Quality Assurance Project Plan (QAPP)

Project # 20-028
Quantification and Characterization of Ozone Formation in Central San Antonio

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

Prepared by

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Principal Investigator (PI)
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Drexel University has prepared this QAPP following Environmental Protection Agency (EPA) guidelines for a Quality Assurance (QA) Category III Project: Measurement. It is submitted to the Texas Air Quality Research Program (AQRP) as required in the Work Plan requirements.

QAPP Requirements: Project Description and Objectives; Project Organization and Responsibilities; Scientific Approach; Sampling Procedure; Measurement Procedures; Quality Metrics; Data Analysis, interpretation, and management; Reporting; and References

QA Requirements:	Technical Systems Audits - Not Required for the Project Audits of Data Quality – 10% Required Report of Findings – Required in Final Report

Project Title and Approvals Sheet

This document is a Category III Quality Assurance Project Plan for the "Quantification and Characterization of Ozone Formation in Central San Antonio" project. The Principal Investigator for the project is Ezra Wood.

Electronic Approvals:

This QAPP was approved electronically on 7/13/2020 by

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

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Ezra Wood
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QAPP Distribution List

Texas Air Quality Research Program
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Texas Commission on Environmental Quality
Erik Gribbin, Project Liaison

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1. Project Description and Objectives

1.1 Description of Environmental system to be evaluated.
Ozone is the main component of smog and has adverse effects on human health and vegetation. Unlike primary pollutants like carbon monoxide or black carbon, ozone is formed by photochemical reactions involving volatile organic compound (VOCs) and nitrogen oxides (NOx).

The rate at which ozone in air is formed is referred to as the ozone production rate ("$P(O_3)$") and is effectively equal to the rate at which nitric oxide (NO) is converted to nitrogen dioxide (NO_2) by reaction with peroxy radicals (e.g., the hydroperoxy radical HO_2 and organic peroxy radicals "RO_2" like the methyl peroxy radical CH_3O_2 which is formed by the photo-oxidation of methane):

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

"RO_2" represents all organic peroxy radicals (e.g., CH_3O_2, $C_2H_5O_2$, etc.), k_{HO2+NO} is the rate constant for the reaction between HO_2 and NO, and k_{RO2+NO} is the weighted-averaged rate constant for the reaction between RO_2 and NO.

By measuring total peroxy radicals and NO and evaluating Eq. 1 above, the absolute rates of ozone formation in the greater San Antonio area can be quantified. Comparison of the resulting measurement-based $P(O_3)$ values to those predicted by photochemical models provide information on how accurate our understanding of ozone formation is.

1.2 Purpose of the project
Bexar county has recently been classified by the US EPA as being in violation of the air quality standard for ozone. Although this classification has resulted in a lawsuit, it is likely that policy makers will need to make science-based decisions in the future in order to reduce ozone concentrations. The purpose of this project is to quantify ozone formation rates in central San Antonio in order to assist in addressing the question of how much ozone is formed locally within San Antonio and how much is transported from upwind locations. To accomplish this, Drexel University will deploy its "Ethane Chemical Amplifer" (ECHAMP) peroxy radical sensor alongside researchers from University of Houston, Rice University, and Baylor University at a central site in San Antonio to quantify ozone formation rates.

2. ORGANIZATION AND RESPONSIBILITIES

2.1 *Project personnel and responsibilities.*

The Primary Investigator of this project is Ezra Wood, Associate Professor of Chemistry at Drexel University. Dr. Wood will direct all aspects of the project, mentor the postdoctoral researcher to be hired, and execute the quality assurance (QA) processing of the data.

One of two graduate students - Andrew Lindsay or Alexa Rhoads will conduct much of the day-to-day work for this project, including preparing the ECHAMP sensor for deployment, operating the instrument while in San Antonio, and assisting in the quality assurance of the data.

2.2 *Project schedule and key milestones.*
The project is divided into five tasks as described in the Scope of Work. The timing of these tasks along with key outcomes or milestones are described below. Further information on these tasks is described in the Scope of Work and elsewhere in this document. Due to the COVID-19 pandemic, we are leaving open the possibility of two separate timelines which will be determined by whether we are able to conduct field measurements during September 2020.

Plan A:
Task 4.1 Prepare for the Field Deployment (June 2020 – September 2020).
During this task, the team will prepare the ECHAMP sensor for deployment, conduct laboratory experiments to improve its sensitivity, and work out the logistics for the deployment (exact dates, arrange travel plans and rental of recreational vehicle (RV) for installing the instrumentation).

Task 4.2: Field Deployment (September 2020)
We will deploy the ECHAMP peroxy radical sensor at a site co-located with the University of Houston mobile laboratory at a site in central San Antonio (possibly the same Traveler's World RV resort that the Houston team used in 2017). We will conduct measurements for 7-10 days.

