Quality Assurance Project Plan

Project 14-009
Analysis of Surface Particulate Matter and Trace Gas Data Generated During the Houston Operations of Discover-AQ

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Summary of Project

QAPP Category Number: III
Type of Project: Secondary Data

QAPP Requirements: This QAPP requires descriptions of project description and objectives; organization and responsibilities; scientific approach; quality metrics; data analysis, interpretation, and management; reporting; and references.

QAPP Requirements:
Audits of Data Quality: 10% Required
Report of QA Findings: Required in final report

May 29, 2014

TITLE SHEET

This document is a Level III Quality Assurance Project Plan for the Analysis of Surface Particulate Matter and Trace Gas Data Generated during the Houston Operations of DISCOVER-AQ project. This project is managed by the staff at Rice and the University of Houston.

Distribution List

Below is a list of individuals and their organizations that need copies of the approved Quality Assurance (QA) Project Plan and any subsequent revisions, including all persons responsible for implementation (e.g., project managers), the QA managers, and representatives of all groups involved. Paper copies need not be provided to individuals if equivalent electronic information systems can be used.

Air Quality Research Program (AQRP), University of Texas

David Allen, AQRP Manager

Cyril Durrenberger, AQRP Quality Manager

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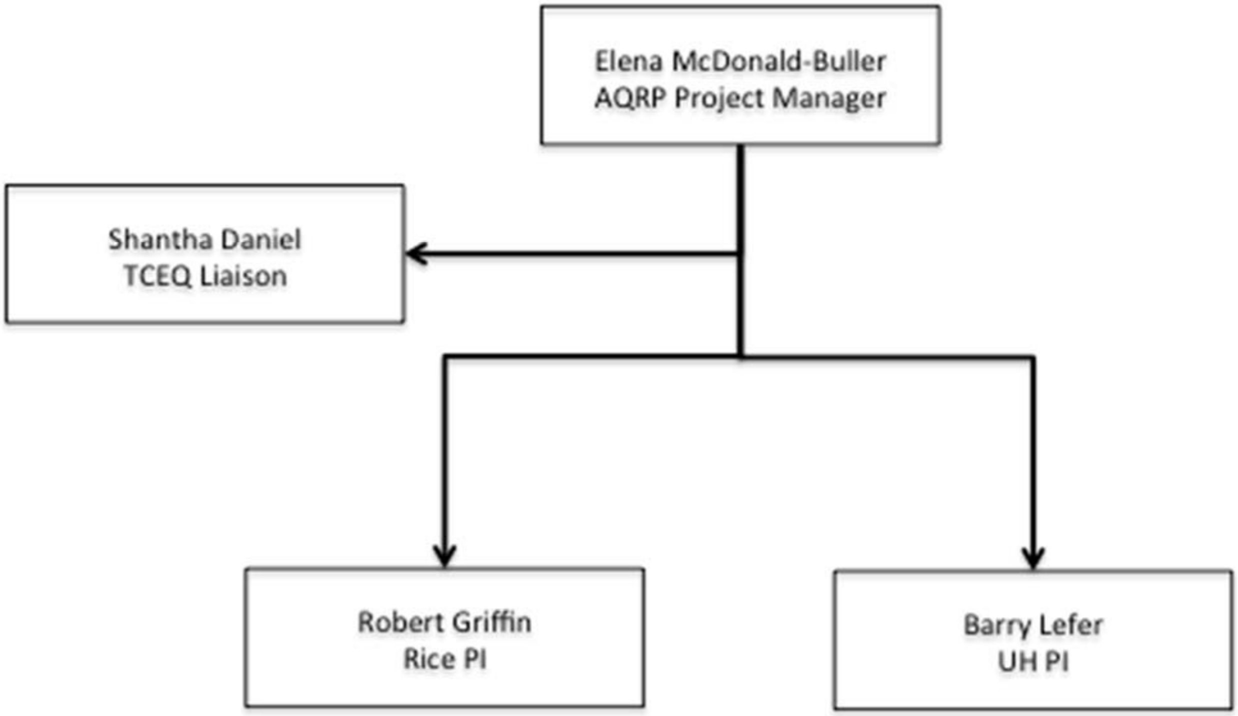
1. PROJECT DESCRIPTION AND OBJECTIVES

To investigate issues associated with direct emission and photochemical formation of air pollution in the Houston area and to support the National Aeronautics and Space Administration (NASA) project DISCOVER-AQ, we deployed a mobile laboratory and established a limited ground site for air quality measurements during September 2013; field operations were conducted by groups from Rice University and the University of Houston (UH). Field measurements included photolysis frequencies, basic meteorological parameters, particle composition, concentration, and size, and the mixing ratios of a suite of relevant trace gases. The current project focuses on analysis of the data collected during DISCOVER-AQ during the previous work. Analysis will focus on temporal and spatial behavior of pollutants, evaluation of pollution formation rates, and investigation of secondary chemical processes that influence air quality in Houston.

