Scope of Work For

Project # 20‐028

Quantification and Characterization of Ozone Formation in Central San Antonio

Prepared for

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

By

Ezra Wood Principal Investigator (PI) Drexel University

7/10/2020 Version #2

Quality Assurance (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 **7/13/20** by

Vincent M. Torres Project Manager, Texas Air Quality Research Program The University of Texas at Austin

This Scope of Work was approved electronically on **07/14/20** by

Erik Gribbin Project Liaison, Texas Commission on Environmental Quality (TCEQ)

Contents

1.0 Abstract

In July 2018 the US Environmental Protection Agency (EPA) classified Bexar County, in which San Antonio is located, as being in nonattainment of the National Ambient Air Quality Standard for ozone $(0₃)$ of 70 parts per billion (ppb). Although the official attainment status will ultimately be determined in the courts, it is possible that regulators will eventually need to make sciencebased decisions on effective mitigation strategies, including emission reduction programs. Since ozone in San Antonio is both transported from outside the city and produced locally by photochemical reactions involving nitrogen oxides (nitric oxide, NO, and nitrogen dioxide, NO2, collectively referred to as "NOx") and volatile organic compounds (VOCs), these decisions will require knowledge of the following:

A. How much ozone and its precursors (NOx and VOCs) are transported into the city,

B. How much ozone is created within the urban core of the city,

C. Information on the spatial and temporal nature of the local and regional ozone formation photochemical "regime", i.e., where and when ozone formation would be responsive to reductions in NOx emissions versus reductions in VOC emissions.

These questions were partially addressed as a result of the TCEQ/AQRP-funded San Antonio Field Study, in which several research groups (including Drexel) collected data at four sites in and around San Antonio during May 2017. The Drexel peroxy radical instrumentation, which enables direct calculation of the ozone production rate, was not deployed to central San Antonio, and photochemical modeling of the air masses there has yielded a wide range of ozone formation rates depending on which chemical mechanism is used in the model. The resulting knowledge gaps regarding how much ozone is formed within the urban core and how it will respond to changes in precursor emissions need to be addressed in order to develop effective ozone mitigation plans.

This research project will address this major shortcoming via analysis of data to be collected in the high-NOx central part of San Antonio during a \sim 7 to 10 day field project during late Summer of 2020. We will quantify the instantaneous ozone production rate, characterize its dependence on NOx and VOCs, determine under what conditions it is VOC-limited vs. NOx-limited, and conduct zero-dimensional modeling of the observed air masses. Comparison of the modeled ozone formation rates to those determined experimentally should identify which chemical mechanism used in photochemical modeling is most accurate for this region and will inform future comprehensive 3-dimensional photochemical modeling of the area.

This project is designed to be conducted in collaboration with measurements to be taken by the research team comprising Rice University, Baylor University, and University of Houston. The importance of this work likely extends beyond San Antonio air quality for two reasons:

1. Photochemical models have been unable to accurately predict ozone formation rates in several other cities under high-NOx conditions, and 2. Since the new O_3 air quality standard is only \sim 20 to 30 ppb higher than background concentrations, an increasing number of US cities are finding that small differences in locally-made O₃ can make the difference between attainment and nonattainment of the air quality standard.

2.0 Background

Introduction

San Antonio was recently classified by the US EPA as being in non-attainment of the National Ambient Air Quality Standard for ozone (O_3) , though the final designation is currently under litigation. As a result, regulators will need to make science-based decisions on effective mitigation strategies, including emission reduction programs. Such decisions will require knowledge of the amount of ozone that is transported into the city from upwind (usually Southeast of San Antonio), the absolute rates of ozone formation in and around San Antonio, the relative importance and interaction of various emission sources (e.g., upwind oil and gas activity and urban emissions from the city itself), and when and where ozone formation is NOx-limited or VOC-limited.

