A. Project Management A1. Title and Approval Sheet

U.S. Environmental Protection Agency Office of Research and Development Center for Environmental Measurement and Modeling

Air Methods and Characterization Division

Source and Fine Scale Branch and Combustion Source Branch

Quality Assurance Project Plan

Title: Verona Ethylene Oxide Project

QA Category: \square A \square B

ORD National Program Project/Task ID: ACE.401.2.1

QAPP was Developed: 🛛 Intramurally 🖄 Extramurally: Jacobs Technology

QAPP Accessibility: QAPPs will be made internally accessible via the <u>ORD QAPP intranet site</u> upon final approval *unless the following statement is selected*.

□ I do NOT want this QAPP internally shared and accessible on the ORD intranet site.

Project Type(s) (check all that apply):

Environmental Measurements
Environmental Technology
Decision Support Tool
Existing Data
Informatics
Geospatial
Method Development
Model Application
Model Development
Software and Data Management
Remote Sensing
Technical Assessment
Other

Disclaimer: This quality assurance project plan (QAPP) is an internal project working group document intended for use by the U.S EPA, Office of Research and Development (ORD), Center for Emission Measurements and Modeling (CEMM), Air Methods and Characterization Division (AMCD), Source and Fine Scale Branch (SFSB), EPA Region 7 (R7) Air and Radiation Division (ARD), R7 Laboratory Services and Applied Science Division (LSASD), and Jacobs Technology under contract 68HERC20D0018, Task Order 68HERC20F0306 (TOP-306), for the execution of a field effort in Verona, Missouri (MO). This is a quality assurance (QA) Category A research project and the procedures utilized and data generated are not intended for regulatory enforcement or compliance purposes. Mention of brand names or vendors does not constitute an endorsement of products or services by the EPA. This QAPP was prepared by EPA with contributions from Jacobs Technology.

QAPP Approval Page		QA Tracking # J-AMCD Date: Ser	-0033761-QP-1-1 otember 30, 2022
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A3.1. Acronyms and Common Terms

Table A3.1: Acronyms and common terms used this QAPP

Term	Definition
3D Sonic	three-dimensional sonic anemometer wind measurement system
ADQs	audits of data quality
AMCD	Air Methods and Characterization Division (EPA/ORD/CEMM)
APSB	Air Permitting and Standards Branch (EPA/R7/ARD)
AQPB	Air Quality Planning Branch (EPA/R7/ARD)
ARD	Air and Radiation Division (EPA/R7)
Cal-check	Picarro calibration check
CCV	continuing calibration verification
CEMM	Center for Emission Measurement and Modeling
CH ₄	methane
CO ₂	carbon dioxide
COC	chain of custody
COR	contracting officer representative

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Term	Definition
CGS	canister grab sample
CRDS	cavity ringdown spectroscopy
Deg C	unit of temperature, degrees Celsius (also °C)
DQI	data quality indicator
DS	dynamic spike
EPA	U.S. Environmental Protection Agency
ERG	Eastern Research Group
EtO	ethylene oxide
eV	electron Volt
FSB	Field Services Branch (EPA/R7/LSASD)
G1-GX	Stands for GMAP stationary observation site #1 (G1), G2, G3, etc.
GC/FID	gas chromatograph / flame ionization detector
GC/MS	gas chromatograph / mass spectrometer
GMAP	geospatial measurement of air pollution
GPS	global positioning system
GS	GMAP survey
H ₂ O	water vapor
HCL	hydrogen chloride
Hz	Hertz
ID	identification (as in sample ID)
IRIS	Integrated Risk Information System
LDAR	leak detection and repair
LPM	litter per minute
LSASD	Laboratory Services and Applied Science Division (EPA/R7)
MDL	method detection limit
MEMS	mobile emissions measurement software (GMAP)
MT	mobile test
MTD	mobile test data form (Appendix E)
MTQ2	mobile test QA form 2 (Appendix D)
mV	millivolt
MFC	mass flow controller
NGEM	next generation emission measurement
OIA	Office of Intergovernmental Affairs
ORA	Office of Regional Administrator
ORD	Office of Research and Development (EPA)
ORISE	Oak Ridge Institute Science and Education
OTM	Other Test Method
PID	photoionization detector
ppb	part per billion, always meaning "by volume" in this QAPP
PN	part number
ppm	part per million, always meaning "by volume" in this QAPP
ppt	part per trillion, always meaning "by volume" in this QAPP
PRT	peak retention time
Press	atmospheric pressure (typically mbar)
QA	quality assurance
QA form 1	QA form 1 (Appendix C) used for MT and FT gas standard challenge tests
QAM	Quality Assurance Manager
QC	quality control
QAPP	quality assurance project plan

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Term	Definition
R7	EPA Region 7
RARE	Regional Applied Research Effort
RPD	relative percent difference
RSD	relative standard deviation
RT	retention time
S1, S2, S3	24-hour canister Site1, Site2, and Site3
SA	standard addition
Sec	second
SEE	Senior Environmental Executive
SFSB	Source and Fine Scale Branch (EPA ORD/CEMM/AMCD)
SIM	selected ion monitoring
SOP	standard operating procedure
SPod	sensor pod
TBD	to be determined
ТО	task order
Picarro	Picarro CRDS
Temp	temperature of the air measured by a Picarro sensor in Deg C
U, V, W	three axis wind speed outputs from 3D sonic anemometer
VOC	volatile organic compound
WS	wind speed (typically m/s or mph)
WD	wind direction (degrees from north)

