I-CIMS PMF analysis (left) and mass spectra (right). PMF factors (bottom 7 traces, black through pink) are shown. The time trace graph also shows solar elevation angle (gold) and Hysplit overlap footprints with oil and gas (purple), oak (green) and urban (grey) landcover.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

Two interesting factors are identified in the data that have opposite behavior relative to sunlight (Figure 2). To delve deeper into the atmospheric chemistry, we can correlate these factors with a wide range of species measured on other instruments.

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 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 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 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 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](https://doi.org/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