San Antonio faces challenges similar to many other cities: background concentrations of ozone are typically 40 – 60 ppb, and so even seemingly modest amounts of ozone created locally can be enough to contribute to 8-hour(hr) concentrations of over 70 ppb. The effectiveness of emissions reductions in mitigating ozone exceedances is uncertain due to the non-linear role of NOx and VOCs in producing ozone, and decreases in NOx, though they decrease ozone production rates, also increase the NOx lifetime and the efficiency by which NOx catalyzes ozone formation (Laughner et al. 2019). Additional challenges potentially facing San Antonio include possible changes in upwind sources, for example oil and gas extraction activity at the Eagle Ford shale play and the increasing role of Corpus Christi as an oil export hub. This project's research plan, based on field measurements in San Antonio as part of a research team, aims to quantify and characterize ozone formation in the urban core of San Antonio. This will address knowledge gaps regarding ozone concentrations in San Antonio that are critical for designing and implementing effective ozone mitigation strategies.

State of knowledge regarding ozone in San Antonio

Ozone concentrations have decreased in San Antonio since 2002, likely in part as a result of decreasing NOx emissions that have occurred throughout the country. The highest ozone concentrations in Bexar County have been observed at sites on the northwest portions of San Antonio at the *Camp Bullis* and *San Antonio Northwest* TCEQ monitoring sites. These two sites are downwind of the city under the prevailing southeasterly wind flow, suggesting that additional ozone is created in the air as it passes over San Antonio. Up until 2017 little was known about the rates and nature of ozone formation in San Antonio. During the 2017 ACRP/TCEQ-funded San Antonio Field Study (SAFS), several research groups made measurement of ozone-relevant compounds at four sites in the greater San Antonio area in order to rectify this paucity of knowledge. The instantaneous ozone production rate $P(O_3)$ was determined using the Drexel measurements of total peroxy radicals (the sum of hydroperoxy radicals HO2 and organic peroxy radicals RO2) using the following equation:

 $P(O_3) = k_{HO2+NO}([HO_2] + [RO_2])[NO]$

where k_{HO2+NO} is the rate constant for the reaction between $HO₂$ and NO to form NO₂ and OH. (The rate-limiting step in ozone formation is the conversion of NO to $NO₂$ by reaction with $HO₂$ or RO2). The main points learned by analyses of these data are summarized below. These points below are described in detail in the final reports for AQRP projects 19-040 and 17-032 as well as Anderson et al (2019):

• At Lake Corpus Christi and Floresville, two sites southeast and therefore usually upwind of the city, instantaneous ozone production rates $P(O_3)$ was rarely above 10 ppb/hr and almost always NOx-limited. At the University of Texas at San Antonio (UTSA), on the northwest portion of San Antonio, P(O3) was usually under 20 ppb/hr (average daytime value 6 ppb/hr) and again usually NOx-limited.

• At all three sites, biogenic VOCs played a large role in the total VOC reactivity. At UTSA, isoprene accounted for slightly over half of the total VOC reactivity. Alkanes (associated with oil and gas activity) and light alkenes (associated with petrochemical emissions) had a small role in ozone formation.

• Zero-dimensional modeling of the data collected at these three sites, which did not have high NOx concentrations (i.e., [NO] was rarely above 1 ppb), was largely able to capture the same trends and values determined directly from the peroxy radical measurements (within the experimental uncertainties). This was the case for four separate mechanisms used, including the explicit "Master Chemical Mechanism", providing confidence that ozone formation can be modeled correctly at those low-NOx locations.

The above results suggest that reducing NOx emissions would be much more effective than reducing VOC emissions at reducing ozone formation rates.

• An extensive set of measurements was taken at the Traveler's World RV resort in central San Antonio by the Rice/University of Houston/Baylor team, in which much higher NOx concentrations were observed ([NO] up to 3-4 ppb). Ozone production rates were not determined directly from measurements as the Drexel peroxy radical measurement was not deployed there. Similar zero-dimensional (0-D) photochemical modeling performed separately by the Drexel and Rice teams indicated much higher values, up to 50+ ppb/hr at times. The different mechanisms used in the models, however, produced different values, with the master chemical mechanisms and the NASA "LaRC" model producing the highest values.

