Quality Assurance Project Plan (QAPP)

Project 22 – 010
Dallas Field Study (DFS); Ozone Precursors, Local Sources and Remote Transport Including Biomass Burning

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

Prepared by

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

QAPP Requirements: Project Description and Objectives, Organization and Responsibilities, Scientific Approach, Sampling Procedures, Measurement Procedures, Quality Metrics (QA/QC checks), 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

Approvals Sheet

This document is a Category III Quality Assurance Project Plan for the Dallas Field Study (DFS); Ozone Precursors, Local Sources and Remote Transport Including Biomass Burning project. The Principal Investigator for the project is Ed Fortner.

Electronic Approvals:

This QAPP was approved electronically on 8/30/2022 by Project Manager Name, The University of Texas at Austin.

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1 PROJECT DESCRIPTION AND OBJECTIVES

1.1 Project Description

1a. Local sources of Volatile Organic Compounds (VOC) and particulates will be evaluated and their role in ozone (O_3) production will be examined.

The sampling of point sources in the Dallas - Fort Worth (DFW) metropolitan area by the Aerodyne Mobile Laboratory (AML) and subsequent measurements downwind of facilities will give insight into both primary gas and particle phase pollution as well as secondary production of O_3 and secondary organic aerosol (SOA).

1b. Biomass Burning influenced airmasses will be evaluated.

The sampling of biomass burning impacted airmasses as they pass through the DFW area will be examined prior to, during and after interaction with the urban plume. Biomass burning events (wildfires) will also be sampled close to their source and downwind when wildfires occur in Texas.

1.2 Purpose and project objectives

The primary purpose of this project is to better understand the role that various point sources in the DFW area play in primary emissions and secondary O_3 and SOA production. The secondary purpose is to better understand the role that biomass burning plays in its interactions with the urban plume. Finally, whenever wildfires occur within the state of Texas, examinations of the biomass burning plume from source to various distances downwind including areas within the DFW area will enhance our knowledge of biomass burning plume evolution.

Project objectives:

1. We intend to identify specific sites of interest (industrial facilities, chemical storage areas, etc.) and measure downwind of those facilities. We will use emission inventories as an initial guide as well as any other information available regarding emission history. A reasonable objective is to successfully characterize 15 to 25 of these sites depending somewhat on their geographical spacing. We will focus on Region 4 in the state of Texas which is centered on the DFW area
2. As a result of the source measurements conducted in Part 1 (above) we will attempt to better apportion the VOC component of regional O_3 production in the DFW area and determine the extent to which the area is nitrogen oxide (NOx) limited versus VOC limited regarding ozone production.

3. We intend to characterize the inflow and outflow of airmasses as they interact with the DFW metropolitan area sources on a broad scale.
4. We will characterize the inflow and outflow of any biomass burning impacted airmasses as they transit the DFW metropolitan area.
5. We will characterize locally produced (within the state of Texas) biomass burning plumes to examine plume evolution with aging conducting transects at varying distances from the source.

2. ORGANIZATION AND RESPONSIBILITIES

2.1 Roles and responsibilities

The roles and responsibilities for each participant of this project are outlined below:

Ed Fortner, Project Principal Investigator (PI), Aerodyne Research Incorporated (ARI)

- Project management and reporting
- Responsible for Field Experiment Execution Planning, Particle phase Soot Particle Aerosol Mass Spectrometer (SP-AMS) operation and data analysis, production of chemically speciated aerosol loading time series.

Brian Lerner, Lead Gas Phase Measurement Scientist, Aerodyne Research Inc.

- Will assist in Field Experiment Execution Planning
- Responsible for Gas Chromatography (GC)/VOCUS operation and data analysis, production of VOC concentration time series.

Tara Yacovitch, Data Quality Manager, Aerodyne Research, Inc.

- Will assist in data analysis
- Data Quality Manager, responsible for 10% data audit of final campaign data.

Conner Daube, Aerodyne Mobile Lab Manager, Aerodyne Research, Inc.

- Responsible for Quantum Cascade Laser (QCL)/Tunable Infrared Laser Direct Absorption Spectroscopy (TILDAS) operation, Mobile Laboratory Readiness
- Will assist in QCL/TILDAS data analysis, Field Experiment Execution Planning

2.2 Project schedule

A schedule of project activities is shown below.

Table 2.2. Timeline of campaign tasks. Note that light shading indicates limited preliminary analysis intended to guide the next day's activities

Task	Description	Year	2022					2023						
		Month	9	10	11	12	1	2	3	4	5	6	7	8
1	Work Plan Including QAPP													
2	Base Site Selection													
3	Campaign Planning													
4	Instrument Integration at ARI													
5	Campaign Execution													
6	Data Analysis													
7	Finalized Dataset													
8	Monthly Reports													
9	Presentation at AQRP Workshop													
10	Draft Final Report													
11	Final Report													

3. SCIENTIFIC APPROACH

We are conducting mobile laboratory measurements during the bulk of this campaign and the number of locations sampled daily will vary, however, the types of missions we will engage in could be categorized into 3 categories and their overall weighting is projected.

1. Source Measurements in the DFW metropolitan area (50-60%)

   In this measurement scenario we will determine facilities of interest to sample on a given day taking into consideration operational status, forecasted wind, and the accessibility of the local road network for the AML. Our schedule for mobile measurements will be flexible with the intent of capturing emissions of interest whenever they occur (e.g., day versus nighttime emissions) as well as building in variety and coverage into our diurnal sampling statistics.

2. Stationary measurements in the DFW metropolitan area (25-40%)

   In this scenario we will position the AML upwind, downwind, or in the middle of the DFW metropolitan area and remain in this position for a period of a few hours (2 to 6). Our intent is to measure the inflow into the DFW metro or alternatively, processing in the DFW and more aged processing downwind of central DFW. We will attempt this scenario in all three measurement stages with both biomass burning impacted airmasses and more typical inflow into the DFW area.

