Scope of Work For

Project 14-026
Quantifying Ozone Production from Light Alkenes Using Novel Measurements of Hydroxynitrate Reaction Products in Houston during the NASA SEAC4RS Project

Prepared for

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

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1.0 STATEMENT OF WORK

1.1 Introduction

This document provides the work plan for the Texas Air Quality Research Program (AQRP) project 14-026 “Quantifying Ozone Production from Light Alkenes Using Novel Measurements of Hydroxynitrate Reaction Products in Houston During the NASA SEAC^{4}RS Project.” The project Principal Investigators (PIs) are Dr. Greg Yarwood (ENVIRON), Dr. Thomas Ryerson (NOAA – participating as an unfunded Federal employee) and Dr. Paul Wennberg (Caltech).

1.1.1 Background

Industrial emissions of highly reactive volatile organic compounds (HRVOCs) can contribute to localized ozone (O_3) production in Houston (Ryerson et al., 2003). Aircraft flights during the National Aeronautics and Space Administration (NASA) Studies of Emissions and Atmospheric Composition, Clouds and Climate Coupling by Regional Surveys (SEAC^{4}RS) project encountered plumes with enhanced O_3 downwind of petrochemical facilities in Houston, such as on 25 September 2013, when ground monitoring downwind of the Ship Channel showed 5-minute average O_3 values peaking at 165 ppb. Historically, direct emissions of HRVOCs (specifically ethene, propene, butenes, and 1,3-butadiene) and formaldehyde (HCHO) have been implicated in these types of high ozone events, but quantifying the relative contributions of different precursors to O_3 formation has been difficult.

1.1.2 Overview of Approach

To address this issue, we will analyze and model new airborne data, taken aboard the NASA DC-8 research aircraft during the 2013 SEAC^{4}RS project in Houston, TX, to determine the amount of O_3 and HCHO produced from industrial emissions of HRVOCs in the Houston area. Information contained in Chemical Ionization Mass Spectrometer (CIMS) measurements of C_2-C_4 hydroxynitrates provides a novel means to link observed O_3 and HCHO enhancements to emissions of specific alkenes.

Analysis of the highly spatially resolved airborne data, combined with known hydroxynitrate yields and in conjunction with O_3, nitrogen oxides (NOx), HCHO, and other chemical tracers measured aboard the DC-8, will permit a robust first-order attribution of observed O_3 and HCHO enhancements to the oxidation of individual alkene precursors emitted from the Houston Ship Channel. Data from Ship Channel plume encounters during DC-8 landing approaches into Ellington Field on multiple flights in August and September 2013 show clear enhancements in the C_2-C_4 hydroxynitrates. A systematic survey capturing plumes from the W.A. Parish power plant, the Houston urban area, and the Ship Channel by the DC-8 aircraft on 18 September 2013 provides further data from which atmospheric reaction rates and yields can be determined. Reactive plume modeling using Revision 2 of the Carbon Bond 6 (CB6r2) chemical mechanism with reactions added for individual HRVOCs will evaluate current chemical mechanisms against in-situ data and test how plume dilution influences chemical processing and therefore how grid model resolution can influence modeled impacts of HRVOC sources. The analyses and modeling, enabled by the novel hydroxynitrate data, will better link industrial alkene emissions to their reaction products O_3 and HCHO and permit a more quantitative assessment of HRVOC sources and their impacts on the Houston atmosphere.

1.2 Task Descriptions

1.2.1 Task 1: QA/QC Alkene Hydroxynitrate Measurements by the Caltech TOF-CIMS aboard the DC-8 during SEAC^{4}RS and Generate Final Data

This task will be conducted by Caltech. Caltech has developed the ability to detect multifunctional organic compounds using chemical ionization mass spectrometry (CIMS). The Caltech CIMS method employs the clustering chemistry of the CF_3O^- reagent ion (Crounse et al., 2006; Paulot et al., 2009) to detect multifunctional OVOC:

$[Z] + CF_3O^- \rightarrow Z\bullet CF_3O^-$ where [Z] is a target analyte.