2. ORGANIZATION AND RESPONSIBILITIES

KEY PERSONNEL

The following flow chart identifies the key personnel at each organization that are responsible for the quality assurance (QA) and deliverables listed in this document.



PROJECT SCHEDULE

The schedule for this project and key milestones are listed in Table 1 below.

Deliverable	**Frequency or Due Date**
Updated Work Plan (Statement of Work, Budget & Justification), QAPP	Prior to start of project
Executive Summary	Within two weeks of start of project
Monthly Technical Reports	Monthly, 8th day of following month
Financial Reports	Monthly, 15th day of following month
Interim Reports	Upon request
Quarterly Reports	At end of every third month
Draft and Revised Final Report	May 18 and June 30, 2015
Presentations in Austin	June 2015 (depending on scheduling and availability)
Final Data in Time-Stamped Delimited Text Format	July 30, 2015
Draft of Journal Manuscripts	Upon Submission to Journal
Task	**Anticipated Completion Date**
Task 1 – Emission factor determination	August 20, 2014
Task 2 – Large emission event investigation	September 15, 2014
Task 3 – Data sharing and comparison	September 30, 2014
Task 4 – Diurnal PM assessment	October 31, 2014
Task 5 – PM composition assessment	November 30, 2014
Task 6 – Oxidation state evaluation	February 28, 2015
Task 7 – Secondary PM analyses	May 31, 2015
Task 8 – Biogenic activity calculations	September 15, 2014
Task 9 – NO_2 spatial variability	December 15, 2014
Task 11 – Ozone production rate modeling	March 15, 2015
Task 12 – Radical source modeling	May 31, 2015

Table 1. Project Deliverables and Tasks, with Due Dates

3. SCIENTIFIC APPROACH

The City of Houston and Harris County have a long history of air quality issues because of their large population, extensive industrial activity, and sub-tropical climate. These issues predominantly have been manifested through ozone (O_3) mixing ratios that exceed the National Ambient Air Quality Standards (NAAQS) established by the United States Environmental Protection Agency. However, recent measurements indicate that Harris County barely achieves compliance with the NAAQS that have been established for particulate matter (PM), specifically for particles with diameters less than or equal to 2.5 micrometers.

In recent years, the National Aeronautics and Space Administration (NASA) has placed considerable emphasis on the use of satellite remote sensing in the measurement of species such as O_3 and PM that constitute air pollution. However, additional data are needed to aid in the development of methods to distinguish between low- and high-level pollution in these measurements. To that end, NASA established a program titled Deriving Information on Surface Conditions from Column and Vertically Resolved Observations Relevant to Air Quality (DISCOVER-AQ). DISCOVER-AQ began in summer 2011 with work in the Mid-Atlantic Coast that featured satellite, airborne, and ground-based sampling. The DISCOVER-AQ program conducted operations in and near Houston in September 2013.

During the Houston operations of DISCOVER-AQ, there was a need for ground-based measurement support. The predecessor to this project filled that need by providing quantitative measurements of sub-micron particle size and composition and mixing ratios of volatile organic compounds (VOCs) and other photochemically relevant gases such as O_3 and oxides of nitrogen (NO_x = nitric oxide (NO) plus nitrogen dioxide (NO_2)). The instrumentation for these measurements was deployed using the University of Houston (UH) mobile laboratory. The current project focuses on the analysis of data generated during the mobile laboratory operations during DISCOVER-AQ.