3. Measurements of biomass burning events in the state of Texas (0-35%)

This will involve driving the AML to wildfire areas in the state of Texas and then conducting transects at varying distances downwind of the fire to characterize the wildfire plume evolution as it ages. We will be safety conscious in this mission ensuring no interference with firefighting efforts while also maintaining safe operating conditions in the AML as we have done in previous wildfire measurement focused campaigns. It is possible that this plume may enter the DFW metropolitan area, and we will prioritize wildfire plumes that are forecast to impact the DFW metropolitan area.

4. SAMPLING PROCEDURES

The AML is outfitted with instrumentation that sample the local air and characterize it for a specific chemical or class of chemicals. The majority run pseudo continuously, with a constant intake flow that is processed to produce 1 second data. Other instrumentation does sample collection, such as gas-chromatography instruments that sample for a discreet period of time, concentrating sample that is released onto the column during a measurement phase. Other integral instrumentation does not fit into either of these categories, such as the anemometers and global positioning system devices.

Once the campaign begins, the instrumentation suite will be operated continuously, switching between pre-arranged “shore” power and the on-board generator. The procedures and protocols for the switch are described in the mobile laboratory manual. Approximately 3 minutes are required to re-establish quality assured data following the power switches

We plan to have shore power and a nominal base at one location in the DFW metropolitan area. We do plan to conduct stationary measurements for extended time periods away from this base and conduct mobile measurements. The AML can operate for 48-72 hours on generator power so it is not necessary to return to shore power nightly. Prevailing and forecast meteorological conditions and the presence of biomass burning impacted airmasses will influence our choice of missions and will dictate where we move the AML daily. For source-related work in the DFW metro (mission 1), we will determine which wind profiles work best for specific sources and plan accordingly. For stationary sampling in the DFW metro (mission 2), we will ensure that we are able to park and sample for some time at either of three nominal positions (upwind, downwind or metro center). When sampling biomass burning plumes (mission 3), we will drive to the wildfire area and then conduct transects along the track of the smoke plume.

The campaign will be conducted during a three-week interval. Aerodyne scientists will analyze the data while in the field and regularly interact with the Project Manager and others to get feedback regarding future planning while considering overall project objectives.

Please note regarding sections 4.3 – 4.6 that we do not actually collect any physical samples for subsequent analysis.

5.MEASUREMENT PROCEDURES

5.1 General Measurement Procedures

The radical termination hydrocarbons that contain a signature of their source and O_3 are high priority measurements in this project. In order to properly evaluate the photochemical environment, speciated NOx and photochemical precursors must also be quantified. The measurements of carbon monoxide (CO) and selected hazardous air pollutant hydrocarbon compounds will also be performed. The core suite of species chosen in the deployment package will enable an understanding of the photo-chemical and radical environment. For the biomass burning investigations we will conduct, hydrogen cyanide (HCN), acetonitrile, CO, black carbon, potassium and certain aerosol organics will be useful source measurements.

The measurement system will include:

- Fast (1s time resolution) combustion tracer species, Carbon dioxide (CO_2), CO, Nitric Oxide (NO), Nitrogen Dioxide (NO_2), HCN
- Rapid measurements of particulate quantities, particulate black carbon mass, particulate sulfate, nitrate and organic matter, metals of interest, total number density (count), particulate size distribution spectra;
- Selected ozone precursors and hazardous air pollutant (HAP) measurements such as, benzene, toluene, ethylene, xylene (BTEX), acetaldehyde and other oxygenated hydrocarbons;
- Meteorological instrumentation to monitor wind speed and direction;
- Global Positioning System (GPS) data for the AML

Table 5.1. Desired Instrument Manifest for the Aerodyne Mobile Laboratory. *

Measurement	Rate	Instrument
Carbon Dioxide (CO_2)	1 s	Licor 6262
Nitrogen Dioxide (NO_2)	1 s	Cavity Enhanced Phase Shift Spectrometer for NO_2 (CAPS-NO_2)
Oxides of Nitrogen (NOx)	1 s	Cavity Enhanced Phase Shift Spectrometer with Ozonator (CAPS-NOx)

Ozone (O_3)	2 s	2B Tech Ozone Monitor
Carbon Monoxide (CO), Nitrous Oxide (N_2O), water vapor (H_2O)	1 s	Tunable Infrared Direct Absorption Spectrometer, Compact Single-Laser (TILDAS-CS): TILDAS-CS CO/N_2O analyzer.
Methane (CH_4), Ethane (C_2H_6)	1 s	TILDAS-CS CH_4/C_2H_6 analyzer.
Hydrogen Cyanide (HCN), acetylene (C_2H_2)	1 s	TILDAS-CS HCN analyzer.
Formaldehyde (HCHO), formic acid (HCOOH)	1 s	TILDAS-CS HCHO analyzer.
Black Carbon Particulate Matter (PM) (70 nm -2.5 µm)	1 s (variable)	Soot Particle Aerosol Mass Spectrometer (SP-AMS) with laser-on mode
Non-refractory PM coating on Black Carbon (70 nm – 2.5 µm)	1 s (variable)	SP-AMS with laser-on mode;
OrganicSulfate, Nitrate, Ammonia, Chloride, metals PM (70 nm – 2.5 µm)	1 s (variable)	Aerosol Mass Spectrometer (AMS) /SP-AMS
Particle Number Density	1 s	Condensation Particle Counter (CPC)
Various Aromatics and Oxygenates such as: Benzene, Toluene, Xylene, Acetone, Acetaldehyde	1 s	Proton Transfer Reaction Mass Spectrometer (PTR-MS)
Alkanes, Selected Alkenes and Aromatics, including alkyl nitrates	30 mins	Gas Chromatogram with Mass Spec. detection

* This list consists of a typical deployment manifest. The exact deployment manifest will be finalized as part of the campaign planning task, prior to campaign execution, and will be communicated to AQRP via the appropriate deliverable. During that planning task, exact power and space requirements will be compared to instrument needs and project measurement priorities.