Task 4.3. Data Quality Assurance (September 2020 – November 2020)
We will quality assure raw data taken by ECHAMP, which largely consists of analyzing the in-field calibration data and applying to the measurements of ambient air.

Task 4.4. Data Analysis (December 2020 – mid July 2021)
We will determine the instantaneous ozone production rates "$P(O_3)$" using the peroxy radical and nitric oxide (NO) data and analyze its dependence on NOx. We will also conduct zero-dimensional photochemical modelling to see if the measurement-based $P(O_3)$ values agree with those produced by our current understanding of urban photochemistry.

Task 4.5. Project Reporting and Presentation (June 2020 – August 2021)
This ongoing Task will generate the following 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 (if any), project data and associated metadata.

Below is an alternate timeline ("Plan B") to be followed in the event that we are unable to follow Plan A above due to the COVID-19 pandemic:

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)

3. SCIENTIFIC APPROACH

3.1 Experimental design.

The Drexel ECHAMP (Ethane CHemical AMPlifier) peroxy radical sensor will be deployed to a measurement site in central San Antonio to quantify concentrations of peroxy radicals ($HO_2 + RO_2$). Nitric oxide (NO) concentrations will be separately quantified using a Thermo chemiluminescence sensor by the University of Houston. This method of quantifying NO is not included in the TCEQ list of NELAP-recognized fields of accreditation. The rate of gross ozone production will be quantified by the following equation:

$$P(O_3) = k_{eff}[HO_2 + \Sigma RO_2][NO]$$

Where $P(O_3)$ is the production rate of ozone (ppb/hr), k_{eff} is the average rate constant for the reaction of HO_2 and individual RO_2 species with NO.

The peroxy radical data will be collected continuously except for when performing maintenance on the instrument (i.e., calibrations). The shortest averaging time used for these measurements is two minutes.

3.2 Specific target analyte.

The target analyte will be the sum of the hydroperoxy radical (HO_2) and organic peroxy radicals (RO_2, where R denotes an organic fragment). Examples of organic peroxy radicals includee the methyl peroxy radical CH_3O_2 and the ethyl peroxy radical $C_2H_5O_2$.).

4. SAMPLING PROCEDURES

4.1 Site preparation

The ECHAMP peroxy radical sensor will be integrated into a measurement platform such as a shipping container or a rented RV. The inlet box will be mounted on top to sample air, and is connected to the rest of the instrument (NO_2 sensors, electronics, gas cylinders) via a conduit comprising 12 Teflon or copper sampling tubes. As the air is continuously sampled and measured, there are no discrete air samples collected that need to be transported or labeled.

5. MEASUREMENT PROCEDURES

5.1. ECHAMP method.

ECHAMP (*Ethane CHemical AMPlifier)*[2] is a peroxy radical detection method based on the "chemical amplification" technique which has been used with variable success for several decades (a.k.a. the "CHemical AMPlifier (CHAMP)" technique and the "PERoxy Radical Chemical Amplifier "PERCA")[3-5]. Ambient air is drawn into two FEP (Teflon) reaction tubes and mixed with high concentrations of ethane (C_2H_6) and nitric oxide (NO). These reagents participate in the following radical propagation reactions with the sampled peroxy radicals, involving the hydroxyl radical OH, the ethyl peroxy radical $C_2H_5O_2$, the ethoxy radial C_2H_5O, molecular oxygen O_2, and acetaldehyde CH_3CHO:

$HO_2 + NO \rightarrow OH + \mathbf{NO_2}$	R1
$OH + C_2H_6 + O_2 \rightarrow C_2H_5O_2 + H_2O$	R2
$C_2H_5O_2 + NO \rightarrow C_2H_5O + \mathbf{NO_2}$	R3
$C_2H_5O + O_2 \rightarrow CH_3CHO + HO_2$	R4

The HO_2 produced by reaction 3 can then react with NO again (reaction 1). For each completion of the chain represented by the four reactions above, two NO_2 molecules are produced. Due to radical termination steps (not shown) the effective amplification factor is 15 at a relative humidity (RH) of 50%, meaning that for each HO_2 sampled, 15 NO_2 molecules are produced. This NO_2 amplification product is then detected by cavity attenuated phase shift spectroscopy (CAPS) – a highly sensitive NO_2 detection method [6]. Two reaction chambers are required – at any given point in time, one is in "amplification mode" while the other is in a background mode.

5.2. Calibration procedures.

The ECHAMP sensor is calibrated by two methods: the water photolysis method (Dusanter et al., 2008), which is a well-established method used by almost all HOx measurement groups in the world, and a methyl iodide (CH_3I) photolysis method. Both are described in Anderson et al[7]. We typically perform four calibrations each week and will plan to conduct them mainly at night to not interrupt the collection of the important daytime data. The CAPS sensors are calibrated to NO_2 as well as described in section 6.

