AQRP Monthly Technical Report

PROJECT TITLE	Analysis of Ozone Production Data from the San Antonio Field Study	**PROJECT #**	19-040
PROJECT PARTICIPANTS	Ezra Wood, Shannon Capps, Daniel Anderson	**DATE SUBMITTED**	7/8/2019
REPORTING PERIOD	**From:** 6/1/2019 **To:** 6/30/2019	**REPORT #**	9

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

The goal of Task #1 is to quantify the dependence of the ozone production rate on the concentrations of NOx, VOCs, and other measurements at the three SAFS sites where peroxy radical concentrations were measured. Most of this work has been collected into a paper which was submitted to the journal *Atmospheric Chemistry and Physics* in October of 2018. The final revised paper has been accepted and published and can be accessed at https://www.atmos-chem-phys-discuss.net/acp-2018-1083/. Remaining parts of Task #1 are to investigate the influence of biomass burning on ozone formation in the San Antonio area and to investigate to what extent the time averaging of the NO and peroxy radical measurements affects the calculated ozone production rates. Preliminary analysis for the first biomass burning topic is presented below. We have not yet worked on the time averaging topic yet.

Task #2 consists of conducting 0-D photochemical modeling constrained by the Aerodyne/Drexel and Rice/Baylor/U. Houston measurements with several model chemical mechanisms for four SAFS measurement sites, spanning a large range of NOx values. We have spent little time on task #2 during this reporting period, though it is nearly complete.

The goal of Task #3 is to apportion ozone concentrations to location-specific emission sources using 3-D air quality modeling with the instrumented Community Multiscale Air Quality model (CMAQ). Investigation of the vertical variation in ozone formation appears below in the "preliminary analysis" section.

Preliminary Analysis

To investigate the impact of biomass burning on ozone concentrations and formation rates in San Antonio we investigated correlations of various relevant measurement-based metrics from the San Antonio Field Study with biomass burning tracers. Figure 1 below shows the time series of *in situ* observations of O_3, XO_2 ($[HO_2] + [RO_2]$), $P(O_3)$, and the biomass burning tracers HCN and black carbon. The tight correlation and elevated concentrations of HCN and BC suggest that the AML measured biomass burning influenced air on multiple occasions at both the Floresville and UTSA sites.

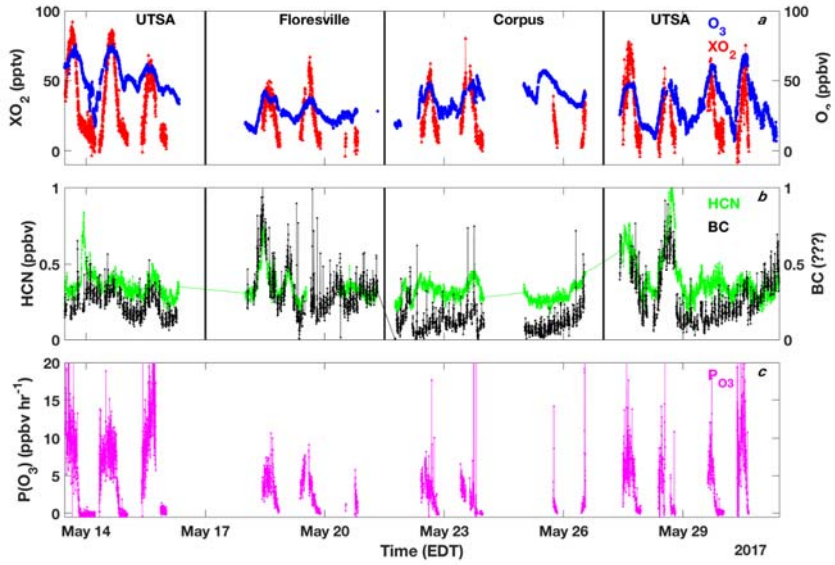

Figure 1.

Figure 2 shows the distribution of O_3 and $P(O_3)$ for biomass burning influenced air as well as air not influenced by biomass burning emissions. We define 75th and 95th as air parcels where both HCN and BC were both above the 75th and 95th percentile of observations for the duration of the campaign. "No fire" indicates observations where both HCN and BC were below the 75th percentile. At the UTSA site, both O_3 and $P(O_3)$ were depressed in the biomass burning air parcels as compared to the "No fire" case, with median O_3 lower by ~10 ppbv and median $P(O_3)$ lower by 2 ppb/hr for the 75th percentile case. The opposite signal was observed at Floresville, with higher O_3 and $P(O_3)$ for the biomass influenced air parcels.