The mobile laboratory suite includes sampling instrumentation, ambient meteorological measurements, and global positioning system

The following general tasks will be completed as part of the daily deployment activity. The manual for the mobile laboratory is included as Appendix 1 and contains much more specific instructions for the operational procedures.

1. The truck infrastructure instrumentation, GPS, clock synchronization software and time stamped notes stations are verified.
2. Quality Control checks are performed on all analyzers. The real-time display of all measured vectors is used to verify that all instruments are recording data with the predicted time response, and that they are all responding to on-board inlet based zero air or particle free air events.
3. Ambient monitoring analysis will be performed to account for the wind condition and total status of the truck. For any instrumentation requiring corrective actions, a judgement will be made regarding the instrument priority within the study objectives and the current sampling condition.

4. When at the base facility, the mobile lab will be docked to shore power and sampling will continue. At this time, detailed calibration and QA procedures can be performed according to specific instrument demands.

The manuals or documents describing the various operational procedures are attached as appendices.

Appendix 1: AML Power Instructions
Appendix 2: Calibration Procedures.
Appendix 3: VOCUS Product Sheet
Appendix 4: Licor 6262 (CO_2 analyzer)
Appendix 5: 2B Tech O3 Monitor Manual
Appendix 6: Ecotech Serinus Cal 3000 Manual
Appendix 7: TILDAS-CS hardware manual
Appendix 8: TDLWintel Software Manual (for TILDAS instruments)
Appendix 9: CAPS NO_2 Product Sheet
Appendix 10: HR-ToF Aerosol Mass Spectrometer Manual
Appendix 11: GC-EI-ToF-MS Product Sheet

The main truck notes log is similar to a chat system, where notes entered at any terminal are time stamped and recorded in a centralized file. Specific calibration procedures and instrument evaluation notes are also recorded on the computer which is responsible for acquiring or logging the data from that instrument.

5.2 Specific calibration procedures

Trace Gas Instrument Calibration Procedures (excluding VOC measurements by the GC-EI-ToF and Vocus PTR-MS)

Each real-time instrument operates on different physical principles; however, they all require established baselines for quantitative measurements. True “no signal” baselines are established periodically during mobile lab operation by introducing zero air into the mobile laboratory-sampling manifold, exposing all instruments to a “no pollutant” stable air sample. Background ambient air and plume pollutant levels are measured from the zero air baseline. Each instrument can then be calibrated by introducing known levels of gaseous or particulate matter (PM) species into the sampling manifold. In the case of the major trace gases (CH_4, HCN, CO and CO_2), calibration gas cylinders with known trace gas levels, traceable to analytical lab verifications and precise to 1 to 10% depending on species, are used for absolute calibration. Calibrations are periodically performed using calibration gas cylinders carried onboard the mobile laboratory. Some of the standards that will be carried require quantitative dilution using two flow controllers (1 for standard and 1 for diluent). Other calibration tanks operate as a single point ‘overblow”. In all cases, the continuous sampling gas phase instruments are calibrated by introducing the standard at the inlet tip. Instruments are never removed from the sample line and calibrated at different pressures of flows. Standard operating procedures for calibration of gas phase instruments are included in Appendix 2.

Particle Measurement Calibration Procedures

The commercial Thermo-Systems Incorporated (TSI) condensation particle counter (CPC) is factory calibrated and is periodically returned for refurbishment and recalibration. The calibration of the ARI Aerosol Mass Spectrometer (AMS) is a more complex procedure. In order to minimize uncertainties in the reported mass concentrations, it is desirable that the fluctuations of the detection efficiency of the AMS are closely monitored and properly corrected throughout the whole campaign. The parameters that capture the AMS detection efficiency are IE_{NO3-}, which is the ionization efficiency (IE) of a reference compound—NO_3^-, and the air beam signal (AB), which is the ion rate (Hz) detected for a major air signal, e.g. N_2^+ in this study[*Allan et al.*, 2003; *Jiménez et al.*, 2003]. While AB can be monitored continuously during instrument operation, the determination of IE_{NO3-} requires interruption of sampling to perform a calibration experiment (typically 1 – 2 hours). Given this restriction and the expectation (based on previous experience) that IE would not be highly variable, periodic IE_{NO3-} calibrations will be conducted during this study. Because the ratios of IE_{NO3-} to AB remains remarkably constant (r.s.d. < 1%) the continuous AB signal can be used to correct for the variations in the AMS detection efficiencies to a very good approximation.

Two other AMS parameters significantly influence the absolute values of its PM measurements: the collection efficiency (CE) and relative ionization efficiency (RIE). CE is introduced to correct for incomplete detection of nonrefractory particles, NR-PM, by the AMS, e.g., due to irregularly shaped particles that do not completely reach the vaporizer [*Jayne et al.*, 2000; *Tobias et al.*, 2000]. Although strictly speaking CE should be a function of particle size and shape, at present it is defined as the correction factor for the bulk mass concentrations, i.e., the fraction of the particle mass that is measured by the AMS.

A CE value of 0.5 is assigned to sulfate, based on extensive observations from several laboratory and field tests for sulfate aerosols. The same CE value (i.e., 0.5) is applied to particles containing nitrate and ammonium, because they appear to be internally mixed with sulfate particles most of the time.