6. QUALITY METRICS (QA/QC CHECKS)

Quality Control (QC) metrics are listed below:

A. The CAPS NO_2 sensors must be calibrated to NO_2. This is accomplished by having the instrument sample ozone prepared by UV photolysis of zero air, quantifying the ozone concentration using a standard UV-absorbance ozone instrument, and simultaneously recording the NO_2 signal from the CAPS sensor. The ozone is quantitatively converted into NO_2 by the reaction $NO + O_3 \rightarrow NO_2 + O_2$. This NO_2 calibration is performed once per week, consistent with the negligible calibration drift observed over years of operation of these instruments.

B. All flow rates from the flow controllers and into the reaction chambers are measured with two separate BIOS flow meters to ensure consistency in flow rates between the two reaction channels.

As required by this category of QAPP, an audit of 10% of the data will be performed. A report of the results of the Data Quality Audit will be included in the final report.

7. DATA ANALYSIS, INTERPRETATION, AND MANAGEMENT

7.1 Data processing

The calculation of peroxy radical concentrations from the raw data is accomplished using the following steps, all of which are executed using Matlab software: 1. The difference between the raw one-second NO_2 data from each of the two ECHAMP CAPS sensors are calculated. 2. Data from the first 15 seconds of each 45 second “valve state” (when one reaction channel is in amplification mode and the other in background mode) are expunged. 3. The remaining NO_2 difference values in ppt are averaged over the remaining 30 seconds. 4. Consecutive 30-second average values are averaged with each other, as described in detail in Wood and Charest (2014). 5. The resulting values from step 4 (in 1.5 minute increments) are divided by an RH-dependent amplification factor based on separate in-field calibrations and the relative humidity measured by the inlet system’s RH probe.

NO data from the chemiluminescence sensor will be corrected to account for instrument baseline drifts (quantified by hourly measurements of “zero air”) and the instrument calibration (quantified by bi-weekly calibrations of the instrument with a standard NO cylinder diluted with dry or humid synthetic air using mass flow controllers).

7.2 Data validation procedures.

The MATLAB code used to calculate the peroxy radical concentrations generates graphs of the partially analyzed data at each of the steps described above. These are visually inspected to ensure correct synchronization of the solenoid valve timing and the averaging routine.

7.3 Data analysis.

The ozone production rates $P(O_3)$ in ppb/hr in the air masses intercepted will be calculated by the following equation:

$$P(O_3) = k_{eff}[HO_2 + \Sigma RO_2][NO]$$

where k_{eff} is the average rate constant for the reaction of HO_2 and individual RO_2 species with NO, $[HO_2 + \Sigma RO_2]$ is the measurement of total peroxy radicals by the ECHAMP instrument, and [NO] is the concentration of NO measured by the chemiluminescence sensor.

7.3.1 Statistics and experimental uncertainties.

The uncertainty (accuracy) at the two sigma level of the peroxy radical data is expected to be in the range of 20 to 25%, and the NO uncertainty is expected to be 5%. By standard propagation of errors this leads to an uncertainty in the calculated ozone production rates of 21% to 25%.

7.4 Data storage requirements.
The peroxy radical and NO measurements generate raw data every second (including NO_2 concentrations, cell pressures and temperatures, flow rates, etc.). Total data storage required from a month-long deployment in Michigan during summer 2016 was 1 GB and we estimate that the San Antonio deployment will produce approximately one-third that amount (~300 MB). This is easily stored on USB storage devices ("thumb drives"), on computer hard drives (both internal and external), and on a secure cloud back-up service. The PI will retain all data, results of measurements and reports, whether in electronic or hard copy format, for a minimum of five years.

8. REPORTING

8.1 Deliverables and expected final products.
The main deliverables resulting from this project will be the quality-assured data (time series) of total peroxy radical concentrations during the 7-10 days of measurements in central San Antonio. Additionally, we will calculate the ozone formation rates, and analysis of the ozone formation rates on NOx concentrations. This analysis will be summarized in the project final report, presented at the August 2021 AQRP meeting, and time allowing submitted as a manuscript for peer review. Monthly and Quarterly reports will also be prepared and submitted in accordance with the schedule described in the accompanying Scope of Work document.

