AQRP Monthly Technical Report

PROJECT TITLE	Spatial Mapping of Ozone Formation near San Antonio	**PROJECT #**	17-032
PROJECT PARTICIPANTS	Ezra Wood	**DATE SUBMITTED**	8/8/2017
REPORTING PERIOD	**From:** 7/1/2017 **To:** 7/31/2017	**REPORT #**	8

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 "Recruit Post-doc" has been accomplished. Additionally, Jessica Pavelec, a 4th year chemistry major at Drexel, started work on April 3 as a full-time "co-op" student. Both the post-doc and undergraduate participated in the May field deployment in the greater San Antonio area.

Task 2 "Laboratory preparation" has been completed. Both the ECHAMP peroxy radical sensor and TD-CAPS organic nitrate instrument were tested in the laboratory, prepared for field deployment, and integrated into the Aerodyne Mobile Laboratory (AML). The main obstacle encountered was electrical noise encountered in the CAPS systems initially at Aerodyne during the integration. This noise was resolved in San Antonio.

Task 3 "Field Deployment" was completed from May 8 – 31 in and around San Antonio. The Aerodyne mobile laboratory deployed to the following three sites: 1. University of Texas at San Antonio (Northwest of the city), 2. Floresville, and 3. Mathis (near Corpus Christi).

Task 4 "Follow-up laboratory work" has commenced. This work focused on performing both NO_2 calibrations and HO_2 calibrations over a wider range of relative humidities than performed in San Antonio during the May field measurements.

Task 5 "Data work-up and analysis" has commenced, and has focused on working up the calibration and ambient data collected during the field measurements. We anticipate having the dataset finalized by the end of July.

Preliminary Analysis

The ozone production rate $P(O_3)$ for all the data collected during the San Antonio Field Study (see next section, Data collected) has been calculated by the following equation:

$P(O_3) = 8.5 \times 10^{-12}$ ([RO_2]+[HO_2])][NO], where the coefficient 8.5×10^{-12} is an average value for the rate constant for HO_2 + NO and RO_2 + NO for small organic RO_2 [8], in cm^3 $molecule^{-1}$ s^{-1}, with an estimated 2σ uncertainty of 15%. Additionally, the HOx radical production rate P(HOx) has been calculated using measurements of photolysis rates (e.g., "j_{HCHO}") and concentrations of water vapor, formaldehyde, ozone, acetaldehyde, and hydrogen peroxide:

$$P(HOx) = 2j_{(O1D)}[O_3](k_{O1D+H2O}[H_2O]/(k_{O1D+H2O}[H_2O] + k_{O1D+O2}[O_2] + k_{O1D+N2}[N_2]) + 2j_{HCHO\rightarrow H + CHO}[HCHO] + 2j_{CH3CHO \rightarrow CH3 + HCO}[CH_3CHO] + 2j_{H2O2}[H_2O_2]$$

The figure below shows the dependence of $P(O_3)$ on NO and P(HOx).