For the NASA SEAC^{4}RS campaign, the Caltech mass analyzer was upgraded from a quadrupole to a time-of-flight (ToF) analyzer (Figure 1-1). The ToF admits the sample ion beam to the ion extractor, where a pulse of high voltage orthogonally deflects and accelerates the ions into the reflectron, which in turn redirects the ions toward the multichannel plate detector. Ions in the ToF follow a V-shaped path from extractor to detector, separating by mass as the smaller ions are accelerated to greater velocities by the high voltage pulse. The detector collects the ions as a function of time following each extractor pulse. Critically for this study, the rapid-scan collection of the ToF guarantees a high temporal resolution (speeds of 10 Hz or faster) and simultaneous data products from the instrument for all masses (Drewnick et al., 2005).

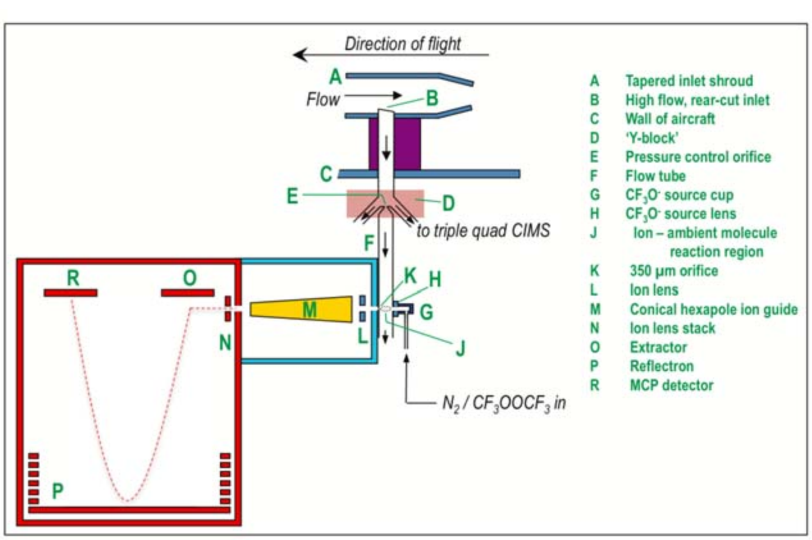

Figure 1-1. Airborne measurements of C_2-C_4 hydroxynitrates by the Caltech chemical ionization time-of-flight mass spectrometer in SEAC^{4}RS in 2013 permit a new and quantitative attribution of O_3 and HCHO produced from HRVOCs in Houston, TX.

During the SEAC^{4}RS flights over Houston, the Caltech instrument detected the presence of β-hydroxynitrates produced in the gas-phase oxidation of alkenes, including those produced from the oxidation of ethene, propene, butenes, and 1,3-butadiene. While these small β-hydroxy nitrates have been previously observed in the laboratory, this is the first systematic detection of their presence in ambient air. An example is shown in Figure 1-2 where the DC-8 sampled air across the city. β-hydroxy nitrates produced from ethene, propene, butenes, and butadiene were all present and detected with excellent signal-to-noise ratios.