A4. Project Organization

Table A4.1: Project roles and primary responsibilities

Project Personnel	Role	Responsibilities
Eben Thoma	ORD/CEMM/AMCD Project Lead, TOCOR, ORISE Mentor, Documentation Steward	Overall project management, preparation and approval of QAPP, Jacobs Technology task order contracting officer's representative (TOCOR), ORISE mentor for M. MacDonald, ORD documentation Steward, contributes to interpretation of data and reporting.
Alireza Gitipour	ORD/CEMM/AMCD Field Lead	ORD/CEMM project field lead, technical expert for Picarro 2920, responsible for project execution in the field, training of personnel, interpretation of data, reporting, review and approval of QAPP.
Ingrid George	ORD/CEMM/AMCD VOC Lead	ORD/CEMM VOC measurements lead contributing to project planning for VOC sampling and analysis, responsible for CGS preparation and analysis, training of lab and field personnel on canister sampling/analysis, interpretation of data and reporting, review and approval of QAPP.
Megan MacDonald	Oak Ridge Science and Engineering (ORISE) researcher	Researcher potentially contributing to data analysis for this project
Lillian Alston	Senior Environmental Executive (SEE) scientist	Research scientist providing laboratory support in canister preparation and analysis
Michael Hays	ORD/CEMM/AMCD/SFSB Branch Chief	First line management oversight, review and approval of QAPP
Laura Nessley	ORD/CEMM/AMCD Quality Assurance Manager	EPA/ORD QAM Lead and Signatory, review and approval of QAPP and data produced, performs QA audit of data quality
Lara Phelps	ORD/CEMM/AMCD Division Director	Second line management oversight, review and approval of QAPP

Project Personnel	Role	Responsibilities	
Michael F. Davis	EPA R7 Co-lead	Contributes to project planning and interpretation of data and reporting, R7 communications, review and approval of QAPP.	
Alexander Edwards	EPA R7 Co-lead	Contributes to project planning and the execution of the field study, interpretation of data and reporting, data analysis, review and approval of QAPP, R7 documentation steward	
Adam Zachary	EPA R7 Field Team	Contributes to the execution of the field study	
Leland Grooms	EPA R7 Field Team	Contributes to the execution of the field study	
Andrew Hawkins	EPA R7/ARD Contributor	Contributes to project planning and interpretation of data, summary, reporting, and communications, review and approval of QAPP	
Amy Algoe- Eakin	EPA R7/ARD Branch Chief	Contributes to project planning, execution, data analysis and interpretation, summary and reporting, communications, review and approval of QAPP	
Michael Jay	R7/LSASD Deputy Director	R7 management oversight, review and approval of QAPP	
Jerome Gilberry	Jacobs Task Order (TO) Lead	Responsible for project execution as per QAPP and TO technical direction, trains personnel, and development of the safety plan. Responsible for managing subcontracts and overall field team lead	
Stella McDonald	Jacobs Technical Lead	Technical assistance in project planning and execution, management of 24-hr canister effort and Jacobs supplied data	
Russel Logan	Jacobs Technical Support	Preparation of equipment, transportation to the field, set up of sites, execution of initial field trials	
Stacy Cross	Jacobs QA Officer	Review and approval of QAPP and data produced by Jacobs. Auditing of procedures and training certification	
Jerry Revis	Jacobs Health and Safety Officer	Responsible for safe operations of Jacobs personnel	
Julie Swift	Eastern Research Group (ERG) Technical Director	ERG) Responsible for preparation, shipping, and analysis of 24-hr canister samples, and Review and approval of QAPP	
Donna Tedder	ERG QA Coordinator	Responsible for QA of 24-hr canister samples	

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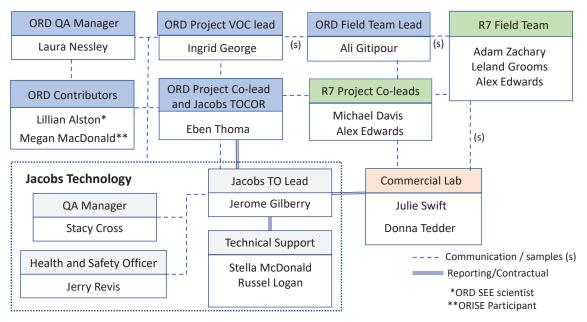


Figure A4.1: Organizational chart for primary project personnel

A5. Problem Definition and Background

Ethylene oxide (EtO, C₂H₄O, CAS #75-21-8) is a hazardous air pollutant¹⁻³ used by chemical facilities as a feedstock and by commercial operations as disinfectant/sterilant. Each year, the BCP Ingredients Inc. chemical facility (BCP), located at 299 Extension St, Verona, MO 65769, processes >100 tank railcars of EtO in the repackaging and production of various industrial and commercial products.

This QAPP describes a limited scope field effort conducted by EPA R7 and EPA ORD CEMM, with the support of Jacobs Technology and ERG, that aims to improve understanding of EtO concentrations in the City of Verona, MO located adjacent to BCP. One motivation for this field effort is concern by the community of Verona regarding potential exposure to EtO. This field effort is an observational study with a primary goal to develop initial information on EtO concentrations near the facility using best available technologies and laboratory analysis methods.

The study will use two independent EtO monitoring technologies to characterize the concentration and geospatial distribution of EtO within the community. This field effort centers on the acquisition and analysis of 24-hr time integrated evacuated canister samples at multiple sites near BCP and in Verona. Canister sampling will occur approximately every three days for a three-month period (nominally 10/3/2022 through 12/31/22). The changeout of the completed (also called acquired) 24-hr canister samples with newly prepared canisters will be performed each week by an EPA R7 field team deployed from Kansas City, KS. As part of the canister changeout visits, the field team will generate several hours of EtO concentration data using a mobile system and acquire a limited number of short-duration canister grab samples (CGS) for comparison purposes. The field effort also includes acquisition of meteorological data that will help provide context to the EtO concentration measurements.

This field effort is not designed to generate continuous emissions monitoring or comprehensive exposure information. This project is not designed to produce data for enforcement or compliance purposes. Based on the findings of this field effort, the emerging availability of new high sensitivity EtO monitoring technologies, and available resources, additional field projects may be pursued in 2023.