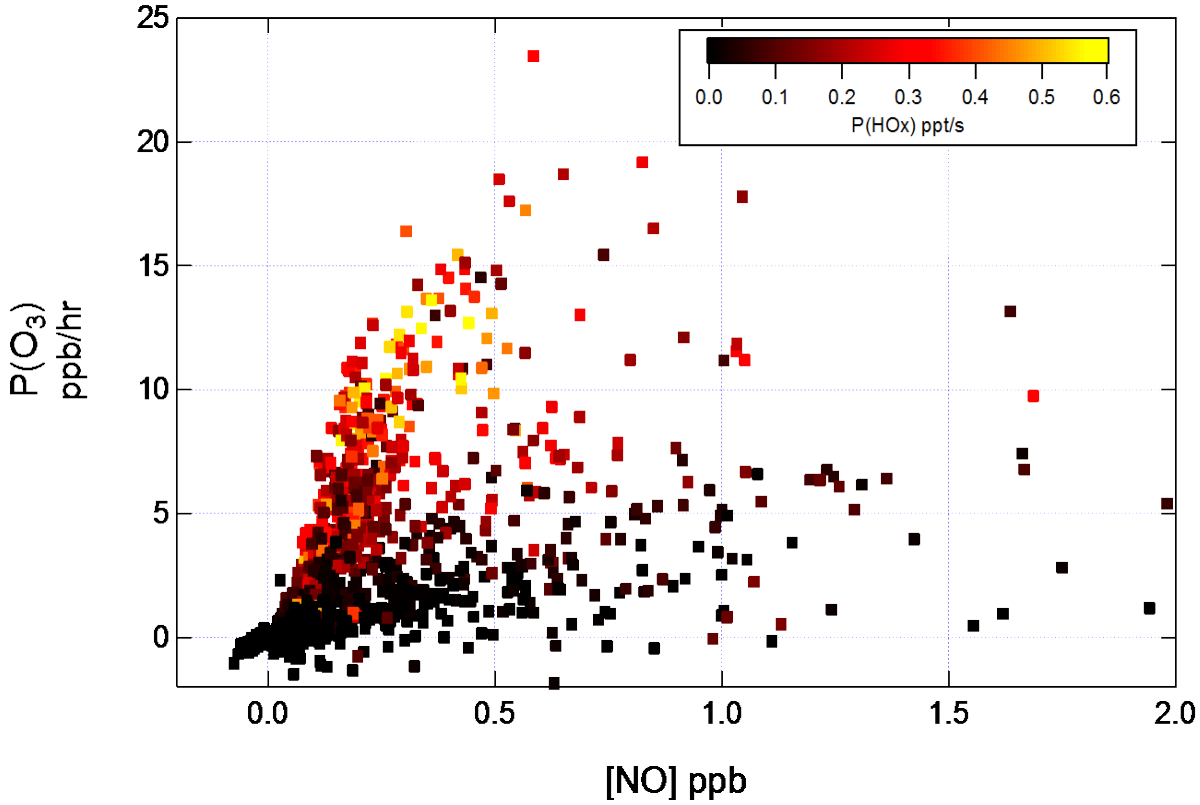

Figure 1. Dependence of $P(O_3)$ on NO, colored by P(HOx), for all the data collected during the San Antonio project. 10 minute average measurements were used.

The data in figure 1 can be divided into two main regimes: data with "low" P(HOx) (less than 0.2 ppt/s), and those at "high" P(HOx), (greater than 0.2 ppt/s). For both categories, $P(O_3)$ increases with NO at low NO values, with the high P(HOx) values much higher. For the high P(HOx) data, there are few points with [NO] greater than 0.5, but it appears that above ~0.5 ppb, $P(O_3)$ does not increase as much with NO as it did for [NO] less than 0.5 ppb. In figure 2, the median $P(O_3)$ values from figure 1 over "bins" of 50 ppt NO width are displayed vs. NO:

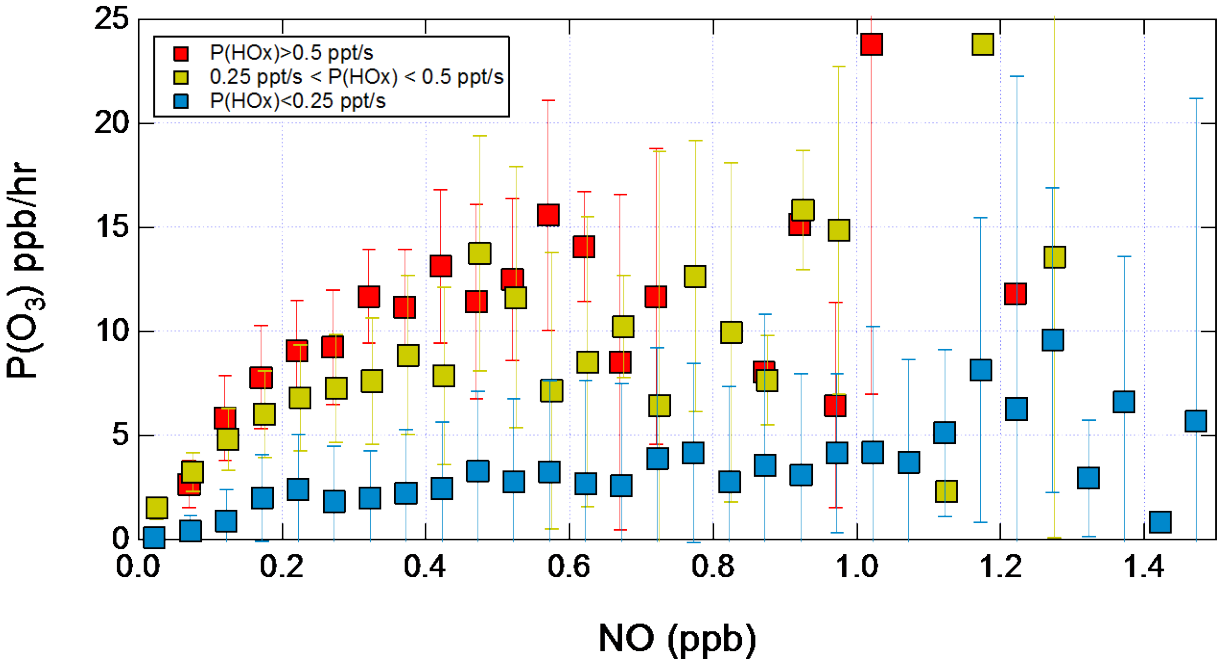

Figure 2. Dependence of $P(O_3)$ on NO and P(HOx). Each point is the median value within 50 ppt NO increments.

In figure 2, the data is collected into three P(HOx) ranges – low, medium, and high as indicated in the legend for figure 2. This shows that at low P(HOx), $P(O_3)$ no longer increases with NO for NO values greater than 0.2 ppb, whereas for the high P(HOx) values $P(O_3)$ no longer increases with NO for NO values greater than ~0.6 ppb. The scatter at higher values of NO is likely caused both by the few number of points at those higher NO values and the fact that the VOC concentrations might vary greatly for those high NOx concentrations. This is a topic for future analysis.

Data Collected

The time series for [ROx] (or equivalently $[HO_2] + [RO_2]$), NO and O_3 (measurements by Aerodyne Research), O_3 photolysis rate "jO1D"), and the calculated ozone production rate are displayed in figures 3 – 5.

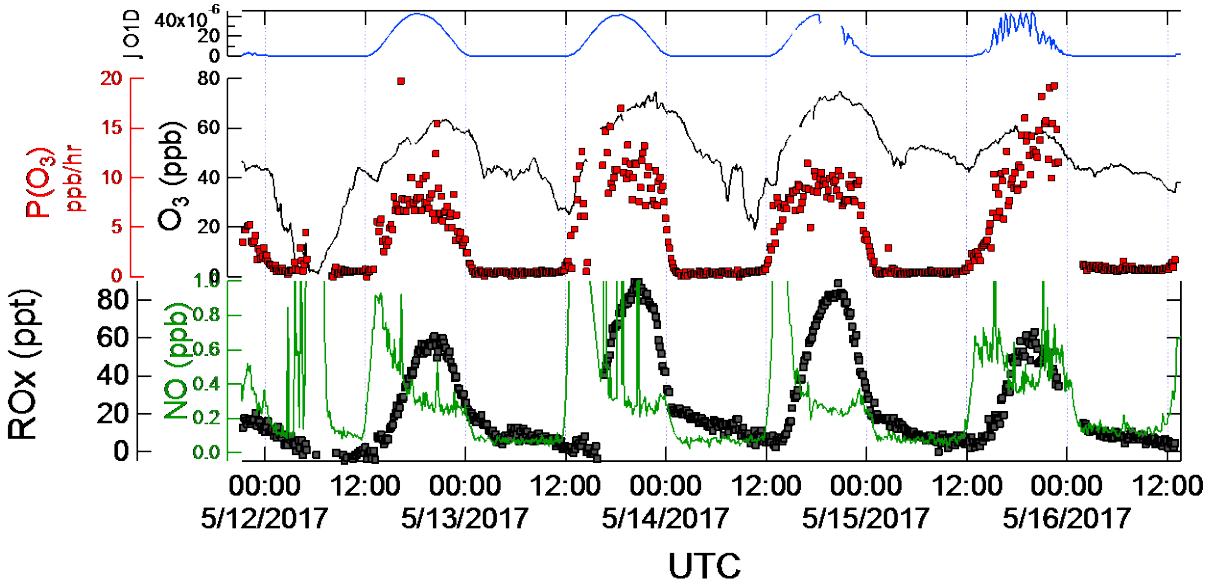

Figure 3. Time series of [NO], [ROx], [O_3], jO1D, and P(O_3) at the UTSA site.