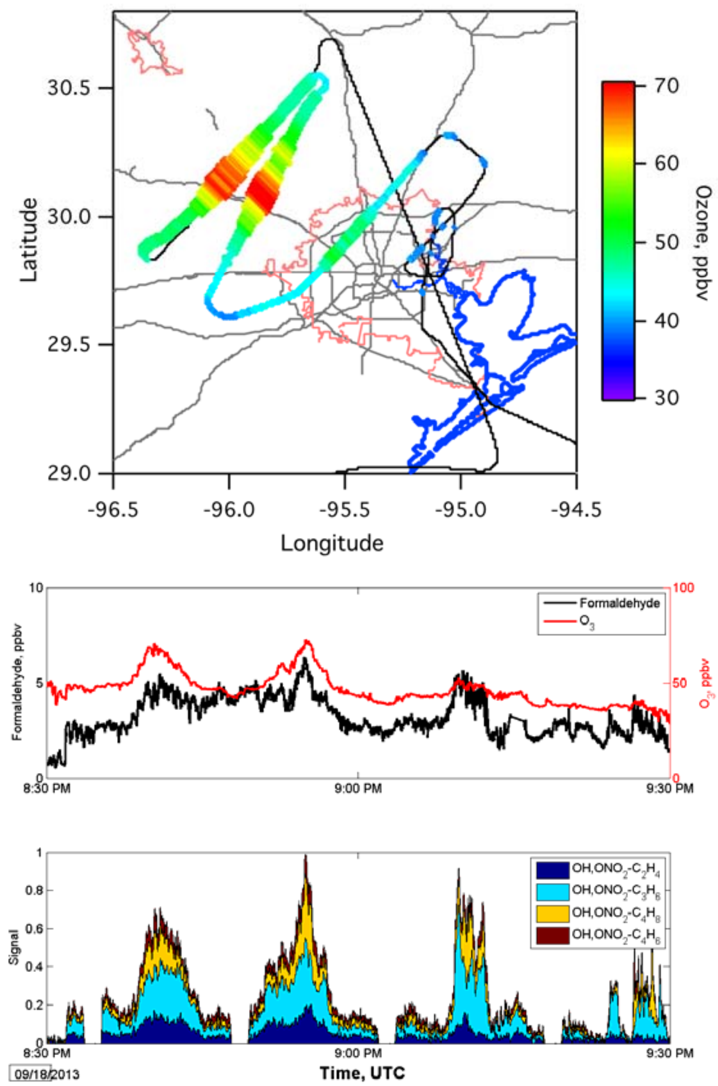

Figure 1-2. (*Upper panel*) NASA DC-8 flight track (black line) on 18 September 2013 colored by O_3 measured in the boundary layer. (*Lower panels*) Time series data showing that observed enhancements in hydroxynitrates are correlated with O_3 and HCHO. Plume analysis and modeling will use these newly-measured products to better quantify emissions of specific HRVOCs.

In Task 1, Caltech will undertake QA/QC of the β-hydroxy nitrates produced from ethene, propene, butenes, and butadiene, producing calibrated measurements for all SEAC[4]RS flights over Texas. These data will enable in Tasks 2 and 3 the quantification of the role of HRVOCs in forming HCHO and O_3.

Deliverables: The final nitrate data will be publicly released via submission to the SEAC[4]RS data archive at the end of Task 1 (August 2014, assuming a start date of May 1, 2014). Caltech will contribute to the Executive Summary that will be prepared at the initiation of the project, as well as to the quarterly reports, the monthly technical reports, and the draft final and final reports. In addition, Caltech will submit separate monthly Financial Status Reports (FSR) according to the schedule provided in Table 1-1 to the AQRP Grant Manager (Maria Stanzione) using the AQRP FY14-15 FSR Template found on the AQRP website. A Caltech representative will also attend the AQRP Workshop in June 2015.

Table 1-1. Reporting Schedule for FSRs

Report	Period Covered	Due Date
FSR #1	Project Start - May 31	Monday, June 16, 2014
FSR #2	June 1 - 30, 2014	Tuesday, July 15, 2014
FSR #3	July 1 - 31, 2014	Friday, August 15, 2014
FSR #4	August 1 - 31, 2014	Monday, September 15, 2014
FSR #5	September 1 - 30, 2014	Wednesday, October 15, 2014
FSR #6	October 1 - 31, 2014	Monday, November 17, 2014
FSR #7	November 1 - 30 2014	Monday, December 15, 2014
FSR #8	December 1 - 31, 2014	Thursday, January 15, 2015
FSR #9	January 1 - 31, 2015	Monday, February 16, 2015
FSR #10	February 1 - 28, 2015	Monday, March 16, 2015
FSR #11	March 1 - 31, 2015	Wednesday, April 15, 2015
FSR #12	April 1 - 28, 2015	Friday, May 15, 2015
FSR #13	May 1 - 31, 2015	Monday, June 15, 2015
FSR #14	June 1 - 30, 2015	Wednesday, July 15, 2015
FSR #15	Final FSR	Wednesday, August 15, 2015

1.2.2 Task 2: Analysis of DC-8 airborne data to quantify plume initial conditions, production rates, and yields of O_3 and HCHO from parent alkenes

This task will be conducted jointly by NOAA, under a Purchase Order (PO) from ENVIRON, and Caltech. The calibrated 1-Hz hydroxynitrate data produced in Task 1 will be used in conjunction with 1-Hz observations of NOx, nitric oxide (NO), peroxyacetyl nitrate (PAN), nitric acid (HNO_3), total reactive nitrogen oxides (NOy), O_3, HCHO, acetaldehyde (CH_3CHO), and other chemical and meteorological parameters measured aboard the NASA DC-8 to determine net O_3 production rates and yields for the airborne Houston study of 18 September 2013 (Figure 1-2). A simple analysis based on known hydroxynitrates yields following OH-initiated reactions of their parent alkenes (Teng, Crounse, Lee, St. Clair, Cohen, Wennberg, submitted, 2014) will permit a first-order attribution of the O_3 and HCHO formed as a result of earlier emissions of each specific alkene. This simple measurement-based analysis will be augmented by the modeling efforts that explicitly treat hydroxynitrate losses and 2nd-generation reaction products, described in Task 3, below.