A6. Project/Task Description

This project consists of three phases: (1) planning and preparation, (2) field effort execution, and (3) report generation phases, with the target timing for these phases described in the Table A6.1. This field effort consists of four measurement tasks:

- 24-hr canister EtO measurements at three sites
- Supporting GMAP survey real-time EtO and other measurements
- Supporting CGS EtO and other VOC measurements
- Supporting meteorological measurements

2022	2022 2023									
Aug.	Sept.	Oct.	Nov.	Dec.	Jan.	Feb.	March	April	Мау	June
	QAPP development/approval, equipment preparation, site set up, and safety planning									
	Field effort execution and regular updates of QA-screened draft data									
	Data analysis and final report generation (draft report for external peer review)									

Table A6.1: Target project timing through June 2023

24-hr canisters:

This field project will deploy 24-hr whole air canisters fitted with automatic acquisition timers at three sites near BCP in Verona, MO, called Site 1 (S1), Site 2 (S2), and Site 3 (S3). The locations of S1, S2, and S3 are indicated in Figures A6.1-A6.3 as yellow squares. Canister acquisitions will occur simultaneously at S1, S2, and S3 approximately every three days using a modified 1 in 3-day sampling schedule. The acquired 24-hr canisters will be picked up and replaced with freshly prepared canisters once each week (on average). The acquired 24-hr canisters will be shipped to ERG for EtO analysis by Gas Chromatography/Mass Spectrometry (GC/MS) following a modified version of EPA Method TO-15/TO-15A.⁴⁻⁸ It is a goal to achieve a TO-15/TO-15A EtO method detection limit (MDL) of <50 pptv for valid 24-hr samples. The project team will work to understand and document any sampling or analysis issues that result in invalid or higher uncertainty data and to produce a 24-hr canister dataset with quality flags for incorporation into the overall project dataset.



Figure A6.1: Overhead view showing BCP facility, 24-hr canister sites (yellow squares at S1, S2, and S3) and example GMAP stationary sites (red circles, G1 – G12).



Figure A6.2: Expanded overhead view showing BCP facility, 24-hr canister sites (yellow squares at S1, S2, and S3) and several example GMAP stationary sites.



Figure A6.3: Expanded view with example mobile routes added (indicated by red arrows).

Supporting Measurements:

During the weekly visits to Verona for 24-hr canister changeout, the field team will conduct several hours (typically) of supporting mobile and stationary EtO concentration measurements using EPA Geospatial Measurement of Air Pollution (GMAP) OTM 33.⁹ The mobile and stationary GMAP surveys will use a Picarro model G2920 (Picarro, Sunnyvale, CA), cavity ringdown spectroscopy (CRDS) EtO measurement system.^{10,11} With knowledge of wind conditions during the time of the GMAP survey, the field team will position the GMAP vehicle at a subset of safe and legally accessible stationary measurement locations [e.g., Figure A6.1 red circles labeled GMAP 1 (G1) through GMAP 11 (G12)]. Mobile measurements on public roadway driving routes near BCP (e.g., red arrows of Figure A6.3) will also be conducted. The goals of the GMAP surveys are to achieve EtO measurement MDLs of <2.0 ppbv at 1 Hz (mobile and stationary mode) and to continuously acquire valid time synchronized wind and GPS GMAP survey data. The typical MDL for this this system ~1.2 ppbv. As with any remote measurement approach, the observational effectiveness of time-resolved downwind sampling is a function of meteorological conditions, system MDLs, and emission source factors.

During the stationary portion of the GMAP surveys, the vehicle engine will be turned off and ~30-second duration CGS acquisitions will be executed with laboratory analysis of EtO and other VOCs conducted by the EPA/ORD/CEMM VOC Laboratory following a modified TO-15/TO-15A. The goal of supporting CGS acquisitions is to improve knowledge of instantaneous upwind and downwind concentrations of EtO and other VOCs near BCP. The CGS samples may be acquired in locations of elevated EtO concentration conditions using real-time data from the GMAP to position the CGS acquisition within an apparent advected emission plume. The CGS samples provide complementary measurements to the 24-hr canisters. The CGS samples also provide QA comparisons for EtO, and other compounds to the real-time data provided by the GMAP measurements that cannot be accomplished with the 24-hr canisters. A project goal is to achieve TO-15/TO-15A EtO MDLs of <100 pptv for valid CGS samples.

Supporting meteorological and non-speciated (non-EtO) VOC fenceline sensor measurements will be made continuously at S1. Supporting meteorological data will also be acquired periodically during GMAP vehicle mobile and stationary sampling to help provide context in the interpretation of other data

acquired. Supporting meteorological data will also be retrieved from the nearest airport location, the Monet Municipal Airport located 14.4 miles away from the following site:

<u>https://mesonet.agron.iastate.edu/request/download.phtml?network=MO ASOS</u>. The supporting meteorological and potentially the non-EtO VOC fenceline measurements will help the project team provide context to the EtO observations. For all supporting measurements, it is a goal of the project to identify and document any sampling artifacts or analysis issues that may occur that result in invalid or higher uncertainty data and to produce a supporting measurement dataset with quality flags for incorporation into the overall project dataset.

A7. Quality Objectives and Criteria for Measurement Data

This field project will generate the following four data types:

- 24-hr canister EtO measurements at three sites (Section A7.1)
- Supporting GMAP survey real-time EtO and other measurements (Section A.2)
- Supporting CGS EtO and other VOC measurements (Section A7.3)
- Supporting meteorological measurements (Section A7.4)

This field project will produce EtO and other VOC concentration mixing ratios expressed in ppbv, along with associated supporting mobile survey and meteorological data. The quality objectives and criteria to meet the goals of this project are based on accuracy, precision, and completeness metrics defined as:

<u>Accuracy</u>: the accuracy of measurement parameters is determined by comparing a measured value to a known standard, assessed in terms of percent bias using Equation B-1:

$$\left[\left(\frac{\text{Measurement}}{\text{Standard}}\right) - 1\right] \times 100 \quad \% \text{ Bias} \tag{B-1}$$

The percent bias measurements are expected to fall within the tolerances stated in subsequent sections pertaining to each approach where applicable.