The CE value for total NR-PM_1 organics is estimated based on their size distributions, which often show two modes – a larger accumulation mode of ambient background particles that appears to be internally mixed with SO_4^{2-}, NO_3^- and NH_4^+, and a smaller ultra-fine mode that seems to be mainly emitted from combustion-related sources. A CE value of 0.5 is thus applied to the accumulation mode organics (due to the internal mixing with SO_4^{2-}) and CE for the smaller mode is assumed to be 1.0 because laboratory studies have shown close to 100 % AMS transmission for sooty combustion particles. By studying the size distributions of total organics, as well as individual organics mass fragments averaged over the whole sampling period, we have found that these two modes can be best separated at Dva = 160 nm and that the mass ratio of the smaller (Dva < 160 nm) to the larger mode (Dva > 160 nm) is roughly 2/3. The CE value of the bulk organics is therefore set at 0.7.

Relative ionization efficiency (RIE) is the ratio of the electron impact ionization efficiency of a given species to IE_{NO3}^- on a per unit mass basis. Note that IE_{NO3}^- is the IE of NO_3^- measured based on two major ions, m/z's 30 and 46, instead of all the mass fragments. RIE values of individual species representative have been determined in a range of laboratory measurements and tabulated [*Zhang et al.*, 2006].

The Soot Particle Aerosol Mass Spectrometer (SP-AMS) has the additional capability of measuring refractory black carbon, and this measurement is calibrated by sampling atomized, dried and differential mobility analyser (DMA) (TSI Model 3081) size selected black carbon (BC) particles into the SP-AMS and a CPC. The ions per picogram of black carbon detected is then compared with the ions per picogram of ammonium nitrate and the RIE of BC is determined by this comparison [*Onasch et. al*. 2012]

Finally, two other key AMS parameters require calibration. The AMS volumetric sampling flow rate and the particle velocity. The sample flow rate will be determined using a Gilibrator (bubble flowmeter). The particle aerodynamic size reported by the AMS is based on measured particle velocities. The size – velocity calibration is performed using an atomizer with an ammonium nitrate (NH_4NO_3) solution followed by DMA size selection in the range 60 -700 nm.

Proton Transfer Reaction Mass Spectrometer (PTR-MS) Instrument Assessment

The PTR-MS instrument provides a measurement of a selected set of organic gases possessing proton affinities greater than water. Most non-alkane organics possessing more than 2 carbons can be detected using the PTR-MS. This instrument is located

immediately behind the driver in the mobile laboratory to minimize the length of the sampling inlet.

Specific step-by-step instructions for bringing this instrument on-line and a copy of the instrument manual are available elsewhere (Appendix 3 in the context of this QAPP). The description provided in this document pertains to the normal operation of instrument. Details of the instrument have been previously published in *Krechmer et al.* [2018].

The PTR-MS draws sample from the main gas phase sample inlet through a short length, ~ 4 feet, of 1/4" outer diameter (OD) perfluoro alkoxy(PFA) tubing at 4.5 standard liters per minute (SLPM) to minimize residence time but maintain laminarity. 0.1 SLPM of this flow is subsampled into the instrument for analysis and the rest is thrown away.

The PTR-MS has three modes of operation: measure, zero and calibrate. Zero and calibration periods are automatically actuated at pre-defined intervals using electronically controlled solenoid valves. The measure and zero modes are automated, while the calibrate mode requires the instrument to be taken off-line. The PTR-MS parameters drift tube pressure, detection region pressure, drift tube temperature and reagent ion intensity should always be within the following specifications:

Drift tube pressure = 2.1 (± 0.05) mbar
Detection region pressure < 45 x 10^{-6} mbar
Drift tube temperature 60 (± 1) ^{o}C

The drift tube pressure and temperature are automatically controlled and maintained via a proportional integral derivative (PID) feedback loop.

Instrument zeros are software controlled and scheduled to occur at a regular specified interval using an on-board zero air generator. The PTR-MS uses a series of 3-way solenoid valves to redirect the inlet flow from the sample inlet to zero gas inlet. This allows the PTR-MS to evaluate the instrument background independently without affecting any of the other gas phase measurements. VOC free air is produced by pulling filtered ambient air through a heated oxidation catalyst. A ¾"OD stainless steel tube packed with a 50:50 mix of Platinum and Palladium coated alumina beads is housed within a small oven that is heated to 400 ^{o}C and oxidizes any VOCs to CO_2. Instrument background is mass dependent with some ions having non-zero values. Atmospherically persistent compounds such as acetone (m/z 59) should exhibit discernable decreases in their ion intensities when the PTR-MS is sampling zero air.

Instrument calibrations are performed at regular intervals (generally every 4 hours around the clock) by serially diluting the PTR-MS multi-component calibration gas with VOC free air from the on-board zero air generator. Instrument calibration is accomplished with the PTR-MS operated in the zero-mode so that the calibration procedure does not affect any of the other gas phase measurements. The flows of the calibration gas and the

VOC free dilution gas are controlled via mass flow controllers. Serial dilutions are performed by mixing 2-10 ml/min of the calibration gas into a zero-gas dilution flow of 400 – 1000 ml/min.

Gas Chromatography Electron Impact Time of Flight (GC-EI-ToF) Instrument

The Thermal Desorption Pre-Concentrator (TDPC)-GC-EI-TOF instrument is a 2-channel GC system that provides semi-continuous quantitation of trace organic gases within the volatility ranges of each chromatograph channel. The instrument has a "high-volatility" VOC channel and a "mid-volatility" channel as configured for this field campaign. Each channel relies upon a two-stage adsorbent / thermal desorption pre-concentration system to provide adequate analyte for separation and analysis by the GC-EI-TOF.

The GC system shares a common inlet with other gas-phase instruments and is located directly behind the PTR-MS instrument inside the mobile laboratory to reduce the inlet length, and to allow for simpler temporal correlation with real-time VOC measurements made with the PTR-MS system.

