Scope of Work For

# Project # 19-040
# Analysis of Ozone Production Data from the San Antonio Field Study

Prepared for

Air Quality Research Program (AQRP)
The University of Texas at Austin

By

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QA Requirements: Audits of Data Quality: 10% Required
Report of QA Findings: Required in Final Report

**Approvals**

This Scope of Work was approved electronically on **September 12, 2018** by Elena McDonald-Buller, The University of Texas at Austin

Elena McDonald-Buller
Project Manager, Texas Air Quality Research Program

This Scope of Work was approved electronically on **September 13, 2018** by Mark Estes, Texas Commission on Environmental Quality

Mark Estes
Project Liaison, Texas Commission on Environmental Quality

# Contents

**1.0 Abstract**

San Antonio experiences ozone ($O_3$) concentrations very close to the National Ambient Air Quality Standard of 70 ppb. Regulators will likely need to make science-based decisions on effective $O_3$ mitigation strategies in the current environment of declining urban nitrogen oxide emissions and variable oil and gas exploration activity. Much less is known about the mechanisms and rates of ozone formation in San Antonio than for Houston, which has been studied for decades. To address this paucity of knowledge, researchers from Drexel University, Aerodyne Research, Inc., the University of Houston, Rice University, and Baylor University deployed a large suite of analytical instrumentation to the greater San Antonio area as part of the 3-week "San Antonio Field Study" (SAFS) during May 2017. During SAFS, a large dataset of chemical composition and supporting parameters was acquired at four locations in the greater San Antonio area, from Lake Corpus Christi (150 km Southeast of San Antonio) to the University of Texas at San Antonio (20 km Northwest of the city center).

The proposed research directly responds to the first of the seven priority research areas identified in the AQRP Strategic Research Plan FY 18-19: "2017 San Antonio Field Study (SAFS) data analysis". Our work comprises the following analysis tasks, which will elucidate and quantify the contribution of emission sources to ozone concentrations in San Antonio:

1. 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.

2. Conduct 0-D photochemical modeling constrained by the Aerodyne/Drexel and Rice/U. Houston measurements with several model chemical mechanisms for four SAFS measurement sites, spanning a large range of NOx values, and compare modeled $P(O_3)$ rates to those calculated using the peroxy radical measurements where available.

3. Apportion ozone concentrations to location-specific emission sources using 3-D air quality modeling with the instrumented Community Multiscale Air Quality model (CMAQ).

These three tasks will quantify which emission source categories affect $O_3$ formation in the greater San Antonio area and address the relative importance of upwind and urban emission sources.

**2.0 Background**

Ozone ($O_3$) is the main component of photochemical smog and is classified as a "criteria" pollutant by the US Environmental Protection Agency. Ozone is formed by photochemical reactions involving volatile organic compound (VOCs) and nitrogen oxides (NOx) – it is not emitted directly into the atmosphere. The generalized reactions that lead to ozone formation are described below, where "$RO_2$" is an organic peroxy radical, e.g. $CH_3O_2$, $C_5H_8(OH)O_2$, etc.: (Atkinson, 2000):

$VOC + OH + O_2 \rightarrow RO_2$ R1
$RO_2 + NO \rightarrow RO + NO_2$ R2
$RO + O_2 \rightarrow carbonyl + HO_2$ R3
$HO_2 + NO \rightarrow OH + NO_2$ R4

The $NO_2$ formed by reactions 2 and 4 will undergo photolysis during the day, thereby forming ozone ($O_3$):

$NO_2 + sunlight \rightarrow NO + O$ R5
$O + O_2 + M \rightarrow O_3 + M$ R6

Thus the rate at which ozone is formed is effectively equal to the rate at which NO is converted to $NO_2$ by reaction with peroxy radicals ("$RO_2$" and $HO_2$):

$$P(O_3) = k_{HO2+NO}[HO_2][NO] + k_{RO2+NO}[RO_2][NO] \qquad \text{Eq. 1}$$

"$RO_2$" represents all organic peroxy radicals (e.g., $CH_3O_2$, $C_2H_5O_2$, etc.)