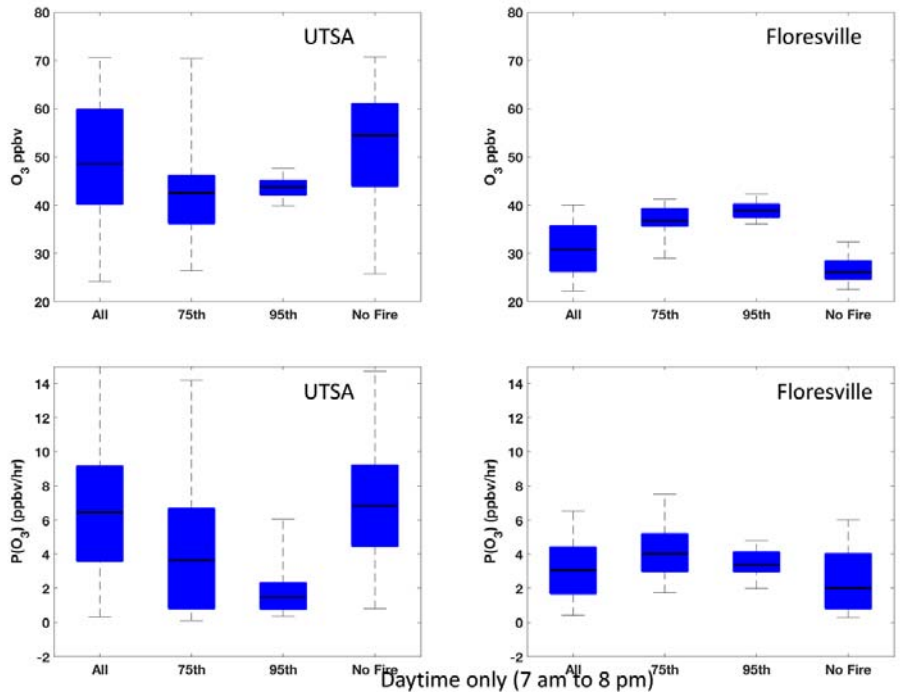

Figure 2.

To determine the source of these differences, we can explore variations in P(HOx), as higher P(HOx) tends to lead to higher O_3 production. Figure 3 shows the distribution of P(HOx), J(O^1D), and HCHO (the two dominant terms in calculating P(HOx)) for the UTSA site. Again, P(HOx) is depressed for the biomass burning cases as compared to the "no fire" air parcels. This decrease is being driven, however, by decreases in J(O^1D), which affects the P(HOx) term more strongly than the increase in HCHO. The opposite trend is seen at Floresville. This suggests that the differences in O_3 and $P(O_3)$ at the two sites for the biomass burning influenced air parcels are likely driven by differences in insolation (i.e., the smoky days might have happened to also have been less sunny days)

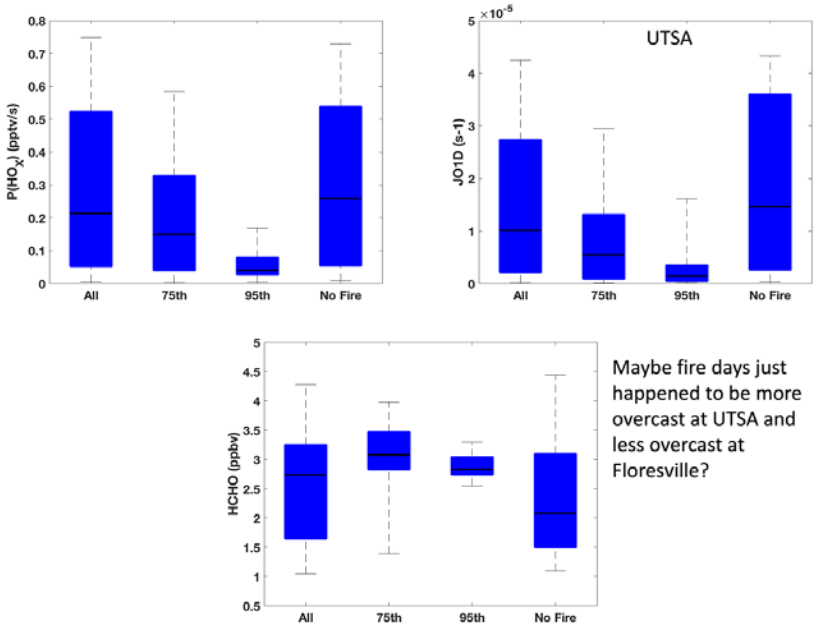

Figure 3

Figure 4 compares two CMAQ runs, a base run, with all emissions, and a "No biomass burning" run, in which all biomass burning emissions within the model domain were turned off. The figure shows the difference between the two runs. No grid cell saw any change in O_3 concentration greater than 0.1 ppbv, suggesting that biomass burning within the modeling domain does not influence O_3 production in San Antonio during SAFS. Influence from outside the modeling domain, particularly from the Yucatan, would not be evident in this analysis, and we are currently exploring ways to determine the importance of these fires for O_3 production.