• Three-dimensional modeling of the area with EPA's Community Multiscale Air Quality (CMAQ) model suggested that reducing NOx emissions by 30% across Texas would decrease O3 concentrations in San Antonio (and elsewhere in the state) by only \sim 2 ppb. This model, however, utilized a coarse grid cell size of 12 km \times 12 km, and thus cannot capture the spatial heterogeneity in ozone formation rates within Bexar county.

Gaps regarding ozone formation in San Antonio

As noted in the fourth bullet point above $P(O_3)$ has not been experimentally determined in the central core part of San Antonio in which NOx concentrations are highest. The accompanying figure summarizes the P(O3) values predicted by the 0-D modelling at Traveler's World with four different mechanisms, along with the experimentally determined $P(O_3)$ values at the lower-NOx UTSA site. Independent

modeling with a different mechanism and modeling platform by the Rice team produced results

similar to the high results shown here which utilized the near-explicit Master Chemical Mechanism (MCM). The main points to conclude are that 1. At the low-NOx sites, the measured $P(O_3)$ agreed with the modeled $P(O_3)$ to within experimental uncertainties, regardless of mechanism. 2. At the higher NOx site, the different mechanisms produced a diverging range of results, with some values extremely high (over 40 ppb/hr). Measurements were not available to determine $P(O_3)$ directly.

 At first glance, these high ozone production rates seem incompatible with the ozone concentrations measured downwind. In only two hours, an ozone formation rate of 50 ppb/hr would seemingly increase the O_3 concentration from $~40$ to 140 ppb – concentrations rarely (if ever) seen at the "high ozone" downwind sites in northwest San Antonio (i.e., *Camp Bullis* and *San Antonio Northwest*). These formation rates are not spatially homogeneous, however, as there are both horizontal and vertical variations in the formation rate. CMAQ results from our prior

According to the traditional understanding of O3 photochemistry, reducing NOx emissions leads to decreases in P(O3) at low-NOx locations ("A") but increases in $P(O_3)$ *at high-NOx locations (B). If the red curve more accurately depicts the actual dependence of P(O3) on NO, then NOx emissions reductions are more effective than currently predicted. During the 2017 San Antonio Field Study, experimentally determined P(O3) was only characterized largely in the low-NOx "A" regions.*

project indicated that, spatially averaged over the 12 × 12 kilometer (km) horizontal grid cell size, between 12:00 and 16:00 local time $P(O_3)$ is 7 ppb/hr at the surface but only 4 ppb/hr at 1 km altitude – mainly due to the vertical gradient in NOx. In contrast, CMAQ predicts HOx radical production rates ("P(HOx)") values that are relatively constant up to 1 km due to much smaller variations in the HO_x radical precursors O₃, H2O, and HCHO. The true values (i.e., not spatially averaged) undoubtedly show additional horizontal variation as well given the horizontal inhomogeneity in surface NOx emissions and concentrations. In summary, although the peak modeled ozone formation rates at Traveler's World are seemingly very high, they are not necessarily wrong as they are confined to a limited volume of air. The high ozone values observed at the Camp Bullis and San Antonio Northwest sites result from ozone produced in air masses that experience a wide range of ozone production rates.

 These obstacles encountered with accurately modeling P(O3) under high-NOx conditions are not limited to the San Antonio dataset - several other research groups have recently encountered similar problems. In Wangdu, China, when NO was 0.6 ppb, P(O3) was on average 10 ppb/hr as determined by both measured peroxy radicals and a 0-D photochemical model. At higher NO of 2 ppb, however, the model predicted lower values $({\sim}8$ ppb/hr) whereas the measurements showed an increase to \sim 25 ppb/hr P(O₃)

(Tan et al. 2017). Similar discrepancies have been found for air masses studied in Golden, Colorado (Baier et al. 2017); Bakersfield, California (Brune et al. 2016); and London, United Kingdom (Whalley et al. 2018). These studies all suggest that NOx reductions are likely to be more effective than predicted by models that are unable to capture these increased $P(O_3)$ values at elevated NOx concentrations. Thus, our CMAQ results from AQRP project 19-040, which suggested very modest decreases in ozone after large (30%) decreases in state-wide NOx emissions, may well be underestimating the efficacy of NOx emissions reductions.