The value of $P(O_3)$ does not always simply increase with increased concentrations of VOCs or NOx, because NOx is involved in some of the radical termination steps that remove OH, $HO_2$, and $RO_2$ from the air. Ozone production is said to be "NOx-limited" if, due to low NO concentrations, HOx radicals (OH, $RO_2$, $HO_2$) are mainly removed by self-reactions (e.g., $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$). Ozone formation is "VOC-limited" (or "NOx-saturated") if HOx radicals are main lost via reactions with $NO_X$ (e.g., $OH + NO_2 + M \rightarrow HNO_3 + M$). Knowing in which chemical regime an air mass resides is crucial for designing effective ozone abatement strategies, since reducing NOx emissions can lead to undesirable *increases* in ozone formation rates if the air is in a VOC-limited state. This is the case in southern California, evident by the higher ozone observed on weekends when there is reduced NOx emissions due to lower diesel truck traffic (Pollack et al., 2012).

Analysis conducted at the end of AQRP project 17-032 "Spatial Mapping of Ozone Formation in San Antonio" generated the preliminary conclusions listed below regarding ozone formation at the University of Texas at San Antonio, Floresville, and Lake Corpus Christi measurement sites. Under normal Southeasterly winds, these three sites are downwind, upwind, and upwind of central San Antonio, respectively.

1. Calculated gross ozone production rates using measured peroxy radical and nitric oxide concentrations at were at most 20 ppb/hr and usually less than 10 ppb/hr. These values are lower than the highest values (over 50 ppb/hr) that have been observed in Houston (Mao et al., 2010). Net ozone formation rates (i.e., gross ozone formation rates minus ozone destruction

rates) were not explicitly determined but were likely 10 to 20% lower than the gross ozone formation rates. Ozone formation rates of 10 ppb/hr are still sufficient to increase ozone concentrations from background concentrations (~20-50 ppb) to values exceeding the 70 ppb air quality standard given certain meteorological conditions.

2. Ozone formation rates increased with increases in HOx radical production rates – mainly due to ozone photolysis (and subsequent reaction of electronically excited oxygen atoms with water vapor) and formaldehyde photolysis. Photolysis of nitrous acid (HONO) was unlikely an important HOx radical precursor.

3. Nitric oxide (NO) concentrations were usually less than 300 ppt, and as a result ozone formation was almost always NOx-limited. The time periods when ozone formation was VOC-limited usually occurred during overcast days when the absolute ozone formation rates were low (less than 3 ppb/hr).

As noted above this analysis is preliminary and the full dependence of ozone formation on other species (NOx, VOCs, other compounds) has not been explored. Furthermore, an important gap in the analysis is that it only uses data collected at measurement sites located upwind and downwind of central San Antonio, all of which had lower NOx concentrations than have been measured at the central urban sites operated by TCEQ.

**3.0 Objectives**

The overall objectives of this project are to elucidate the sources of high ozone concentrations in the greater San Antonio area and to conduct analyses that determine if our understanding of ozone formation is accurate. More detailed objectives are to answer the following science questions (and are closely related to the tasks described in section 4):

1. What is the dependence of ozone formation in the greater San Antonio area on concentrations of NOx, VOCs, and “HOx” radical precursors? Where and during what times of day is ozone formation “NOx-limited” vs. “VOC-limited”?

*These questions will be addressed by analyzing the mobile and stationary measurements of total peroxy radicals, nitrogen oxides, volatile organic compounds, and other measurements from the 2017 San Antonio Field Study. We will calculate instantaneous rates of ozone formation ($P(O_3)$) using equation 1 ($P(O_3) = k_{HO2+NO}([RO_2]+[HO_2])[NO]$). The NOx-limited or VOC-limited nature will be investigated by the relationship between $P(O_3)$ and [NO]. Preliminary analysis conducted shortly after the 2017 SAFS using only the Drexel/Aerodyne data indicated that ozone formation was usually NOx-limited in the upwind and downwind measurement sites. This preliminary analyst will be finalized as part of this project, and we will expand the analysis to include the data collected by the Rice / U. Houston teams which were in the higher-NOx urban core of San Antonio – a much needed complement to the Drexel/Aerodyne datasets which were only collected in lower-NOx locations (i.e., upwind and downwind of San Antonio).*

*2. Do current chemical mechanisms used in 0-D models correctly predict radical concentrations? This will be accomplished during Task 2 as described in the next section. Verifying agreement between measured and modeled radical concentrations will greatly support the results of the 3-D air quality modeling (Task 3).*

3. What are the relative contributions of different emission sources to ozone concentrations in San Antonio?
*This question will be addressed primarily through the use of CMAQ – EPA's 3-dimensional air quality model.*