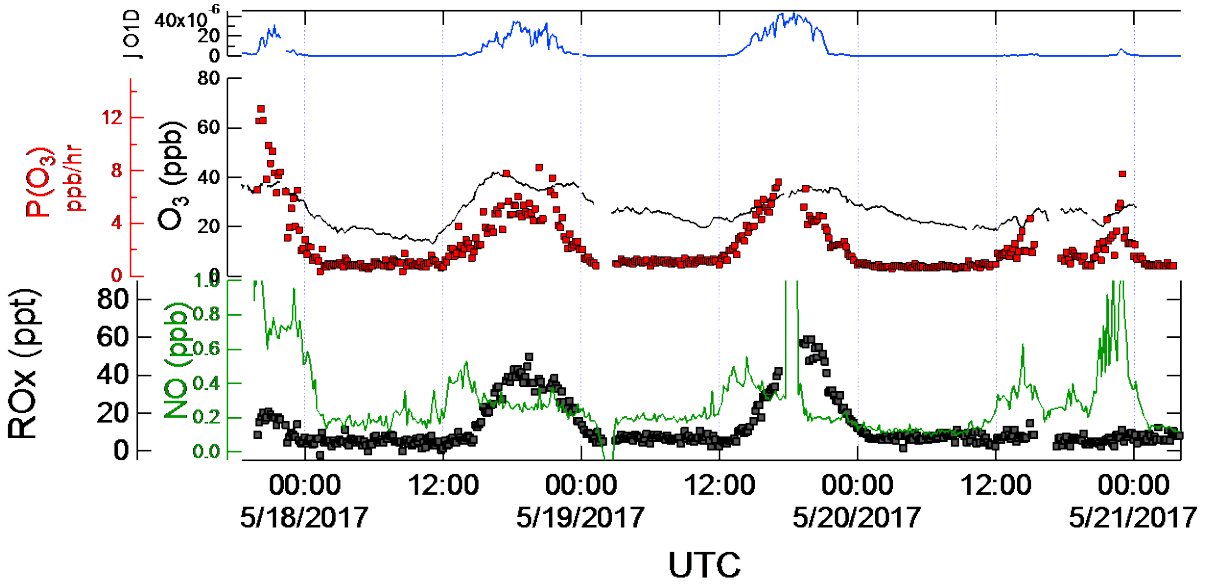

Figure 4. Measurements at the Floresville site.