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:

Report	Period Covered	Due Date
Quarterly Report #1	May, June, July 2020	Friday, July 31, 2020
Quarterly Report #2	August, September, October 2020	Friday, October 30, 2020
Quarterly Report #3	November, December 2020, January 2021	Friday, January 29, 2021
Quarterly Report #4	February, March, April 2021	Friday, April 30, 2021
Quarterly Report #5	May, June, July 2021	Friday, July 30, 2021
Quarterly Report #6	August, September, October 2021	Friday, October 29, 2021

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:

Report	Period Covered	Due Date
Technical Report #1	Project Start - June 30, 2020	Wednesday, June 10, 2020
Technical Report #2	July 1 - 31, 2020	Friday, July 10, 2020
Technical Report #3	August 1 - 31, 2020	Monday, August 10, 2020
Technical Report #4	September 1 - 30 2020	Thursday, September 10, 2020
Technical Report #5	October 1 - 31, 2020	Friday, October 9, 2020
Technical Report #6	November 1 - 30, 2020	Tuesday, November 10, 2020

Technical Report #7	December 1 - 31, 2020	Thursday, December 10, 2020
Technical Report #8	January 1 - 31, 2021	Friday, January 8, 2021
Technical Report #9	February 1 - 28, 2021	Wednesday, February 10, 2021
Technical Report #10	March 1 - 31, 2021	Wednesday, March 10, 2021
Technical Report #11	April 1 - 30, 2021	Friday, April 9, 2021
Technical Report #12	May 1 - 31, 2021	Monday, May 10, 2021
Technical Report #13	June 1 - 30, 2021	Thursday, June 10, 2021
Technical Report #14	July 1 - 31, 2021	Friday, July 9, 2021

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:

Report	Period Covered	Due Date
FSR #1	Project Start - June 30	Wednesday, July 15, 2020
FSR #2	July 1 - 31, 2020	Friday, August 14, 2020
FSR #3	August 1 - 31, 2020	Tuesday, September 15, 2020
FSR #4	September 1 - 30 2020	Thursday, October 15, 2020
FSR #5	October 1 - 31, 2020	Friday, November 13, 2020
FSR #6	November 1 - 31, 2020	Tuesday, December 15, 2020
FSR #7	December 1 - 31, 2020	Friday, January 15, 2021

FSR #8	**January 1 - 31, 2021**	**Monday, February 15, 2021**
FSR #9	**February 1 - 28, 2021**	**Monday, March 15, 2021**
FSR #10	**March 1 - 31, 2021**	**Thursday, April 15, 2021**
FSR #11	**April 1 - 30, 2021**	**Friday, May 14, 2021**
FSR #12	**May 1 - 31, 2021**	**Tuesday, June 15, 2021**
FSR #13	**June 1 - 30, 2021**	**Thursday, July 15, 2021**
FSR #14	**July 1 - 31, 2021**	**Friday, August 13, 2021**
FSR #15	**August 1 - 31, 2021**	**Wednesday, September 14, 2021**
FSR #16	**Final FSR**	**Friday, October 15, 2021**

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.

9. REFERENCES

1. Kleinman, L. I.; Daum, P. H.; Lee, Y. N.; Nunnermacker, L. J.; Springston, S. R.; Weinstein-Lloyd, J.; Rudolph, J., A comparative study of ozone production in five U.S. metropolitan areas. *Journal of Geophysical Research-Atmospheres* **2005,** *110* (D02301), doi:10.1029/2004JD005096.
2. Wood, E. C.; Deming, B. L.; Kundu, S., Ethane-Based Chemical Amplification Measurement Technique for Atmospheric Peroxy Radicals. *Environmental Science & Technology Letters* **2017,** *4* (1), 15-19.
3. Cantrell, C. A.; Shetter, R. E.; Calvert, J. G., Dual-Inlet chemical amplifier for atmospheric peroxy radical measurements. *Anal. Chem.* **1996,** *68* (23), 4194-4199.
4. Green, T. J.; Reeves, C. E.; Fleming, Z. L.; Brough, N.; Rickard, A. R.; Bandy, B. J.; Monks, P. S.; Penkett, S. A., An improved dual channel PERCA instrument for atmospheric measurements of peroxy radicals. *Journal of Environmental Monitoring* **2006,** *8* (5), 530.
5. Wood, E. C.; Charest, J., Chemical Amplification – Cavity Attenuated Phase Shift Spectrometer Measurements of Peroxy Radicals. *Anal. Chem.* **2014,** *86* (20), 10266-10273.
6. Kebabian, P. L.; Wood, E. C.; Herndon, S. C.; Freedman, A., A Practical Alternative to Chemiluminescence-Based Detection of Nitrogen Dioxide: Cavity Attenuated Phase Shift Spectroscopy. *Environ Sci Technol* **2008,** *42* (16), 6040-6045.
7. Anderson, D. C.; Pavelec, J.; Daube, C.; Herndon, S. C.; Knighton, W. B.; Lerner, B. M.; Roscioli, J. R.; Yacovitch, T. I.; Wood, E. C., Characterization of Ozone Production in San Antonio, Texas, Using Measurements of Total Peroxy Radicals. *Atmos. Chem. Phys.* **2019,** *19* (5), 2845-2860.