The GC system pulls approximately 1-2 slpm of ambient air from the main inlet via 1/4" OD PFA tubing, typically less than 4 feet in length. A subset of this sample flow (100-200 sccm) is directed to the GC inlet for analysis, with the rest of the flow vented. The air is passed through an oxidant scrubber (a quartz tube packed with sodium sulfite) to reduce ozone, which can produce significant artifacts in the pre-concentration system when in high abundance.

After the oxidant scrubber, the gas sample is split to separate multibed sample tubes, which are held at fixed temperature (typically 20 °C) during sample collection. The flow to each tube is controlled by calibrated mass flow controllers (MFCs) to provide known sample volumes. After sample collection (typical 100 sccm for 10 min), the sample tubes are forward-flushed with carrier gas to reduce the water-loading in the tubes. The tubes are then heated with a controlled temperature ramp to 300 °C in 60 seconds to transfer analyte to narrow-bore focusing traps (Markes International U-T15ATA-2S) held at 20 °C, using low flow-rate carrier gas (typically 2 sccm). The analyte is held on the focus trap until flash-heated and injected upon the respective separation column, for separation and detection.

Sample tubes and the sodium sulfite used in the oxidant trap must be changed routinely to maintain quantitative instrument response. For the Dallas FS campaign, sample tubes will be replaced every 4th day, to maintain <200 samples collected per tube. Quartz tubes packed with sodium sulfite will be replaced every 2nd day.

The TDPC-GC-EI-TOF is operated in three modes: ambient sampling, calibration mode and zero mode. The calibration and zero modes enable internal solenoid valves to overflow the GC inlet with a mixture of calibrant gas and zero gas, or just zero gas, respectively.

The GC system operates on a 20-hour sequence, with 18 hours of ambient sampling (2 samples / hr) followed by a single zero sample, a single cal sample and then two zero samples. This provides 90% data coverage over a 10-hour sampling period. Within each individual sample period, the GC collects sample gas for 10-minutes of the 30-minute analytical cycle.

The calibrant used for this campaign is a gas cylinder purchased from Apel-Riemer Environmental Inc, with a mixture of 19 VOCs diluted to nominal 1 ppm in nitrogen (with one component nominal 100 ppb due to low volatility). The mixing ratios of the analytes in the gas cylinder are certified by the vendor prior to delivery, with accuracy ±5% for all species. The GC flows this calibrant gas continuously at nominally 0.5 sccm via critical orifice and is occasionally directed to the GC inlet (see above). This flow rate is controlled by the gas cylinder regulator pressure and will be checked daily via bubble flow meter.

The TPDC-GC-EI-TOF system records temperatures, flows and pressures relevant to the sample collection and chromatographic analysis. The following parameters should be maintained throughout the campaign:

Sample flow rate = 100[†] sccm (± 1 sccm)
Sample tube temperature = 20 (± 1) °C during sample collection
Focus trap temperature = 20 (± 1) °C during sample focusing

[†]*Sample flow rate may be adjusted during ambient sampling in rare instances, to accommodate exceptionally high or low VOC mixing ratio (e.g. near-source plume measurement). In these cases, flow rate is controlled ± 1 sccm.*

6. QUALITY METRICS (QA/QC CHECKS)

6.1 Quality control checks

QC metrics are listed below:

The QC checks used in the field to assess the QA Objectives for this mission are tabulated in three tables. They have been divided into the following categories: a) core gas phase measurements, b) core particulate measurements and c) truck infrastructure data and additional measurements including VOCUS and GC-EI-ToF-MS .

The core gas phase measurement assessment notes are tabulated in Table 6-1a.

The core particulate measurement assessment notes are tabulated in Table 6-1b.

The truck infrastructure measurement and additional measurement assessment notes are tabulated in Table 6-1c.

Table 6.1a Procedures to Assess QA Objectives for Core Gas Phase Measurements

Measurement Parameter	Analysis Method	Assessment Method
Carbon Dioxide	Nondispersive Infrared (IR)	Flow check [1] Span Checks/Calibration at least twice during campaign Zero checks every 15 minutes
Ozone	Ultraviolet (UV) Absorption	Zero checks every 15 mins with Ultra Zero Air (UZA). Instrument calibrated in the laboratory pre- campaign using Ecotech Serinus Cal 3000 (See Appendix 6)
CO, N_2O, CH_4, C_2H_6; HCN; HCHO	TILDAS	See Table 6-1a(b) for TILDAS assessment procedures Calibrations described in Appendix 2 at least twice during campaign
NOx, NO_2	Cavity Enhanced Phase Shift (CAPS), with or without ozonator	Regular Zero checks (15 mins) with NOx-free air. Internal zeroes (scrubber-based); NO_2 span check performed in-field, at least twice. CAPS flow check described in Table Note[1]

Table Notes

[1] Sample Flow Rates Designated with this note entry are set using critical apertures that are protected by a high surface area particle filter. The aperture is chosen according to its size designation; however all flow rates are measured using a certified mass flow meter to quantify the actual flow rate. Note that the total flow where multiple instruments are joined to the same sample trunk line is also measured. The small disparities (<10%) between the measured total and sum of the Individual flow are due to small pressure drop along the truck sample line. Whenever possible, the calibrations, zeros or instrument span checks are all performed at the inlet tip to ensure the instrument operating pressure and flows are as similar as possible. None of the instruments used in the truck show a systematic dependence on the flow rate and thus, the flow checks are generally performed during the common inlet synthesis. The total flow rate is checked semi-daily along with the examination of the common time response to 'zero' gas overblow. Only if there is an inconsistency or a change of the internal plumbing are the individual instrument flows re-measured.