<u>Precision</u>: Precision is evaluated by making replicate measurements of the same parameter and assessing the variations of the results. Precision is assessed in terms of relative percent difference (RPD), or relative standard deviation (RSD). The replicate measurement points will be one specific parameter value within the measurement range and replicate measurements are expected to fall within the tolerances described for each approach.

<u>Completeness</u>: This parameter is expressed as a percentage of the number of valid measurements compared to the total number of measurements taken.

Unless otherwise stated, the general accuracy and comparative precision goals for the project are ± 20 % for values above MDL with a data completeness value of > 80%.

A7.1 24-hr Canisters:

The quality objectives and criteria associated with 24-hr canister acquisitions and analysis are as follows:

- Accuracy: the laboratory continuing calibration verifications (CCVs) will be used to assess analytical accuracy of canister analysis with a quality objective criterion of ≤30% from expected concentrations from a known standard
- Precision: achieve collocated canister comparison precision of ≤25% RPD when both measurements are >5 times the MDL (e.g., data greater than analytical quantitation limit)

• Completeness: produce > 22 days of simultaneous 24-hr canister sample data at S1, S2, and S3 over with > 80% data completeness over the 3-month deployment

A7.2 GMAP Surveys:

The target quality objectives and criteria for the GMAP surveys are:

- Accuracy: EtO measurement accuracy within ± 20% of calibration gas checks
- Precision: achieve collocated and time synchronized Picarro to CGS comparison precision of ≤30% (RPD) when both measurements are >5 times the MDL (e.g., data greater than analytical quantitation limit)
- Completeness: >36 hours of GMAP Surveys with >80% data completeness during the 3-month deployment

A7.3 CGS Acquisition and Analysis:

. The quality objectives and criteria associated with CGS canister acquisitions and analysis are as follows:

- Accuracy: the continuing calibration verifications (CCVs) will be used to assess analytical accuracy of canister analysis with a quality objective criterion of ≤30% from expected concentrations from a known standard
- Precision: achieve collocated and time synchronized Picarro to CGS comparison precision of \leq 30% (RPD) when both measurements are >5 times the MDL (e.g., data greater than analytical quantitation limit)
- Completeness: Acquire >50 CGS grab samples with >80% data completeness during the 3-month deployment

A7.4 Supporting Meteorological and VOC Measurements:

The target quality objectives and measurement criteria supporting meteorological data include:

- Accuracy (meteorological data): The 3D sonic anemometers were calibrated in the U.S. EPA wind tunnel on 9/12/22. The wind speed and wind direction of the SPod fenceline sensors will be compared to the collocated 3D sonics as an accuracy transfer standard with expectation of agreement to within < 20% RPD in wind speed and +/- 15 degrees in wind direction for 5-minute averages with both units showing wind speeds means above 1 m/s for select open-fetch directions at S1. Similarly, the GMAP vehicle will be sited at SI for the same comparison of mobile meteorological gear as part of daily QA checks. SPod and GMAP temperature, atmospheric pressure, relative humidity (as available) will also be compared to each other and Airport data for reasonableness with expectation of agreement to within < 20% RPD.
- Accuracy (non-EtO VOC): SPod calibration check to within +/- 20% of isobutylene gas standard and background correct baseline = 0 ppbv +/- 50 ppbv
- Precision (wind): collocated unit to unit < 20% RPD in wind speed and +/- 15 degrees in wind direction for 5-minute averages with both units showing wind speeds means above 1 m/s for select open-fetch directions at S1
- Precision (non-EtO VOC): background corrected theoretical MDL (VOC baseline stability) < 100 ppbv under "no source" conditions.

• Completeness: Time-resolved local temperature, pressure, relative humidity, wind speed, wind direction, and SPod VOC data >80% data completeness

A8. Special Training/Certifications

General field safety training with emphasis on the hazards associated with mobile measurements and field activities conducted near roadways and general laboratory safety training (Method TO-15/TO-15A) are required for all personnel but are outside the scope of this QAPP. This project includes task-specific field sampling and laboratory analysis procedures. Prior to executing a specific field or laboratory activity, personnel must be appropriately trained, and this training must be documented. Appendix A identifies training leads for this project and a form for QAPP-specific training documentation for field activities. Procedures relevant to this project are:

- <u>24-hr canister and CGS preparation and analysis</u>: Laboratory-specific training and experience with laboratory work practices, documentation, and standard operating procedures (SOPs) for canister cleaning and analysis performed by method TO-15/TO-15A.⁴⁻⁸
- <u>24-hr canister deployment including timer set up, COC documentation, and shipping/receiving:</u> Documented training/experience using procedures summarized in Appendix B and knowledge of manufacturer equipment manuals and procedures described therein.^{12,13}
- <u>GMAP survey operation</u>: Documented training/experience using procedures summarized in this QAPP and referenced materials, with QA and data forms contained in Appendix C.^{9-11,14-17}
- <u>CGS acquisition including COC documentation and shipping/receiving</u>: Documented training/experience using procedures summarized in this QAPP and Appendix D.
- <u>3-D sonic anemometer set up and operation</u>: Documented training/experience using procedures summarized in Appendix E and knowledge of equipment manuals referenced therein.^{17,18}
- <u>SPod operation</u>: Documented training/experience using procedures of Appendix F which reference SPod SOP ID: J-AMCD-SFSB-SOP-4380-2 and associated information.¹⁹⁻²¹

A9. Documents and Records

The following records and documentation will be generated for this project:

- 1. EPA and Jacobs Technology field and safety plans (not covered in this QAPP)
- 2. Personnel training documentation (Appendix A)
- 3. 24-hr canister chain of custody (COC) forms
- 4. 24-hr canister summary record (Appendix B)
- 5. GMAP survey daily QA form (Appendix C, Table C1)
- 6. GMAP survey data acquisition form (Appendix C, Table C2)
- 7. CGS COC forms
- 8. CGS summary record (Appendix D)
- 9. 3D sonic anemometer QA form (Appendix E)
- 10. SPod QA forms SOP ID: J-AMCD-SFSB-SOP-4380-2
- 11. EPA Field Notebook (PDF copies)
- 12. Gas standard certifications
- 13. Equipment calibration records
- 14. GMAP survey system data files
- 15. Raw data files from Picarro G2920
- 16. Raw data files from 3D Sonic anemometer(s)

- 17. Raw data files from SPod(s)
- 18. Processed data files
- 19. Laboratory SOPs and other operational documentation
- 20. Laboratory data analyses, log sheets, and QA reports
- 21. Laboratory 24-hr canister analysis records
- 22. Laboratory CGS analysis records
- 23. Surveillance audit memos to the project file
- 24. GMAP vehicle records specifying which vehicle was used for the survey
- 25. Possible information on BCP process operations (to be determined)

Approved electronic copies of this QAPP, related SOPs, and any associated audit reports, will be maintained in the ORD QA Track database to ensure data backup. E. Thoma (ORD), A. Edwards (R7), and S. McDonald (Jacobs) will be responsible for ensuring distribution of the current version of the QAPP within their respective organizations. These persons will ensure timely communications with all involved participants and will retain copies of all management reports, memoranda, and correspondence between research task personnel. Records will be maintained in accordance with EPA record schedule 1035a for records retention. Laboratory and field notebooks and other hard copy and electronic records will be retained by the generating organization where these operations are performed until the conclusion of the project. Project record files will be maintained by the documentation stewards E. Thoma (ORD) and A. Edwards (R7) and by the Jacobs technical lead (S. McDonald) where applicable.

B. DATA GENERATION AND ACQUISITION

B1. Experimental Design

The experimental design includes 24-hr canister measurements (Section B1.1), GMAP surveys (Section B1.2), with CGS acquisitions (Section B1.3), and supporting meteorological measurements (Section B1.4).

B1.1 24-hr Canisters:

The project team will deploy 24-hr canister sampling systems consisting of a Silonite[®] -coated CS1200ES sampler that controls sampling flow rate (Entech Instruments, Simi Valley CA, USA), Figure B1.2(a)] connected to Entech model TM12000 canister sampling timer that controls sampling start and end date/times,^{12,13}[Figure B1.2(b)]. Entech Silonite[®] coated 6 L stainless steel canisters [Figure B1.2 (c)] will be used for the 24-hr time-integrated sample collection. Further details on 24-hr canister system deployment/retrieval are contained in Appendix B.

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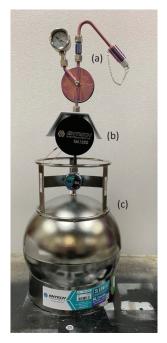


Figure B1.1: 24-hr canister systems (a) sampler, (b) timer, and (c) 6L canister

B1.2 GMAP Surveys:

GMAP mobile and stationary observations will be conducted from an EPA R7 fleet vehicle with an example of roof equipment position shown in Figure B1.2(a). The GMAP system is modular and can be moved to different vehicles. The vehicle shown is not the vehicle that will be used. A Picarro model G2920 (Picarro, Sunnyvale, CA) CRDS will provide ~1 Hz measurements of EtO [Figure B1.2(b)] sampling through unheated 6.4 mm outer diameter, 3.2 mm inner diameter high density polyethylene (HDPE) sampling line (50375K41, McMaster-Carr, Atlanta, GA, USA), 10 m in length (coiled up on roof). The air sample is drawn through the Picarro instrument via a Picarro A2000 external diaphragm pump. The G2920 has a manufacturer stated EtO measurement precision of 0.4 ppbv, defined as one standard deviation (1 σ) noise at the base time resolution of ~1 second per data point (~1 Hz). The G2920 has a stated EtO measurement range from zero to 2,000 ppbv. The G2920 also measures carbon dioxide (CO₂), methane (CH₄), and water vapor (H₂O), which are necessary for spectroscopic determination within the instrument but also provide useful data for QA and source diagnostic purposes.

Motion-corrected wind measurements and GPS data will be provided by an AirMAR®200WX Weatherstation® [AIRMAR Technology Corp., Milford, NH, Figure B1.2(c)] or a Hemisphere R100 [NavtechGPS, Alexandria, VA, Figure B1.2(d)], as a backup. A control computer (laptop) running a custom LabVIEW (National Instruments, Austin, TX, USA) data acquisition program [EPA Mobile Emissions Measurement Software (MEMS) version 6.2.1-1.7.0]¹¹ will record time-aligned data from all instruments at a 1 Hz rate. The MEMS system records only EtO, CO₂, and CH₄ from the Picarro and wind data, temperature, and pressure from the AirMar. During some stationary measurements, an 81000V 3D sonic anemometer [RM Young Co., Traverse City, MI, USA, Figure B1.2(e)] will be deployed to collect local wind data. The instruments and sampling pumps will be powered by multiple Yeti 1400X or 3000X battery supplies (Goal Zero, Bluffdale, UT).

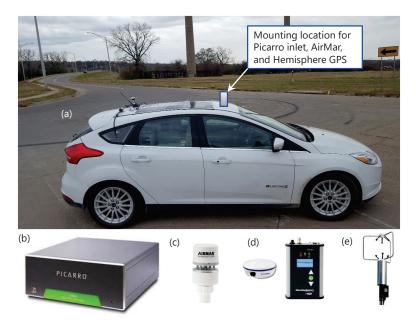


Figure B1.2: Overview of equipment used in the GMAP survey (not actual vehicle used)

The GMAP survey experiment design consists of two operational modes, mapping/transect surveys and stationary observations. Using knowledge of forecasted and real-time measured wind conditions, EtO concentrations, and potentially available and relevant BCP process operation information, the decision will be made by the field team lead to conduct GMAP mapping and/or transect surveys or stationary observations along selected routes and at selected positions (see default survey plan).