Three instruments were used to characterize the chemical composition and size of aerosol particles in Houston. The Rice team performed measurements of size-resolved aerosol chemical composition at high time resolution (10 minutes) using an Aerodyne (Billerica, MA) high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS). In this instrument, sub-micron particles are classified by size according to their speed within a vacuum chamber, which will allow estimation of their vacuum aerodynamic diameter. Non-refractory material is vaporized, ionized by electron impact, and detected using a time-of-flight mass spectrometer. The HR-ToF-AMS provides chemical speciation for ammonium, nitrate, chloride, sulfate, and several classes of organic matter. The Rice team also deployed a TSI, Inc. (St. Paul, MN) Model AE51 to measure black carbon (BC) in a manner similar to an aethalometer. Lastly, a particle-into-liquid sampler (PILS) (Brechtel Manufacturing, Oakland, CA) connected to ion chromatographs (ICs) (Dionex, Sunnyvale, CA) was used at a stationary site (Manvel Croix) to collect one-hour resolution measurements of water soluble ionic aerosol composition to focus on materials that are not amenable to measurement by the HR-ToF-AMS and to provide a basis for calculating the collection efficiency of the HR-ToF-AMS. In the PILS, particles are collected on an impaction plate that is washed by clean water; soluble material dissolves in the wash water, which is then collected and injected directly into the ICs. Species measured by the PILS-IC include sulfate, nitrate, chloride, ammonium, calcium, potassium, magnesium, and sodium. The inlet on the PILS-IC included a 1-μm cyclone.

Measurement of VOCs conducted by the UH team used a proton transfer reaction mass spectrometer (PTR-MS) manufactured by IONICON Analytik (Austria) in which target gas molecules are ionized by proton transfer from protonated water. The ionized material is then detected and quantified using a time-of-flight mass spectrometer. The PTR-MS is a form of chemical ionization mass spectrometry. Data were collected in thirty-second averages, but these data will be averaged to longer time scales in order to match the output from other instruments.

In situ O_3 measurements were performed with a Thermo Scientific (Franklin, MA) Model 49C O_3 ultraviolet photometric gas analyzer. The NO, NO_2, and total active nitrogen (NO_y) measurements were made with three modified Thermo Scientific Model 42 trace level chemiluminescence NO-NO_2-NO_x analyzers with a blue light converter (BLC) from Air Quality Design (Wheat Ridge, CO, USA) for photolysis conversion of NO_2 to NO and a Thermo molybdenum (Mo) converter heated to 320°C for conversion of odd nitrogen species to NO. The BLC is more specific in that it essentially converts only NO_2 to NO, compared to the standard Mo-based NO_2-to-NO converter used in most EPA and Texas Commission on Environmental Quality (TCEQ) air monitoring sites that also converts nitric acid (HNO_3) and peroxy acyl nitrates to NO and as a consequence tends to over estimate NO_2. Ambient levels of carbon monoxide (CO) were measured with a Thermo Scientific CO Analyzer (Model 48C-Trace Level Enhance) with a gas correlation wheel cell that detects CO via the absorption of infrared radiation at a wavelength of 4.6 microns. Ambient levels of sulfur dioxide (SO_2) were monitored using the pulsed ultraviolet fluorescence technique employed in the Thermo Scientific Model 43i-TLE instrument, which takes advantage of the characteristic that SO_2 molecules absorb ultraviolet radiation and then fluoresce in the range of 220 to 240 nm. These basic ambient trace level chemical instruments were queried serially every second with DAQFactory data acquisition software (Azeotech, Ashland, OR). The UH Atmospheric Radiation Laboratory also deployed a Diode Array Actinic Flux Spectroradiometer to measure the solar actinic flux in the wavelength range of 290 to 560 nm. Photolysis frequencies of at least 20 important photolytic processes were calculated from the actinic flux spectra using the most recent Jet Propulsion Laboratory and International Union of Pure and Applied Chemistry recommendations for absorption cross section and quantum yield data. The trace gas and actinic flux data were post-processed and averaged into a format suitable for storage and use in a database with software such as Igor Pro and MATLAB. Data were saved at 10-second, one-minute, and five-minute resolutions.

The data were provided in time-stamped delimited (resolution described above) text format suitable for use in a database to the AQRP. Data included the time series (and relevant global positioning system information) of all parameters discussed above. At least 10% of the data will be audited by members of the relevant group who did not generate the time series to ensure that proper data were included, that the appropriate time period is addressed, that the correct units and limits of detection are used, and that the data points are easily viewed when plotted.

Further analyses of these data will include fundamental statistical analyses including averaging, median, and percentile anlaysis, and correlation/regression between measured parameters (slope, regression coefficient, and p-value). More advanced techniques will include derivation of diurnal profiles (average, mean, and percentile analysis within a given hour for every day of the campaign) and spatial distributions.