3.0 Objectives

The overall objectives of this project are the following:

1. Quantify the instantaneous rates of ozone formation (" $P(O_3)$ ") in central San Antonio where NOx concentrations can be relatively high.

2. Compare these observation-based P(O3) values to those predicted by zero-dimensional photochemical models constrained by measurements of relevant compounds (e.g., NOx, VOCs). Modeled and measured $P(O_3)$ values have been shown to agree within uncertainties under low-NOx conditions (when nitric oxide mixing ratios are less than 1 ppb) but, in many cases, not under higher NOx conditions

3. Use the results of #1 and #2 above to inform strategies for addressing exceedances of the ozone air quality standard in the greater San Antonio area.

4.0 Task Descriptions

Task 4.1: Prepare for the Field Deployment

During Task 1, to be conducted in close collaboration with colleagues from Rice/U. Houston / Baylor, we will decide on overall logistical plans, including determination of deployment dates and locations, and determine plans for how to co-locate the Drexel "Ethane Chemical Amplifier" (ECHAMP) peroxy radical sensor with the UH mobile laboratory at the measurement site in central San Antonio. We will plan on renting some sort of measurement platform such as a recreational vehicle (RV) or shipping container that can house the instrument with the requisite holes for connecting the inlet box (mounted on the roof) to the rest of the instrument inside.

Field deployment preparation to be conducted in the home laboratory at Drexel University will include testing an improved method for scrubbing ethane from ECHAMP's exhaust pump. Past attempts to chemically remove the ethane used in the ECHAMP amplification chemistry were not sufficient to fully remove the ethane, resulting in occasional interferences in supporting ethane measurements. Given the importance of high–quality ethane measurements for discerning possible influence of emissions from oil and gas activity it will be critical for this type of self-sampling to be eliminated. The revised method relies on supplementing the oxidation catalyst used in the past with additional scrubbing using a small stove and/or an activated carbon trap. An additional laboratory task, to be conducted if time allows, is to test the operation of ECHAMP at reduced pressure which is predicted to greatly reduce the impact of relative humidity on the instrument's sensitivity and uncertainty.

The ideal schedule for this task will be from June 2020 through early September 2020, though if the COVID19 pandemic does not allow this schedule it will effectively continue through April 2021. The expected milestone for this task is readiness to deploy the instruments to San Antonio.

Task 4.2: Field Deployment

The field deployment is tentatively planned for September of 2020. The University of Houston mobile lab is planning a \sim 3-week deployment that will include sampling in Austin, San Antonio, and Corpus Christi. We will co-locate ECHAMP with the UH mobile laboratory for 7 to 10 days at a central site in San Antonio, likely Traveler's World RV resort (2617 Roosevelt Ave, San Antonio). ECHAMP will not join the UH mobile laboratory for its planned measurements in Austin or Corpus Christi. The expected milestone for this task is successful deployment of the ECHAMP peroxy radical sensor instruments in central San Antonio. Ideally the deployment will occur during September 2020, though if the COVID19 pandemic does not allow this schedule it will be rescheduled for Spring 2021 (May-June).

Task 4.3: Data Quality Assurance

For Task 3, the raw data from ECHAMP will be converted into concentrations (mixing ratios in parts per trillion) based on the in-field calibrations and, if needed, post-deployment follow-up experimental work. Calibrating instruments that measure HOx radicals, i.e. generating accurately known concentrations of these extremely reactive radicals, is one of the most challenging aspects of measuring the compounds. We routinely calibrate ECHAMP with two separate calibration methods. Both methods, though very different, are ultimately traced to the accuracy for which our Cavity Attenuated Phase-shift Spectroscopy (CAPS) monitors can measure NO2, which in turn is traced to an ozone calibration source. We compare our portable field O3 source to two other ozone quantification systems in our laboratory at Drexel to maximize the accuracy of our peroxy radical measurements. The deliverable for this task is the quality assured data collected during the deployment. This task will occur after the deployment (September 2020 – November 2020, or June $2021 - mid July 2021$ if necessary).