Alkene emissions inferred from hydroxynitrate observations will be compared to the DC-8 whole-air-sample (WAS) data on ethene, propene, butene, and butadiene in these plumes, and linked to the original emission ratio for individual plumes by the observed NOx/ethene ratio, which is preserved during transport from the source (Ryerson et al., 2003).

Overall plume O_3 production rates and yields deduced from airborne measurements during $SEAC^4RS$ in 2013 will be compared to rates and yields deduced from airborne measurements in Ship Channel plumes under similar flow patterns, ambient temperatures, and solar insolation during the 2000 Texas Air Quality Field Study (TexAQS) (Ryerson et al., 2003; Wert et al., 2003) and the Second Texas Air Quality Study (TexAQS II) (Washenfelder et al., 2010). Changes in plume reaction rates between these earlier studies were noted and ascribed, in part, to the decrease in HRVOCs as a result of mandated control strategies to control ozone formation in Houston (Washenfelder et al., 2010). Analysis of the 2013 NASA airborne data will highlight the effects of over a decade of control strategies focusing on mitigating ozone formation in industrial plumes in the Houston area. The fractional contribution of PAN and HNO_3 to the plume NOy budget, among other chemical diagnostics, will be examined to evaluate changes in OH reactivity and plume chemistry between these studies.

The work in Task 2 will define measurement-based estimates of plume initial conditions, background concentrations, and dispersion as constraints for the Task 3 modeling, discussed below.

Deliverables: The results from Task 2 will be used to prepare a manuscript for publication in a peer-reviewed journal. NOAA will also contribute to the Executive Summary that will be prepared at the initiation of the project, as well as to the quarterly reports, the monthly technical reports, and the draft final and final reports. A NOAA representative will also attend the AQRP Workshop in June 2015.

1.2.3 Task 3: Photochemical plume modeling to assess effects of hydroxynitrate sinks and 2nd-generation reaction products on inferred plume ozone production

This task will be conducted by ENVIRON. Reactive plume modeling will be performed for selected days of the $SEAC^4RS$ measurement period using the SCICHEM Lagrangian puff model with explicit photochemistry. SCICHEM is a state-of-the science puff model using second-order closure with an advanced chemistry module that represents chemical interactions between plume pollutants and the surrounding atmosphere. SCICHEM has previously been successfully evaluated using helicopter measurements of power plant plumes, including plume widths and plume chemistry (Karamchandani et al., 2000). SCICHEM was also applied in AQRP Project 10-020 conducted by NOAA and ENVIRON to study NOx reactions and transport in nighttime plumes and their impacts on next-day ozone. The model currently uses the CB05 gas-phase chemistry mechanism and will be updated to the CB6r2 mechanism (developed in AQRP Project

12-012) with additional explicit reactions to represent hydroxynitrate production from individual HRVOCs, leveraging the work done for AQRP Project 12-006.

Task 1 will identify flight dates and plume transects of interest during the SEAC^{4}RS measurement period. Task 2 will provide information on emission rates (based on initial plume concentrations), background concentrations for the plume chemistry calculations, and the plume spread or width at various downwind distances from the Houston Ship Channel. This information will serve as input for Task 3 plume modeling with SCICHEM. A similar approach was adopted in AQRP Project 10-020 to constrain the dispersion of the plume, resulting in much better agreement between predicted plume concentrations and observations made by the NOAA WP-3D aircraft in the TexAQS II study.

The hydroxynitrate and ozone concentrations predicted using SCICHEM will be compared with data from the DC-8 flight transects to evaluate whether the model chemistry is consistent with SEAC^{4}RS observations. In addition, the results from the plume modeling will be analyzed to compare modeled yields of O_3 and HCHO from the parent alkenes for comparison with the yields obtained in Task 2 from the analysis of the DC-8 measurements. The model will be used to explore the effects of hydroxynitrate deposition, HCHO losses, and constrain the impact of product reactions on the conclusions of the Task 2 analysis, which implicitly assumes negligible product losses over the 2-3 hour plume reaction and transport time scales sampled by the DC-8.