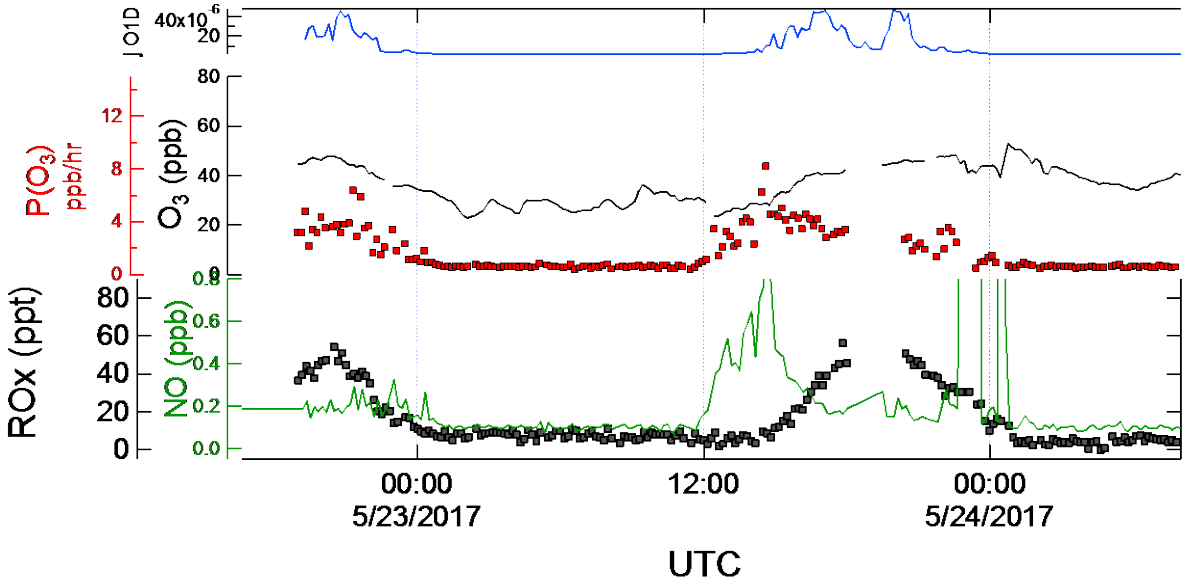

Figure 5. Measurements at the Corpus Christi site.

$P(O_3)$ values for the entire project, along w/ P(HOx), are shown in figure 6:

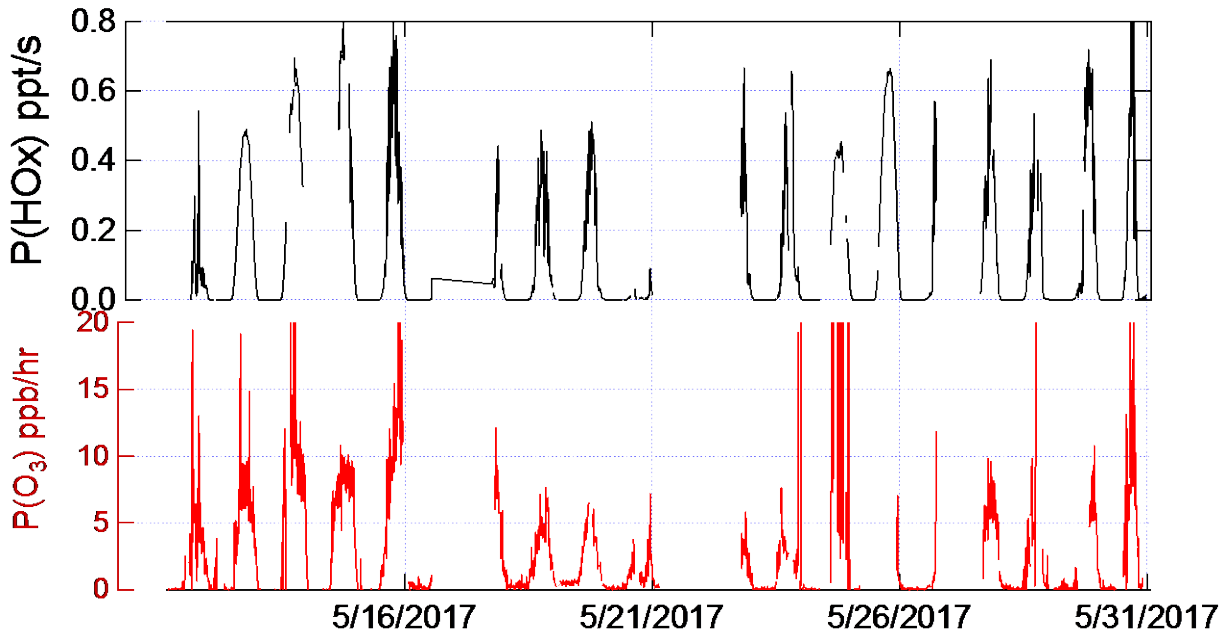

Figure 6. P(HOx) calculated using measured photolysis rates and radical precursors (O_3, H_2O, HCHO, CH_3CHO, H_2O_2) and $P(O_3)$.