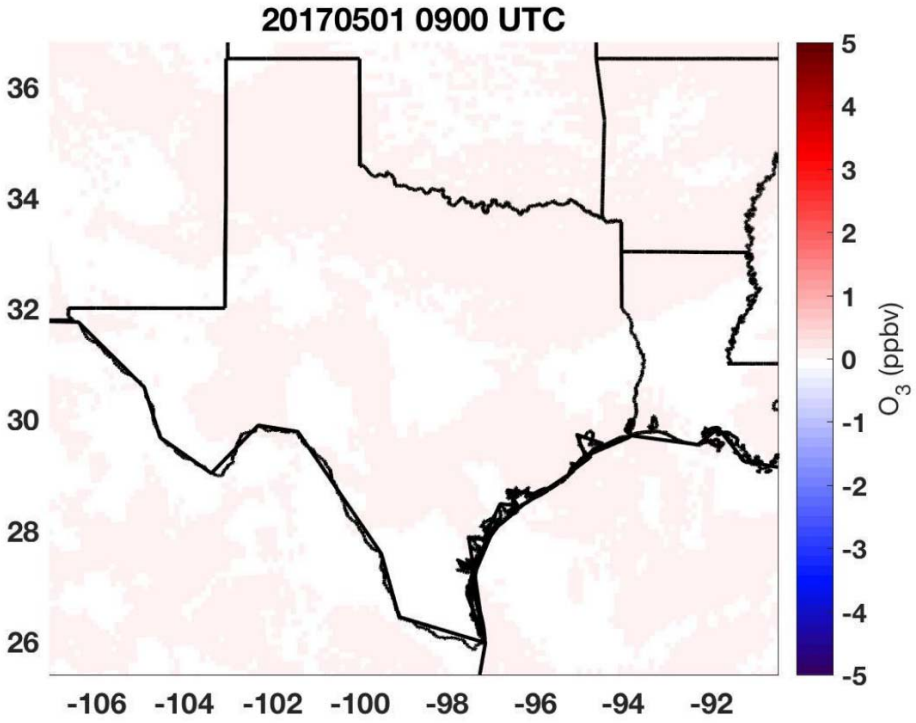

Figure 4.

We also investigated the vertical distribution of $P(O_3)$ in San Antonio using CMAQ. Most of our prior analysis based on the SAFS measurements were based on the surface-measurements, which can overemphasize the importance of the photochemistry occurring at the surface at the expense of the rest of the boundary layer.

Figure 5 shows the vertical $P(O_3)$ profile from CMAQ for a representative day over Bexar County. For most of the day, there is a significant decrease in $P(O_3)$ with decreasing pressure. This suggests that high $P(O_3)$ rates near the surface, such as those seen at the Travelers' World site, might be confined to the surface, and are not necessarily representative of the rates seen throughout the mixed layer.

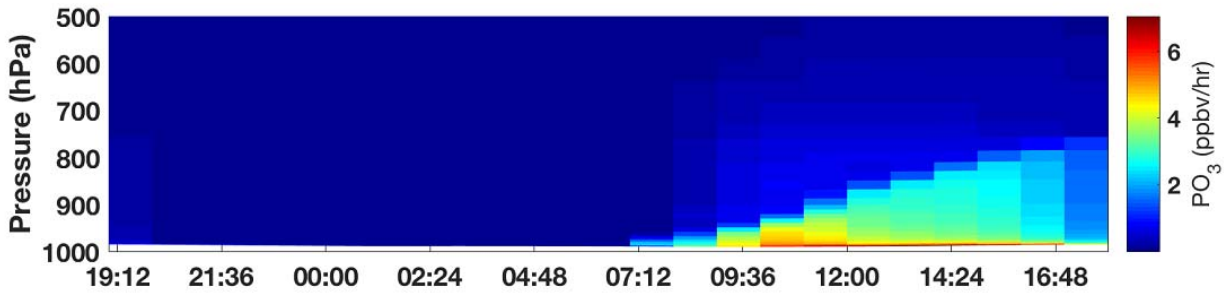

Figure 5.

Data Collected

No additional data have been collected.

Identify Problems or Issues Encountered and Proposed Solutions or Adjustments

The federal government shutdown delayed our work on task 3 as described in an earlier report. Additionally, our plans to utilize CMAQ's Integrated Source Apportionment Method (ISAM) are in jeopardy as its release has been delayed until late July 2019 which will not leave us enough time to use it. Instead we are planning on conducting forward emission sensitivity tests in CMAQ, especially for NOx.

Goals and Anticipated Issues for the Succeeding Reporting Period

We will focus on the forward emission sensitivity tests in CMAQ.

Detailed Analysis of the Progress of the Task Order to Date

Tasks 1 and 2 are near-complete. Task 3 is making progress.

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?

__X_Yes __ _No

The title is "Characterization of Ozone Production in San Antonio, Texas Using Observations of Total Peroxy Radicals", submitted and accepted to *Atmospheric Chemistry and Physics*, accessible at https://www.atmos-chem-phys-discuss.net/acp-2018-1083/. This manuscript was sent to Gary McGaughey (Project Manager for project 17-032, during which most of the analysis was conducted) and Mark Estes (TCEQ) prior to submission.

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

Ezra Wood,
Principal Investigator