Model sensitivity tests with different initial plume dimensions will evaluate how the rate of plume dilution influences chemical processing in order to assess how grid model resolution (e.g., 4 km^2 vs. 1.3 km^2) is likely to influence modeled impacts of HRVOC sources on downwind concentrations of O_3 and HCHO. The results from this sensitivity analysis will help in understanding the effect of grid resolution on Eulerian model results and will benefit future grid modeling conducted for the region.

Deliverables: ENVIRON will prepare an Executive Summary at the initiation of the project that will be submitted to the AQRP Project Manager for use on the AQRP website. The Executive Summary, to be delivered by May 30, 2014, will provide a brief description of the planned project activities, and will be written for a non-technical audience.

ENVIRON will also deliver Monthly Technical Reports (MTRs) to the Project Manager and TCEQ Liaison as a Word doc using the AQRP FY14-15 MTR Template found on the AQRP website based on the schedule shown in Table 1-2. The MTRs will include a summary of work accomplished on Tasks 1, 2, and 3 by the team members in each month. ENVIRON will also submit monthly FSRs according to the schedule shown in Table 1-1 to the AQRP Grant Manager (Maria Stanzione) using the AQRP FY14-15 FSR Template found on the AQRP website.

ENVIRON will prepare Quarterly Reports with the contributions of the team members according to the schedule shown in Table 1-3. The Quarterly Reports will provide a summary of the project status for each reporting period. They will be submitted to the AQRP Project Manager as Word doc files. They will not exceed 2 pages and will be text only, without a cover page. Each Quarterly Report document will be inserted into an AQRP compiled report to the TCEQ.

Table 1-2. Reporting Schedule for MTRs

Report	Period Covered	Due Date
Technical Report #1	Project Start - May 31	Monday, June 9, 2014
Technical Report #2	June 1 - 30, 2014	Tuesday, July 8, 2014
Technical Report #3	July 1 - 31, 2014	Friday, August 8, 2014
Technical Report #4	August 1 - 31, 2014	Monday, September 8, 2014
Technical Report #5	September 1 - 30, 2014	Wednesday, October 8, 2014
Technical Report #6	October 1 - 31, 2014	Monday, November 10, 2014
Technical Report #7	November 1 - 30 2014	Monday, December 8, 2014
Technical Report #8	December 1 - 31, 2014	Thursday, January 8, 2015
Technical Report #9	January 1 - 31, 2015	Monday, February 9, 2015
Technical Report #10	February 1 - 28, 2015	Monday, March 9, 2015
Technical Report #11	March 1 - 31, 2015	Wednesday, April 8, 2015
Technical Report #12	April 1 - 28, 2015	Friday, May 8, 2015
Technical Report #13	May 1 - 31, 2015	Monday, June 8, 2015

Table 1-3. Reporting Schedule for Quarterly Reports

Report	Period Covered	Due Date
Quarterly Report #1	March, April, May 2014	Friday, May 30, 2014
Quarterly Report #2	June, July, August 2014	Friday, August 30, 2014
Quarterly Report #3	September, October, November 2014	Monday, December 1, 2014
Quarterly Report #4	December 2015, January & February 2015	Friday, February 27, 2015
Quarterly Report #5	March, April, May 2015	Friday, May 29, 2015
Quarterly Report #6	June, July, August 2015	Monday, August 31, 2015
Quarterly Report #7	September, October, November 2015	Monday, November 30, 2015

ENVIRON will prepare the Draft Final Report, with contributions from the team members, that will be submitted to the Project Manager and the TCEQ Liaison on May 18, 2015. The draft report will include an Executive Summary. It will be written in the third person and will follow the State of Texas accessibility requirements as set forth by the Texas State Department of Information Resources.

An ENVIRON representative will attend the AQRP Workshop in June 2015 to present study results. ENVIRON will prepare a Final Report incorporating comments from the AQRP and TCEQ review of the Draft Final Report. The Final Report will be submitted to the Project Manager and the TCEQ Liaison on June 30, 2015. It will be written in the third person and will follow the State of Texas accessibility requirements as set forth by the Texas State Department of Information Resources.