The TD-CAPS system suffered a few experimental setbacks and as a result data are only available for the last few days of the project. Measurements of total acyl peroxy nitrates ("ΣPNs") were successful and showed adequate signal-to-noise, however the alkyl nitrate ($RONO_2$) measurements showed much lower concentrations and will require more refined analysis. Overall it is apparent, however, that alkyl nitrates were a much smaller component of NO_Y than peroxy nitrates.

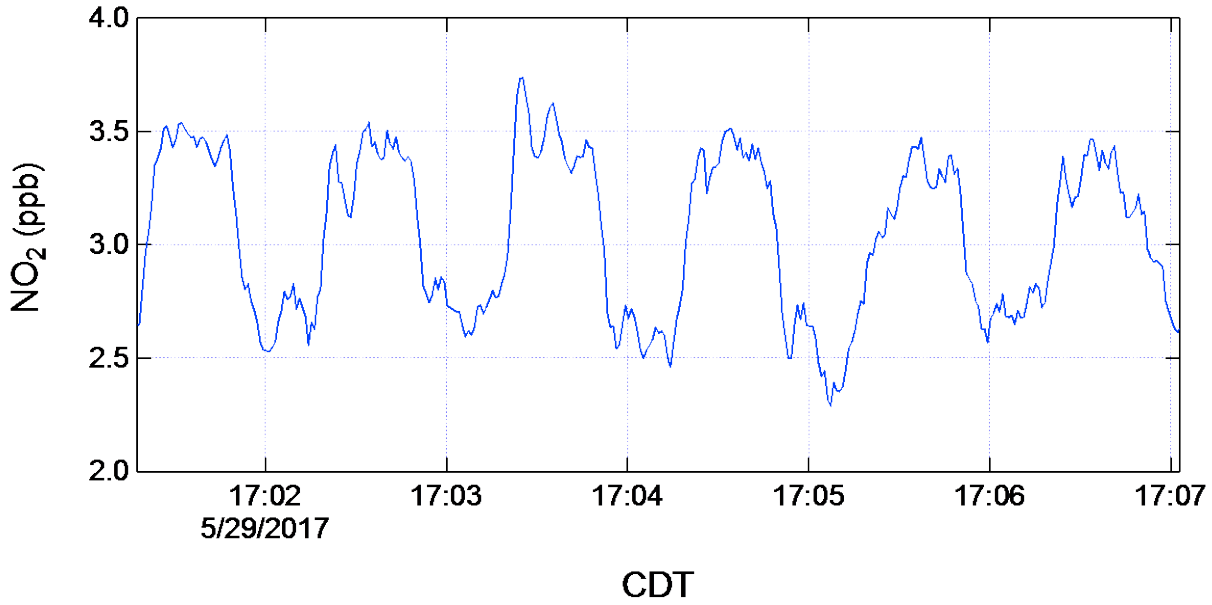

Figure 7. TD-CAPS measurements of total peroxy nitrates (PAN, PPN, MPAN, etc.). [ΣPNs] is equal to the difference in [NO_2] between sampling through the 200 °C quartz tube and unheated quartz tube, and equal to 0.8 ppb in the time window shown.

Identify Problems or Issues Encountered and Proposed Solutions or Adjustments

No new problems have been encountered during the month of July.

Goals and Anticipated Issues for the Succeeding Reporting Period

The follow-on calibrations will be finished during the month of August, with a goal to finalize the May dataset by the end of August. This work is continuing during a separate field deployment to Indiana that started in mid-July and will end mid-August.

Detailed Analysis of the Progress of the Task Order to Date

Task 1 “Recruit Post-doc”, Task 2 “Laboratory Preparation”, and Task 3 “Field Deployment” have been completed. Task 4 “Follow-up laboratory work” and Task 5 “Data work-up and analysis” commenced in June. Task 6 “Project Reporting and Presentation” are partially complete but will continue until the end of the project.

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).

__X_Yes ___No

We (Dan Anderson and Ezra Wood) have submitted an abstract for an eventual poster or oral presentation at the American Geophysical Union in New Orleans, December 2017. We submitted the abstract to AQRP (Gary McGaughey and Mark Estes) for approval, prior to the submission deadline.

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