## 4.0 Task Descriptions

*Task 4.1: Analyze the 2017 SAFS data collected by Drexel and Aerodyne to quantify the dependence of the ozone production rate on supporting measurements. (September 2018 – December 2018)*
The focus of our analysis will be the Drexel measurements of peroxy radicals which were taken at three measurement sites. These peroxy radical measurements enable the ozone chemical production rate "$P(O_3)$" to be quantified. We will investigate the dependence of $P(O_3)$ on supporting measurements, including concentrations of nitrogen oxides, HOx radical precursors, volatile organic compounds (VOCs), and tracers for specific emission sources (e.g., $SO_2$ from coal combustion, HCN from biomass burning). This task will be conducted by the PI and postdoc at Drexel University. The deliverable resulting from this task will be analysis that will be documented in the form of text and accompanying figures and tables and will be included in the final report. The results may also be prepared as a manuscript for submission to a peer-reviewed journal such as "Atmospheric Chemistry and Physics".

*Task 4.2: Conduct 0-D photochemical modeling using data from four SAFS measurement sites and compare modeled ozone production rates and peroxy radical concentrations to those calculated using the peroxy radical measurements where available. (September 2018 – March 2018)*
We will compare the measurement-based ozone production rates at the UTSA, Floresville, and Lake Corpus Christi sites to those produced by 0-dimensional photochemical models constrained by the supporting measurements. We will conduct the same 0-D modeling using the U. of Houston / Rice University data from the centrally located (higher NOx) Traveler's World RV resort location. Multiple chemical mechanisms will be evaluated (e.g., MCMv3.3.1 and CB6r3) in our 0-D model activities. This task will be conducted by the PI and postdoc at Drexel University. The deliverable resulting from this task will be analysis that will be documented in the form of text and accompanying figures and tables and will be included in the final report. The results may also be prepared as a manuscript for submission to a peer-reviewed journal such as "Atmospheric Chemistry and Physics".

*Task 4.3. Apportion ozone concentrations to location-specific emission sources using 3-D air quality modeling with the instrumented Community Multiscale Air Quality model (CMAQ). (November 2018 – July 2019)*

Finally, we will use CMAQ, a 3-dimensional chemical transport model developed and maintained by the US EPA, to investigate ozone formation and concentrations in San Antonio. By using CMAQ source apportionment tools and by varying emissions, we will assess the impact of current and future emission sources and emission rates, especially for NOx, on resulting $O_3$ concentrations in San Antonio. We will evaluate CMAQ's chemical mechanism with field-based measurements of the ozone production rate, and similarly we will evaluate its NOx emissions by comparison to NOx and CO measurements and $NO_2$ column satellite retrievals. This task will be initiated by the co-I, who will train the postdoc to use CMAQ. The continuing analysis will be conducted primarily by the post-doc with mentoring and input from the PI and co-I. The initial set-up of the model will start in November; more focused effort and analysis will follow in January 2019. The deliverable resulting from this task will be analysis that will be documented in the form of text and accompanying figures and tables and will be included in the final report. The results may also be prepared as a manuscript for submission to a peer-reviewed journal such as "Atmospheric Chemistry and Physics"

*Task 4.4: Project Reporting and Presentation (September 2018 – August 2019)*

As specified in Section 7.0 "Deliverables" of this Scope of Work, AQRP requires the regular and timely submission of monthly technical, monthly financial status and quarterly reports as well as an abstract at project initiation and, near the end of the project, submission of the draft final and final reports. Additionally, at least one member of the project team will attend and present at the AQRP data workshop. For each reporting deliverable, one report per project will be submitted (collaborators will not submit separate reports), with the exception of the Financial Status Reports (FSRs). The lead PI (or their designee) will electronically submit each report to both the AQRP and TCEQ liaisons and will follow the State of Texas accessibility requirements as set forth by the Texas State Department of Information Resources. The report templates and accessibility guidelines found on the AQRP website at http://aqrp.ceer.utexas.edu/ will be followed. Draft copies of any planned presentations (such as at technical conferences) or manuscripts to be submitted for publication resulting from this project will be provided to both the AQRP and TCEQ liaisons per the Publication/Publicity Guidelines included in Attachment G of the subaward. Finally, our team will prepare and submit our final project data and associated metadata to the AQRP archive.

Deliverables: Abstract, monthly technical reports, monthly financial status reports, quarterly reports, draft final report, final report, attendance and presentation at AQRP data workshop, submissions of presentations and manuscripts, project data and associated metadata

Schedule: The schedule for Task 4.4 Deliverables is shown in Section 7.