<u>Mapping and Transect Surveys</u>: The GMAP moves along a mapping route or drives back and forth on publicly accessible roadways (called transects) downwind or upwind of BCP to geospatially characterize EtO concentrations near the facility and/or demonstrate that concentrations over GMAP detection limitations are not present. Each mapping or transect survey will be saved as an individual MEMS data file. The data file will be saved initially on the MEMS control computer and then copied to the project dives.

<u>Stationary Observations</u>: Depending on conditions, one or more stationary observations may be conducted from the GMAP platform. For this measurement, the GMAP vehicle will remain parked, with the engine turned off, at a strategically selected location and will acquire data for a minimum of 15 minutes. The 10 m long HDPE sampling line, normally coiled-up and mounted to the roof of the GMAP vehicle may be moved to a temporary tripod that may also carry a 3D sonic anemometer that will be connected to and recorded by the MEMS system. Each 15-minute measurement will be saved in a separate MEMs data file. The data file will be saved initially on the MEMS control computer and then copied to the project dives.

The default GMAP survey plan will be executed only to the east of BCP as there are no nearby roadways to the west. In the below procedure, a "significant EtO detection" is defined as a period of elevated EtO concentrations that are easily noticed by the MEMS operator observing the real-time EtO data (multiple elevated data points). This would generally represent peak EtO plume concentrations > 10 ppbv. The default GMAP survey plan is as follows:

(1) Each field test day, the GMAP survey equipment will be prepared and QA-checked to ensure it is ready for operation before starting initial data collection. Information on GMAP operation will be

recorded in the GMAP survey QA and field data acquisition forms of Appendix C. After completion of daily QA checks, proceed to step (2)

- (2) Conduct an engine-off 15-minute stationary observation at S1 (note wind speed and direction)
- (3) Conduct a north to south transect survey on public roads closest to and east of BCP from S1 to southern most turn around location near 36°57'27.64"N 93°48'7.97"W (Figure A6.1 G6)
- (4) Conduct a south to north transect survey on public roads closest to and east of BCP from S1 location near at 36°57'27.64"N 93°48'7.97"W (Figure A6.1 G6) to S1
- (5) Evaluate wind speed and direction and EtO observations.

(5a) If an apparent EtO emission plume is encountered (a significant EtO detection), continue the transect evaluation and shorten travel path as required to fully capture plume. The optimal transect returns to baseline on both sides of the detected plume while maximizing GMAP survey efficiency (maximize number of plume assessments). Attempt position-optimized stationary observations and expanded route maps based on meteorological conditions and EtO observations. For example, move downwind in the same meteorological sector to attempt to characterize the plume physical extent. The field team lead (typically the MEMS operator) will make decisions on survey routes and stationary locations with primary goals (1) to maximize emission plume to unit spatial overlap, (2) assess the temporal constancy of the emission plume, and (3) assess the plume at distance away from BCP (if possible)

(5b) If wind conditions are not conducive to easterly transport and/or if no significant EtO detections are observed, go to Step (6) through Step (9) and return to (5a) optimized positions/routes on any significant EtO detection

- (6) Conduct a full route map of at least 3 parallel roadway segments
- (7) Conduct an engine-off stationary observation at S2
- (8) Conduct an engine-off full route map for at least three parallel roadway segments
- (9) Conduct a stationary observation at S3
- (10) Repeat Steps (2-4) as observation time and battery power allows (target >3 hrs)

If significant detections of EtO concentrations above the GMAP MDL (~1.2 ppbv) are observed and persist more than 10 minutes (are temporally sustained), the field team lead will attempt to notify BCP and offer to provide immediate information on the observations. This notification is performed to alert the facility and also in an attempt to collaboratively improve understanding potential emission sources and opportunities for potential emission reduction. This strategy assumes that periodic short-term episodic releases (e.g., railcar switchover) may (or may not) produce observable concentrations off site but should not be sustained for long periods of time. In addition to EtO, the GMAP system is also sensitive to and will be collecting real time data for methane gas. Methane is a primary component of natural gas and has been detected in prior mobile surveys due to natural gas leaks. The field team will immediately notify the Verona fire department if the team encounters any emission plume of potential concern. For example, a significant natural gas leak along the survey route.

B1.3 CGS Acquisition:

CGS samples [Silonite[®] coated 1.4 L (Entech Instruments, Simi Valley CA, USA)] of approximately 30 seconds in duration will be manually acquired following J-AMCD-SFSB-SOP-1729-0 "*Canister Field Grab Sampling using 1.4 L Canisters*",⁸ typically at a stationary position that is collocated with the sampling inlet

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of the GMAP vehicle (with engine turned off). The exact start and stop time of the CGS acquisition will be carefully recorded so the analyzed results can be directly compared to simultaneously acquired EtO concentration data from the Picarro and other measurements. The decision on when to acquire a CGS sample will be made by the field team lead, in consultation with project team members, using available real-time data and other information. The CGS will be analyzed by GC/MS following TO-15/TO-15A. The grab sampling apparatus includes the following Silonite® coated Entech parts: canister (TOV-2) valve (PN 01-29-TOV-2S), Micro-QT® female fitting (PN FQT-400S); filtered grab sampler (PN 01-39-RS-0), Silonite® 1/4" OD tubing. Procedures for CGS acquisition and CGS master record are contained in MOP 3070 and in Appendix D.