The project data, including the QA/QC measurement data, databases, plume model, and modeling inputs and outputs, will be submitted to the AQRP Project Manager within 30 days of project completion. The data will be submitted in a format that will allow AQRP or TCEQ or other outside parties to utilize the information. The data deliverables include the following:

- QA/QC final nitrate and ancillary data
- Data analysis spreadsheets
- SCICHEM modeling data:
  - SCICHEM source code with updated CB6r2 mechanism
  - SCICHEM run control file and run script
  - SCICHEM inputs
    - Emissions inputs
    - Meteorological inputs
    - Background chemistry inputs
  - SCICHEM outputs
    - Instantaneous puff concentrations
    - Time-averaged concentrations for plume transects
  - Excel spreadsheets for comparison of model outputs with aircraft observations

2.0 PROJECT TIMELINE

The project timeline is shown in Table 2-1 below and assumes that technical work begins on May 1, 2014.

Table 2-1. Project Timeline

	2014									2015					
	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	JAN	FEB	MAR	APR	MAY	JUN
Contract, Work Plan, QAPP															
Task 1 – QA/QC Alkene Hydroxynitrate Measurements															
Task 1. Final Nitrate Data Publicly Released Via Submission to the SEAC^{4}RS Data Archive															
Task 2 – Analysis of DC-8 airborne data															
Task 2. Submit Results from Task 2 for peer-reviewed publication															
Task 3 – CB6r2 mechanism and SCICHEM updates and photochemical plume modeling															
Draft Final Report and AQRP Review															
Final Report															

3.0 PROJECT ORGANIZATION AND RESPONSIBILITIES

This project is being conducted by ENVIRON, NOAA and Caltech under a grant from the Texas Air Quality Research Program. The project Co-Principal Investigators (PIs) are Dr. Greg Yarwood of ENVIRON, Dr. Thomas Ryerson of NOAA, and Dr. Paul Wennberg of Caltech. The Co-PIs will assume overall responsibility for the research and associated quality assurance.

ENVIRON will be responsible for Task 3 as well as for overall project management and submitting periodic technical reports and the Final Report. Dr. Yarwood will be responsible for updating the CB6r2 mechanism with additional explicit reactions to represent hydroxynitrate production from individual HRVOCs, and for overall direction of ENVIRON's task for the AQRP study. Dr. Prakash Karamchandani of ENVIRON will be responsible for day-to-day technical management of the project. Drs. Karamchandani and Yarwood will also be responsible for preparing the Draft Final and Final reports with relevant contributions from NOAA and Caltech, as well as the monthly and quarterly technical progress reports. Dr. Ryerson will lead the scientific analysis of DC-8 measurements (Task 2), described in Section 1 of this work plan, in collaboration with Caltech scientists. Dr. Wennberg will lead the analysis and QA/QC of the raw field data in Task 1.

All Principal Investigators will contribute to the periodic reports (as appropriate) and the Draft Final and Final reports.

The project will be overseen by the AQRP Project Manager, Mr. Gary McGaughey, and the TCEQ Project Liaison, Mr. Chris Kite. The scientists working on this project and their specific responsibilities are listed in the Table below.

Participant	Project Responsibility
Dr. Greg Yarwood (ENVIRON)	Co-Principal Investigator: Project oversight; responsible for updates to CB6r2 mechanism in Task 3
Dr. Thomas Ryerson (NOAA)	Co-Principal Investigator: Lead researcher for Task 2; responsible for scientific analysis of DC-8 measurements and contributions to periodic and final reports
Dr. Paul Wennberg (Caltech)	Co-Principal Investigator: Lead researcher for Task 1; responsible for analysis and QA/QC of raw field data
Dr. Prakash Karamchandani (ENVIRON)	Project Manager: Responsible for day-to-day management of project and technical management of Task 3; responsible for implementing the chemistry updates in SCICHEM, setting up and supervising the SCICHEM simulations, and analyzing the results
Dr. Ilana Pollack (NOAA)	Assist Dr. Ryerson in Task 2
Mr. Jeff Peischl (NOAA)	Assist Dr. Ryerson in Task 2
Mr. Alex Teng (Caltech)	Assist Dr. Wennberg in Tasks 1 and 2
Dr. John Crounse (Caltech)	Assist Dr. Wennberg and Mr. Teng
Ms. Lynsey Parker (ENVIRON)	Assist Dr. Karamchandani in Task 3

4.0 REFERENCES

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