**5.0 Project Participants and Responsibilities**

Provide a table or bulleted list that summarizes the individual participants and their responsibilities.

| Name | Title/Affiliation | Responsibilities |
|---|---|---|
| Ezra Wood | PI, Assoc. Professor, Drexel University Dept. of Chemistry | The PI will oversee, manage, and be directly involved in all tasks. |
| Shannon Capps | Co-investigator, Assistant Professor, Drexel University Department of Civil, Architectural and Environmental Engineering | The co-I will train the postdoctoral fellow to use the 3-D photochemical model CMAQ and advise on the interpretation |
| Daniel Anderson | Postdoctoral fellow, Drexel University Department of Chemistry | The postdoc will conduct most of the day-to-day analysis, including analysis of 2017 field data, the 0-D modeling using both the Drexel/Aerodyne and UH/Rice data, and the 3-D photochemical air quality modeling using CMAQ. |

**6.0 Timeline**

The tasks described in section 4 will be executed following the following timeline:

▪ Task 4.1: Quantify the dependence of ozone production on compounds measured during SAFS (September 2018 – December 2018)

▪ Task 4.2: Conduct 0-D photochemical modeling using data from four SAFS measurement sites (September 2018 – March 2018)

▪ Task 4.3. Apportion ozone concentrations to location-specific emission sources using 3-D air quality modeling with the instrumented Community Multiscale Air Quality model (CMAQ). (November 2018 – July 2019)

▪ Task 4.4. Project Reporting and Presentation (September 2018 – August 2019)

**7.0 Deliverables**

AQRP requires certain reports to be submitted on a timely basis and at regular intervals. A description of the specific reports to be submitted and their due dates are outlined below. One report per project will be submitted (collaborators will not submit separate reports), with the exception of the Financial Status Reports (FSRs). The lead PI will submit the reports, unless that responsibility is otherwise delegated with the approval of the Project Manager. All reports will be written in third person and will follow the State of Texas accessibility requirements as set forth by the Texas State Department of Information Resources. Report templates and accessibility guidelines found on the AQRP website at http://aqrp.ceer.utexas.edu/ will be followed.

**Abstract:** At the beginning of the project, an Abstract will be submitted to the Project Manager for use on the AQRP website. The Abstract will provide a brief description of the planned project activities, and will be written for a non-technical audience.

**Abstract Due Date:** Friday, August 31, 2018

**Quarterly Reports:** Each Quarterly Report will provide a summary of the project status for each reporting period. It will be submitted to the Project Manager as a Microsoft Word file. It will not exceed 2 pages and will be text only. No cover page is required. This document will be inserted into an AQRP compiled report to the TCEQ.

**Quarterly Report Due Dates:**

| Report | Period Covered | Due Date |
|---|---|---|
| Aug2018 Quarterly Report | June, July, August 2018 | Friday, August 31, 2018 |
| Nov2018 Quarterly Report | September, October, November 2018 | Friday, November 30, 2018 |
| Feb2019 Quarterly Report | December 2018, January & February 2019 | Thursday, February 28, 2019 |
| May2019 Quarterly Report | March, April, May 2019 | Friday, May 31, 2019 |
| Aug2019 Quarterly Report | June, July, August 2019 | Friday, August 30, 2019 |
| Nov2019 Quarterly Report | September, October, November 2019 | Friday, November 29, 2019 |

**Monthly Technical Reports (MTRs):** Technical Reports will be submitted monthly to the Project Manager and TCEQ Liaison in Microsoft Word format using the AQRP FY16-17 MTR Template found on the AQRP website.

**MTR Due Dates:**

| Report | Period Covered | Due Date |
|---|---|---|
| Aug2018 MTR | Project Start - August 31, 2018 | Monday, September 10, 2018 |

| | | |
|---|---|---|
| Sep2018 MTR | September 1 - 30, 2018 | Monday, October 8, 2018 |
| Oct2018 MTR | October 1 - 31, 2018 | Thursday, November 8, 2018 |
| Nov2018 MTR | November 1 - 30 2018 | Monday, December 10, 2018 |
| Dec2018 MTR | December 1 - 31, 2018 | Tuesday, January 8, 2019 |
| Jan2019 MTR | January 1 - 31, 2019 | Friday, February 8, 2019 |
| Feb2019 MTR | February 1 - 28, 2019 | Friday, March 8, 2019 |
| Mar2019 MTR | March 1 - 31, 2019 | Monday, April 8, 2019 |
| Apr2019 MTR | April 1 - 28, 2019 | Wednesday, May 8, 2019 |
| May2019 MTR | May 1 - 31, 2019 | Monday, June 10, 2019 |
| Jun2019 MTR | June 1 - 30, 2019 | Monday, July 8, 2019 |
| Jul2019 MTR | July 1 - 31, 2019 | Thursday, August 8, 2019 |

**Financial Status Reports (FSRs):** Financial Status Reports will be submitted monthly to the AQRP Grant Manager (Maria Stanzione) by each institution on the project using the AQRP FY16-17 FSR Template found on the AQRP website.