In addition, positive matrix factorization (PMF) will be applied to the organic fraction of the PM. PMF applied to the HR-ToF-AMS data will allow for separation of the organic matter into various classes (termed factors) including secondary organic aerosol, biomass burning aerosol, etc. (Ulbrich et al, 2009). In this version of PMF, the time series of the signal at various mass-to-charge ratios are investigated to see which vary similarly in time. In this way, ‘typical spectra’ that represent/constitute the bulk HR-ToF-AMS spectra when combined are identified. The time series of each factor can then be determined, with the best results determined by a minimization of errors technique. The time series of each factor are compared to tracer compounds (such as CO for combustion) to identify the likely source/process for each factor.

A zero-dimensional model (Flynn et al., 2010) will be used in O_3 production rate and radical source calculations. This model can be run either in time-dependent mode or using an assumption of instantaneous photostationary state. The reactions used and the kinetics that describe them are those specified by Sander et al. (2006) and are based on the mechanistic scheme of Lurmann et al. (1986). The model is constrained by measurements of O_3, CO, NO_x, and other measurements.

4. QUALITY METRICS

Comparability is achieved when the results are reported in standard units to facilitate comparisons between the data from this project and other similar programs. In order to accomplish this objective, the reporting units for the ambient measurements performed here will adhere to standard units (mixing ratios or number densities for gases, seconds for temporal units, and mass concentration for aerosol composition as a function of size).

Quality control (QC) checks on the instrumentation were critical to successful generation of the data. The QC checks used during generation of original data as well as instrument-specific information are described in the work plan, reports, and QA plan associated with the previous project.

Data acceptability was determined by considering detection limit, blanks/zeros, precision, accuracy, and completeness. Audits of data quality were performed by visual inspection of the data, comparison of the data to the QA/QC criteria described in previous project documentation, and comparison with other measurements, as applicable. Data that passed these examinations were deemed acceptable. Data that failed were further examined by the researchers and as appropriate flagged as invalid, valid, or valid but having failed a check. At least 10% of the valid data will be audited by members of the relevant group who did not generate the time series to ensure that proper data were included, that the appropriate time period is addressed, that the correct units and limits of detection are used, and that the data points are easily viewed when plotted.

Besides the audit, all data that will be used in the analyses for this project already have undergone QA/QC procedures. Therefore, no additional QA/QC will be performed on these data. Because all analyses will be performed using these data, there are no additional project-specific data quality requirements.

5. DATA ANALYSIS, INTERPRETATION, AND MANAGEMENT

Data analysis techniques are discussed in Section 3. The information provided by these data will be useful in understanding pollution dynamics in this region and therefore in developing control strategies and determining whether local or regional controls may be best suited for this area in the State Implementation Plan. Data collected/generated during the course of this project will be backed up on servers in multiple locations at each of the participating institutions and will be maintained for a minimum of 3 years after the completion of the project.

6. REPORTING

Reporting for this project will include:

- Monthly, quarterly, and interim (as requested) reports including accomplishments, problems encountered and corrective actions, goals for the next reporting period, and a description of the project's progress as described above.
- Separate monthly financial reports.
- Draft final and final reports describing all activities and summarizing all findings. The final report will include descriptions of the field campaign including site and instrumental information, time series of all collected data, and preliminary statistical analysis of the data. The final report may also include recommendations for future work (depending on the outcome of this project).

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.

Drafts of journal manuscripts based on the work performed as part of this project will be presented to the TCEQ upon submission to the journal. Manuscripts are likely to include attempts to analyze these data in manners that will elucidate the root causes of pollutant concentrations observed at the various sites.

7. REFERENCES

Flynn, J., et al. (2010), Impact of clouds and aerosols on ozone production in southeast Texas, Atmos. Environ., 44, 4126-4133.

Lurmann, F.W, A.C. Lloyd, and R. Atkinson (1986), A chemical mechanism for use in long-range transport/acid deposition computer modeling, J. Geophys. Res., 91, 10905-10936.

Paatero, P. (1997), Least squares formulation of robust non-negative factor analysis, Chemometr. Intell. Lab. Syst., 37, 23-35.

Sander, S., et al. (2006), Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies, Evaluation Number 15, JPL Publication 06-2.

Ulbrich, I.M., M.R. Canagaratna, Q. Zhang, D.R. Worsnop, and J.L. Jimenez (2009) Interpretation of organic components from Positive Matrix Factorization of aerosol mass spectrometric data. Atmos. Chem. Phys., 9, 2891-2918.