Task 4.4: Preliminary Data Analysis

Task 4 consists of two main sub-tasks:

A. With the collected data, we will be able to greatly extend the analysis of ozone formation presented in Anderson et al. (2019). We will calculate instantaneous ozone production rates $(P(O_3))$ using measured concentrations of total peroxy radicals ($[HO_2] + [RO_2]$) and nitric oxide (NO) and the following equation: $P(O_3)$ $=$ k_{HO2+NO}([HO₂] + [RO₂])[NO]. We will quantify the dependence of $P(O_3)$ on NO, VOC reactivity, and HOx radical production rates $(P(HOx))$. We will be able to determine during what periods of the day ozone formation is NOx-limited vs. VOC-limited.

B. We will conduct zero-dimensional modelling of the sampled air masses. We will use the Framework for 0-D Atmospheric Modeling (F0AM) version 3.1 box model, which is a Matlab-based tool for simulation of photochemical, atmospheric processes (Wolfe et al. 2016).

We will also incorporate satellite retrievals of the NO₂ vertical column density from the recently launched TROPOMI (TROPOspheric Monitoring Instrument) spectrometer to frame our analysis. TROPOMI retrievals have superior spatial resolution and signal-to-noise compared to the older OMI product (Laughner and Cohen 2019). A preliminary retrieval is shown in the accompanying figure, with a pixel size of 7 km \times 3.5 km. The greater San Antonio area, encompassing the Camp Bullis and Northwest monitoring sites, is approximately 20 km \times 20 km. This will provide information on the horizontal distribution of NO2 and, by extension, NO and the ozone production rates. This task will occur from December 2020 – mid-July 2021 ideally, or if the deployment is rescheduled it will occur from June 2021 to mid-July 2021.

Task 4.5: Project Reporting and Presentation

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, PI Ezra Wood 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.

By August 31, 2021 all project tasks will be completed and all project funds will be expended.

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 4.5 Deliverables are shown in Section 7.

5.0 Project Participants and Responsibilities

6.0 Timeline

The tasks described in section 4 will be executed following one of two possible timelines depending on the Drexel and Rice/UH/Baylor team's ability to deploy during the COVID19 pandemic as described below:

Plan A:

▪ Task 4.1 Prepare for the Field Deployment (June 2020 – September 2020)

▪ Task 4.2: Field Deployment (September 2020)

▪ Task 4.3. Data Quality Assurance (September 2020 – November 2020)

▪ Task 4.4. Data Analysis (December 2020 – mid-July 2021)

▪ Task 4.5. Project Reporting and Presentation (June 2020 – August 2021)

Plan B: ▪ Task 4.1 Prepare for the Field Deployment (June 2020 – April 2021)

▪ Task 4.2: Field Deployment (May 2021)

• Task 4.3. Data Quality Assurance (June 2021 – mid-July 2021)

▪ Task 4.4. Data Analysis (June 2021 – mid-July 2021)

▪ Task 4.5. Project Reporting and Presentation (June 2020 – August 2021)

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 AQRP 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 AQRP 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, July 31, 2020

Quarterly Reports: Each Quarterly Report will provide a summary of the project status for each reporting period. It will be submitted to the AQRP 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:

Monthly Technical Reports (MTRs): Technical Reports will be submitted monthly to the AQRP Project Manager and TCEQ Liaison in Microsoft Word format using the AQRP FY20‐21 MTR Template found on the AQRP website.

MTR Due Dates:

DUE TO PROJECT MANAGER

Financial Status Reports (FSRs): Financial Status Reports will be submitted monthly to the AQRP Grant Manager (RoseAnna Goewey) by each institution on the project using the AQRP 20‐ 21 FSR Template found on the AQRP website.

FSR Due Dates:

DUE TO GRANT MANAGER

Draft Final Report: A Draft Final Report will be submitted to the AQRP 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: Monday, August 2, 2021

Final Report: A Final Report incorporating comments from the AQRP and TCEQ review of the Draft Final Report will be submitted to the AQRP 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, August 31, 2021

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 20, 2021). 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 2021.

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.