The 2B Tech ozone monitor will be calibrated once before and once after the field campaign. No calibrations will be done during the campaign, but automated ozone-free air deliveries (ultra-zero air) will be done throughout (see Section 4.2). The calibration is performed using an Ecotech Serinus Cal 3000, which generates ozone and controls output on the fly based on photometer output. Calibrated concentrations can be generated in the range of 3-3000 ppm. The calibration of the Ecotech Serinus Cal 3000 photometer is actively maintained, making it a Level-3 transfer standard. The ozone monitor will subsample the output of the Ecotech unit, allowing for calibrations across the range of O_3 concentrations that are measurable by the instrument: 2 to 250 ppb. Calibration factors will be interpolated between the pre- and post-campaign values over the course of the measurements.

Further details can be found in Appendix 6: "Ecotech Serinus Cal 3000 Manual".

TILDAS instrument assessments will consist of a routine instrument check (aka "Status Check"). All parameters except for flow rate, ultra-zero air (UZA) tank status, and filter cleanliness are accessible remotely. Even flow rate and filter status can be inferred based on cell pressure. More detailed description of the status check procedures is available in Appendix 7. TILDAS Hardware Manual.

Table 6.1a(b). TILDAS Monitor Status Check Steps, Acceptance Criteria and Corrective Action

Status Check Step	Acceptance Criteria	Corrective Action
Confirm Stream Mode is active	Stream Mode Active	Activate Stream Mode and frequency lock.
Check the laser temperature and laser current	Within 5% of expected value shown in notes.txt file	Load old .con file or manually adjust laser settings
Check the light level	Within 20 % of value on first day of field campaign	Assess noise performance per species. If warranted, perform laser alignment
Load and inspect your data	Data is complete. Mixing ratios are not negative or unphysically high. Mixing ratios are not correlated to system conditions. Noise meets specification of 1-sigma 1-second noise (varies per species. 10-200 ppt. See Table Note)	Negative mixing ratios may indicate insufficient or empty UZA tank – change tank. Assess light level and instrument alignment. Inspect and adjust spectral fit.
Check the gas pressure in the sample cell	Within 0.1 Torr of setpoint	Enable pressure lock. Check inlet/filter for clogs. Check filter cleanliness. Change filter and clear inlet if required, following manual procedures.
Check the sample flow rate	Total inlet flow is as expected.	Check sample pressure. Check inlet/filter for clogs. Re-set flow rate using flow meter and ensure complete overblow during UZA autobackgrounds.
Check the temperature of the sample cell	Similar to ambient and/or trailer temperature	Check trailer climate control.
Check the quality of the spectral fit	Blue fit line matches green measured data. Large tuning rate problems may change effective calibration factor.	Load old con file. Check that frequency lock is active. Adjust tuning rate following manual procedures. Adjust fit parameters.
Check the particle filter	Not clogged. Not visibly dirty (grey)	Change filter, following shutdown procedures to safely vent cell.

Status Check Step	Acceptance Criteria	Corrective Action
Check the liquid level of the chiller	Liquid level is visible. Chiller does not read “tank level low”	Check for coolant leaks. Add Koolance chiller fluid to fill-line.
Confirm that proper Toggle controls are active	WD, ASS, FLK4, are active (purple). RS *may* be active. ABG is active for all TILDAS except CO/N_2O	Click button to toggle.
Confirm all required schedules and scripts are activated	Schedules unlikely, but possible. To be determined during instrument install.	Enable checkboxes.

Table Note: The instrument noise is assessed by way of an Allan-Werle variance plot [*Werle*, 2011]. This can be generated on the instrument computer during remote check-ins. An acceptable performance metric during the field campaign will be a noise less than or equal to the specified instrument noise on the relevant product sheet (https://www.aerodyne.com/product/laser-trace-gas-and-isotope-analyzers/, also see appendices) For HCN, an acceptable noise will be 80 ppt for HCN.

Table 6.1b Procedures to Assess QA Objectives involving Particulate Measurement

Measurement Parameter	Analysis Method	Assessment Method
Particle Number Density	Optical Particle Count Condensation Particle Counter (CPC)	Flow Check 300 sccm or 1.5 slpm semi-daily high efficiency particulate air filter (HEPA) filter tozero time response comparison with PM CO_2 (Licor 6262b or 820) as overallperformance check
Black Carbon, Organics, Nitrate, Sulfate, Ammonia, Chloride	SP-AMS/AMS	Flow rate checked continuously by pressure and instrument air beam signal. Ion Signal to mass loading performed with classified ammonium nitrate aerosol (*nitrate equivalent loading*); Black carbon detection sensitivity (ionization efficiency) determined using CaboJet 300.

Table 6.1c Procedures to Assess QA objective for Additional Measurements

Measurement Parameter	Analysis Method	Assessment Method
Mass to charge ratios in the PTR-MS	Sample reaction with proton hydrates	Hourly dedicated sampling of the VOC free air with matched humidity. Daily calibration using standards to determine instrument response.
Carbon Containing Species	Gas Chromatogram with Mass Spectrometer Detector	Daily measurements of VOC free air with matched humidity. Daily calibration standards to track retention times. Pre-campaign determination of the mV*s/g carbon using three different standard tanks. In-field checks of the response per ppmC are done with the calibration chromatograms
Wind Speed and Direction	RM Young or Airmar sonic anemometer	The anemometer direction is checked against a coordinated manual fan blowing on the anemometer along the four quadrants (ahead, driver, passenger, rear). Wind speed calibration is compared by looking at the GPS velocity signal during a mobile condition with light ambient wind.
Position	Global Position System (GPS)	Examining the output from the GPS compared to an online source such as google maps verifies the function. All mobile ground tracks are mapped into the universal transverse Mercator (UTM) coordinate space to put traces onto a georeferenced image of the roadway, terrain, facility boundaries

6.2 QA Objectives and Acceptance Criteria

The data quality indicator goals for accuracy, precision and completeness for this project are listed in Table 6-2. *At the time of this draft, the instrument manifest is not finalized. The noted precisions will be revised based on the pre-deployment precisions of the specific instrument chassis and wavelength selections. The values cited here convey the approximate precision targets.*

During the campaign, any failure of the instrumentation to meet the data quality indicator (DQI) goals will be reported to Ed Fortner, who will be responsible for informing Vince Torres. Data collected during periods in non-attainment with DQI goals will be flagged as questionable, but not necessarily considered invalid. Corrective action will be taken depending on the nature of the problem encountered.