Figure B1.3: 1.4 L Mini-can used for CGS

B1.4 Supporting Meteorological and VOC Measurements:

Supporting meteorological measurements consist of 3-axis 1Hz wind speed data produced by at least one (but typically two collocated) battery-powered 81000V 3D sonic anemometers (RM Young Co. Traverse City, MI),^{10,11} positioned at ~3.0 m above ground level at S1 [Figure B1.4(a)]. At least one SPod fenceline sensor (Sensit Technologies, Valparaiso, IN)¹⁹⁻²¹ producing continuous 1Hz (10-sec avg) 2D wind measurements along with approximate temperature, atmospheric pressure, relatively humidity, and integrated VOC concentration data will be located at S1 [Figure B1.4(b)]. The SPod's 10.6 eV photoionization detector does not respond effectively to EtO but can register other VOCs that may be present in advected emission plumes and add value to the project (secondary data). The system described at S1 can be land-powered but the default will be solar power (with battery storage), as shown in Figure B1.4. Procedures for the 3D sonic Appendix E with SPod procedures contained in SOP ID: J-AMCD-SFSB-SOP-4380-2. Meteorological parameters will also be measured by the GMAP as described in Section B1.2.

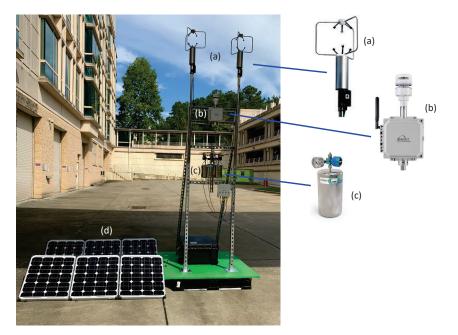


Figure B1.4: Supporting Meteorological Measurements at S1

B2. Sampling Methods

The sampling methods used for this project include: 24-hr canister sampling (Section B2.1), supporting GMAP Mobile Surveys (Section B2.2), with CGS acquisitions (Section B2.1.3), and meteorological measurements (Section B2.4).

B2.1 24-hr Canister sample batch description:

Whole air 24-hr canister sampling systems (Figure B1.1) will be deployed at S1, S2, and S3. There will be two primary samples at each site (labeled A and B), in addition to QA samples, forming a sample shipping batch (sample batch). Each site will contain two primary timer-controlled sampling systems labeled (S1A, S1B, S2A, S2B, S3A, S3B) that will remain at the same locations over the three-month study period (Table B2.1). There will be two additional timer-controlled sampling systems, one called SXC (where X = 1, 2, or 3) that will be moved between the sites for each new sampling batch to provide a collocated QA canister sample with identical acquisition timing to one of the primary samples. The other timer-controlled sampling system is called SXI (where X = 1, 2, or 3) and will serve primarily as a backup to the primary samplers and also be used as for interlaboratory comparisons where EPA Region 4's laboratory will perform the preparation and analysis of the canister, but the sample will be shipped separately as part of the sampling batch to and from EPA Region 4. The implementation of interlaboratory comparisons will be described in an addendum to this QAPP.

On the first sampling day of a batch (labeled A), the automated timers on one sampling system located at each site (S1A, S2A, and S3A) will simultaneously open and acquire air samples starting at midnight (0:00) and ending at 23:59 of that day (default timing). This sampling procedure will produce three spatially separated but time-aligned 24-hr integrated canister samples (i.e., a sampling set).

Primary Sampler and Primary Samples		Sample Batch 1 (Week 1)	Sample Batch 2 (Week 2)	Sample Batch 3 (Week 3)	Sample Batch 4 (Week 4)	
Site	Sampling Set	Sampler ID	Collocated Samples	Collocated Samples	Collocated Samples	Collocated Samples
S1	A	S1A	S1C, S1I*			
S2	A	S2A	S2F	S2C, S2I*		
S3	A	S3A	S3H	S3F	S3C, S3I*	
S1	В	S1B		S1H	S1F	S1C, S1I*
S2	В	S2B			S2H	S2F
S3	В	S3B				S3H

Table B2.1: Labeling convention sample shipping batches 1, 2, and 3, cycle continues (*optional)

On the second sampling day (i.e., approximately three days after the first sampling day), the automated timers on the 2^{nd} set canister samplers (S1B, S2B, and S3B) will simultaneously acquire three additional canister samples to produce a second sampling set. The SXC sampler (and possibly the SXI sampler) will acquire collocated sample(s) coincident with one of the primary samples (Table B2.1). Each sample batch will also include a field travel blank canister called SXF (where X = 1, 2, or 3) that is prepared the same and shipped in the same fashion as the primary canister samples but is not connected to a canister acquisition system and is simply left in the field at field conditions. Additionally, each sample batch will include a humidified field travel blank canister SXH (where X = 1, 2, or 3) that is prepared in the same manner as other samples but is partially filled with humidified air (to final vacuum spec), but not connected to a canister acquisition system and is simply left in the field at field conditions. The purpose of the humidified field travel blank is to improve knowledge of potential low-level EtO growth in-canister, which has a direct bearing on overall measurement uncertainty at low EtO concentration levels. The field travel blank and humidified field travel blank samples are analyzed along with the other samples in the sample batch and are rotated between the sites as indicated in Table B2.1.

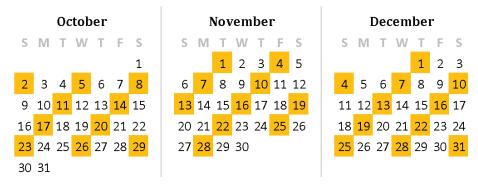
Additionally, one extra fully prepared and certified canister (called a spare canister) will be shipped as part of each sample batch for use if one of the canisters fails pre-deployment acceptance criteria, such as vacuum pressure check. If the spare canister is used, it becomes a sample. If unused, the spare canister will be shipped back to the laboratory along with the other samples in the sample batch and a new spare will be prepared and shipped with the next batch. The spare canister, if unused, will not normally be analyzed.