**FSR Due Dates:**

| **Report** | **Period Covered** | **Due Date** |
|---|---|---|
| Aug2018 FSR | Project Start - August 31 | Monday, September 17, 2018 |
| Sep2018 FSR | September 1 - 30, 2018 | Monday, October 15, 2018 |
| Oct2018 FSR | October 1 - 31, 2018 | Thursday, November 15, 2018 |
| Nov2018 FSR | November 1 - 30 2018 | Monday, December 17, 2018 |
| Dec2018 FSR | December 1 - 31, 2018 | Tuesday, January 18, 2019 |
| Jan2019 FSR | January 1 - 31, 2019 | Friday, February 15, 2019 |
| Feb2019 FSR | February 1 - 28, 2019 | Friday, March 15, 2019 |
| Mar2019 FSR | March 1 - 31, 2019 | Monday, April 15, 2019 |
| Apr2019 FSR | April 1 - 28, 2019 | Wednesday, May 15, 2019 |
| May2019 FSR | May 1 - 31, 2019 | Monday, June 17, 2019 |
| Jun2019 FSR | June 1 - 30, 2019 | Monday, July 15, 2019 |
| Jul2019 FSR | July 1 - 31, 2019 | Thursday, August 15, 2019 |
| Aug2019 FSR | August 1 - 31, 2019 | Monday, September 16, 2019 |
| FINAL FSR | Final FSR | Tuesday, October 15, 2019 |

**Draft Final Report:** A Draft Final Report will be submitted to the Project Manager and the TCEQ Liaison. It will include an Executive Summary. It will be written in third person and will follow the State of Texas accessibility requirements as set forth by the Texas State Department of Information Resources. It will also include a report of the QA findings.

**Draft Final Report Due Date:** Thursday, August 1, 2019

**Final Report:** A Final Report incorporating comments from the AQRP and TCEQ review of the Draft Final Report will be submitted to the Project Manager and the TCEQ Liaison. It will be written in third person and will follow the State of Texas accessibility requirements as set forth by the Texas State Department of Information Resources.

**Final Report Due Date:** Tuesday, September 3, 2019

**Project Data:** All project data including but not limited to QA/QC measurement data, metadata, databases, modeling inputs and outputs, etc., will be submitted to the AQRP Project Manager within 30 days of project completion (September 30, 2019). The data will be submitted in a format that will allow AQRP or TCEQ or other outside parties to utilize the information. It will also include a report of the QA findings.

**AQRP Workshop:** A representative from the project will present at the AQRP Workshop in the first half of August 2019.

**Presentations and Publications/Posters:** All data and other information developed under this project which is included in **published papers, symposia, presentations, press releases, websites and/or other publications** shall be submitted to the AQRP Project Manager and the TCEQ Liaison per the Publication/Publicity Guidelines included in Attachment G of the Subaward.

## 8.0 References

Atkinson, R.: Atmospheric Chemistry of VOCs and $NO_x$, Atmospheric Environment, 34, 2063-2101, 2000.
Mao, J., Ren, X., Chen, S., Brune, W. H., Chen, Z., Martinez, M., Harder, H., Lefer, B., Rappenglück, B., Flynn, J., and Leuchner, M.: Atmospheric oxidation capacity in the summer of Houston 2006: Comparison with summer measurements in other metropolitan studies, Atmospheric Environment, 44, 4107-4115, 10.1016/j.atmosenv.2009.01.013, 2010.

Pollack, I., Ryerson, T., Trainer, M., Parrish, D., Andrews, A., Atlas, E., Blake, D., Brown, S., Commane, R., and Daube, B.: Airborne and ground-based observations of a weekend effect in ozone, precursors, and oxidation products in the California South Coast Air Basin, Journal of Geophysical Research: Atmospheres, 117, 2012.