Table 6.2 QA Objectives and Acceptance Criteria

Measure-ment Parameter	Analysis Method	Assessment	Criteria Accuracy	Comp-letenes	Precision	Corrective Action Given Failure to meet Criteria
CO_2 Carbon diox-ide Licor 6262 (a)	Nondispersive Infrared Sensor (NDIR)	Flow rate measurement Zero check Span Check	Zero Check: ±5 ppmv from zero Span Check: ±3 ppmv of the travel standard tank	90%	130 ppbv at 1s	Flow rate problems, check pumping, check filter Zero problems, check other instruments (is sample line being overblown?); Check internal offset in instrument against lab notebook value Span problems, check sample overblow. Re-calibrate instrument using zero-air and span tank.
Ozone	UV Absorption	Zero Check Intercompare with TCEQ site	Zero Check	90 %	2 ppbv for 0.5 Hz data	Flow rate problems: check pumping, check filter. Zero problems: check other instruments (is sample line being overblown?) Span problems: check sample overblow, leverage reading against other instruments or comparison sites. Note in-field response factor, to be later compared with calibration factor calculated using zero-air and calibration source. Intercomparison with TCEQ site(s): Check zero offset, check calibration values. Determine whether another site can be used for a second intercomparison.
CO, N_2O, CH_4, C_2H_6, HCHO, HCOOH, HCN, C_2H_2	TILDAS	Flow Rate Measurement Zero measurement check Span check	Zero Check: Performance meets or exceeds product specification Span Check: Cal Standard is within tank uncertainty (1-5%)	90%	10 - 200 pptv at 1s (see product specificiatio n sheets) 80 ppt for HCN	See Table 6-1a(b), TILDAS Status Check Procedures
NO_2, NOx	CAPS	Consistent zero value during regular overblow. Span Check with NO_2	Within 10% of previous span check	90%	50-100 pptv at 5-s	Flow problems, check pumping, check inlet line Span problems: check sample overblow. Re-calibrate instrument ensuring NO_2 regulator is well-purged. Noise performance problems: Assess cell cleanliness

PTR-MS all	Reaction with Proton hydrates and classified by mass to charge ratio (parent and daughter ions)	Reagent ion count Ion molecule region pressure Flow rate to instrument	Response Factors should be within 15% of the running instrument performance	85%	Typically 1 ppbv at 1Hz, depends on specific compound	Flow, reagent ion and pressure problem are corrected using procedure described in the PTR-MS manual
GC-EI-ToF all	Preconcentration via adsorbent tube, separation by gas chromatography and detection by electron-impact ionization and time-of-flight mass spectrometry.	Sample flow rate check Trap temperature check Single Ion Strength (SIS) measurement	Flow ± 5%; Temperatures ± 2.5 °C; SIS ± 0.1 mV-nSec	90%	Typically 1-10 pptv at 30 min, compound-specific	Flow: leak check of system, check pumping Temperature: check TDPC cooler, heater temperature sensors, temp controller cabling SIS: adjust detector voltage as needed
SP-AMS	PM focused with aerodynamic lens and 'concentrated' by differential pumping. PM vaporized with laser absorption. Gaseous PM constituents ionized with electron impact and classified by mass to charge ratio	Airbeam signal Flow rate Particle time of flight pressure regime	Calibration of Relative ionization efficiency . SP module laser power meets instrument operational value	80%	NA	Flow rate restored by cleaning the orifice. Calibration performance of collection efficiency and relative ionization efficiency evaluated. Laser re-aligned according to the established procedure in the manual.
Particle Number Density	CPC	Flow Check Daily zero checks	10% of specified flow rate either 300 sccm or 1.5 slpm zero much be less than 100 particles per cm^3	90%	N/A	Inlet pump is verified to be operational. If it fails, truck 'house' pumping can be used. Failure to Zero mandates instrument optics cleaning

[a] The in-field calibration check of NO, NO_2 and O_3 are performed using dilution of a tank standard containing CO and NO. The CO instrument is used to verify the measured flow rate of the standard and diluent because it is verified in the field using a 673 ppbv standard. The NO instrument is calibrated first. To this sample stream varying (and small) flows of concentrated O_3 are added. The NO_2 instrument response is verified against the NO instrument by computing quantitative difference between NO levels, with and without the added O_3. The resulting time series from the calibration procedure is analyzed for consistency among the signal level. Any discrepancies greater than 8% are investigated by checking the calibration protocol, the specific instrument operation and repeated to deduce the source of the disparity.

As required by this category of QAPP, the data quality manager, Tara Yacovitch, will perform a quality audit of 10% of the data. Days of data to be inspected will be randomly chosen from the measurement periods (e.g. 1 24-hour period from a 10-day total). Instrument performance is assessed based on noise during periods of stable ambient concentrations. Lacking such periods due to real variability in the atmosphere, tank air overblows will be sought out within the full dataset. Furthermore, those inspected datasets containing data from routine overblows with zero air will be inspected for problems in the zero levels (these are separate from zero checks, which usually occur prior to calibrations). Relevant notes taken in the field on instrument performance will be reviewed for the audited data, and the issues noted will be checked against the final QA/QC data to make sure they have been corrected, or the affected data excised. Finally, calibration results (which often include zero-checks) will be collected for the whole campaign, and the performance compared to the metrics noted above. 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 raw data, collected using the protocols described in Sections 5 and 6 will be processed with some initial quality assurance procedures to time align, remove the automatic and manually triggered zeros and store the calibration checks separate from the ambient sample data. A merge is produced combing the GPS data (typically using the UTM north and east coordinate system) with the measurement vectors.

7.2 Data validation procedures.

The data quality indicators in Table 6-1a, b and c are used as the primary validation sources. When the time series analysis of the DQI criteria do not flag problems and the time series vectors are consistent on multiple instruments the inlet is casually validated and all instruments on the manifold are reporting the respective outdoor sampled air. Thereafter, the calibration and performance checks for each instrument (Table 6-2) will be evaluated and data will be validated. *None of the methods used in this project are EPA standard protocol techniques. Each measurement will employ a calibration protocol needed to pass scientific peer-review.*

Verification and validation of the procedures used to collect and analyze data are critical to achieving the project objectives. Data validation for this study will be accomplished through a review of the quality control checks conducted daily for the instrumentation as

described in Table 6-2. This review will determine whether instrumentation had acceptable performance.

7.3 Data analysis.

For this study, data analysis after the simple processing steps describe above will include parallel time series and correlation analysis of the air pollutant measurements (following step 1) as well as geospatial and temporal analysis (following step 2 and/or step 3). These and other analyses may lead to further post-processing of data, dependent on project needs. Additional data used for interpretation will include regional meteorology data and other air pollutants measured at other TCEQ sites in the area.

7.3.1 Statistics and experimental uncertainties.

The uncertainty (accuracy) at the two sigma level of the various mixing ratio and particulate data is expected to be in the range of 5 to 15%. Each of the anticipated precisions (typically at 1-sigma) is noted in table 6-2. The systematic uncertainty at 95% confidence limits will be the combination of the method uncertainty and the uncertainty of the calibration standard used in-field, pre- and post- campaign. All errors will be accounted for and estimated.

7.4 Data storage requirements.

The digital data chain of custody is discussed in Section 6.6. The digital data storage requirements are modest by current standards. We anticipate a complete raw data footprint of ~ 150 GB. The quality assured measurement data and pre-process dataset to be used for analysis will be less than ~ 8 GB. The largest data source are the AMS, VOCUS and GC-EI-ToF high resolution data files and the QCL spectra in binary format. 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 Project 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: August 16th, 2022

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.

Table 8.1a Quarterly Report Due Dates:

Report	Period Covered	Due Date
Quarterly Report #1	August, September, October 2022	October 31, 2022
Quarterly Report #2	November, December 2022, January 2023	January 31, 2023
Quarterly Report #3	February, March, April 2023	April 30, 2023
Quarterly Report #4	May, June, July 2023	July 31, 2023

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.

Table 8.1b MTR Due Dates:

Report	Period Covered	Due Date
Technical Report #1	**Project Start - August 31, 2022**	**September 10, 2022**
Technical Report #2	**September 1 - 30, 2022**	**October 10, 2022**
Technical Report #3	**October 1 - 31, 2022**	**November 10, 2022**

Technical Report #4	**November 1 - 30, 2022**	**December 10, 2022**
Technical Report #5	**December 1 - 31, 2022**	**January 10, 2023**
Technical Report #6	**January 1 - 31, 2023**	**February 10, 2023**
Technical Report #7	**February 1 - 28, 2023**	**March 10, 2023**
Technical Report #8	**March 1 - 31, 2023**	**April 10, 2023**
Technical Report #9	**April 1 - 30, 2023**	**May 10, 2023**
Technical Report #10	**May 1 - 31, 2023**	**June 10, 2023**
Technical Report #11	**June 1 - 30, 2023**	**July 10, 2023**
Technical Report #12	**July 1 - 31, 2023**	**August 10, 2023**

DUE TO AQRP 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.

Table 8.1c FSR Due Dates:

Report	Period Covered	Due Date
FSR #1	Project Start - August 31, 2022	September 15, 2022
FSR #2	September 1 - 30, 2022	October 15, 2022
FSR #3	October 1 - 31, 2022	November 15, 2022
FSR #4	November 1 - 30, 2022	December 15, 2022
FSR #5	December 1 - 31, 2022	January 15, 2023
FSR #6	January 1 - 31, 2023	February 15, 2023
FSR #7	February 1 - 28, 2023	March 15, 2023
FSR #8	March 1 - 31, 2023	April 15, 2023

FSR #9	April 1 - 30, 2023	May 15, 2023
FSR #10	May 1 - 31, 2023	June 15, 2023
FSR #11	June 1 - 30, 2023	July 15, 2023
FSR #12	July 1 - 31, 2023	August 15, 2023
FSR #13	August 1 -31, 2023	September 15, 2023
FSR #14	Final FSR	October 15, 2023

DUE TO GRANT MANAGER

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: August 1, 2023

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: August 31, 2023

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, 2023). 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. All data will be retained by ARI for a minimum of three years following project completion.

AQRP Workshop: A representative from the project will present at the AQRP Workshop in the first half of August 2023.

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.

8.2 Expected final product(s) prepared for the project.

We expect that the final products resulting from this project will be the final project report and at least one journal article that describes the most noteworthy results from this project. The most likely target journals are *Environmental Chemistry and Technology*, *Atmospheric Chemistry and Physics*, and *Journal of the Air and Waste Management Association*. These will be prepared and submitted following the Publication/Publicity Guidelines included in Attachment G of the Subaward.

9. REFERENCES

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