The field team visits the sites to retrieve all canister samples (i.e., 1st and 2nd sampling sets and all QA samples) that together form the sample shipping batch. The field team deploys the new canister samples at the appropriate sites and adjusts the acquisition timing determined as per the modified 1 in 3-day sampling plan. The retrieved canister batch will be shipped to ERG for EtO analysis by TO-15/TO-15A (except for the interlaboratory comparison sample which will be transferred to EPA Region 4 for analysis). In summary, each sample batch issued from and returned to ERG contains 6 primary 24-hr canister samples (2 sampling sets of 3), one collocated QA sample, one field travel blank, one humidified field travel blank, one spare canister and one separately prepared and analyzed sample for interlaboratory comparison (i.e., 10 or 11 canisters total per sample shipping batch).

able B2.2: General information for primary 24-hr canister batches				
New canisters shipped from	ERG 1600 Perimeter Park Drive Morrisville, NC 27560			
New canisters shipped to	U.S. EPA Region 7 Science and Technology Center 300 Minnesota Avenue Kansas City, Kansas 66101			
Field site:	Verona, MO			
Number of canisters per shipment:	10 or 11			
Shipment frequency:	Once per week			
Field transport and installation:	Canisters will be hand carried from R7 Lab to Verona field sites			
Acquired canisters shipped from	U.S. EPA Region 7 Science and Technology Center 300 Minnesota Avenue Kansas City, Kansas 66101			
Acquired canisters shipped to	ERG ATTN: Julie Swift 1600 Perimeter Park Drive Morrisville, NC 27560			
RG Laboratory contact: Julie Swift ERG, 1600 Perimeter Park Drive Morrisville, NC 27560 919-468-7924, julie.swift@erg.com				
Address where acquired canisters Will be analyzed:	ERG 1600 Perimeter Park Drive Morrisville, NC 27560 or alternate location for interlaboratory comparison samples			

Table B2.2: General information for primary 24-hr canister batches

The basic 1 in 3-day sampling plan is shown in Figure B1.5. The actual sampling plan may differ from the that shown as it may include a deployment cycle shift by one or more days forward or backward in time. This is done to randomize the acquisition date and to account for variations in field deployment and pickup schedules due to inclement weather and other factors.





B2.2 GMAP Survey:

The G2920 Picarro and GMAP MEMS software will be used to measure and record the concentrations of EtO, CO₂, and CH₄, along with GPS, wind information, and other meteorological data during the GMAP

survey (mobile and stationary). There are no physical samples acquired by the GMAP survey, however CGS acquisitions (Section B2.3) are performed during select GMAP survey stationary observations.

B2.3 CGS Acquisition:

The signal from the Picarro unit will primarily be used to inform the acquisition of ~30 second duration CGSs. If a stationary GMAP observation encounters a significant and temporally stable EtO detection above MDL, an acquired CGS will be used to provide comparison data. In some cases, other factors may contribute to the decision to acquire a CGS (e.g., strong odor, comparison to SPod VOC fenceline sensor data, or decision to acquire an upwind grab sample). The CGS will be prepared, shipped, and analyzed by the EPA ORD CEMM VOC Laboratory by TO-15/TO-15A GC/MS. The CGS samples will be acquired near the inlet (within 2 m) of the Picarro sampling line on the GMAP with precise time alignment to the Picarro units so the EtO data can be directly compared. The laboratory analysis of EtO and other VOCs in the CGS sample will inform and support the measurement interpretation. The acquisition of CGS samples for this project will primarily follow a manual grab sampling approach using evacuated and cleaned 1.4 L Entech Silonite® coated stainless steel canisters. The 1.4 L Entech canisters will be shipped to the R7 lab in a custom Pelican[®] shipping box along with the COC forms, a manual pressure gauge, and return shipping labels. The canisters will be hand-carried from the R7 lab to the Verona field site during the weekly deployment to change-out the 24-hr canisters placed at S1 S2, and S3.

A target quantity of four or more CGS acquisitions per week is the goal. Since 14 canisters total will be shipped every two weeks, only four canisters may be used the first sampling week if detectable EtO signal is not encountered in order to hold additional samples in reserve for the second week (if needed). One canister from each sample batch must not be acquired and represents a field blank. General site and analysis contact information for the CGSs is contained in Table B2.2. Procedures associated with CGS preparation, shipping, and general system cleanliness checks utilized by the EPA/ORD/CEMM/AMCD VOC Laboratory are described in J-AMCD-AAB-SOP-675-0 "Standard Operating Procedure for Cleaning Air Sampling Canisters with the Entech 3100A Canister Cleaner",⁷ and J-AMCD-SFSB-SOP-1729-0 "Canister Field Grab Sampling using 1.4 L Canisters".⁸

New canisters shipped from	U.S. EPA Building E Chemical Services ATTN: Ingrid George 109 T.W. Alexander Drive Durham, NC 27709			
New canisters shipped to	U.S. EPA Region 7 Science and Technology Center 300 Minnesota Avenue Kansas City, Kansas 66101			
Field site:	Verona, MO (canisters hand carried from R7 Lab to Verona field sites)			
Number of canisters per deployment:	14			
Shipment frequency:	Once every two weeks			
Field transport and installation:	Canisters will be hand carried from R7 Lab to Verona field sites			
Acquired canisters shipped from	U.S. EPA Region 7 Science and Technology Center 300 Minnesota Avenue Kansas City, Kansas 66101			
Acquired canisters shipped to	U.S. EPA Building E Chemical Services ATTN: Ingrid George 109 T.W. Alexander Drive Durham, NC 27709			

Table B2.3: General information for CGSs

EPA laboratory contact: (post-collection)	Ingrid George U.S. EPA ORD/CEMM VOC Laboratory Lead 919-541-9780 <u>george.ingrid@epa.gov</u>
Address where acquired canisters Will be analyzed:	U.S. EPA ORD/CEMM VOC Laboratory (E-288) 109 T.W. Alexander Drive Durham, NC 27709

B3. Sample Handling and Chain of Custody

The 24-hr canisters and CGS will be shipped to the R7 lab in Kansas City, KS. The R7 lab will be responsible for shipping 24-hr canisters back to ERG weekly and shipping the 1.4 L canisters to the EPA ORD CEMM VOC Laboratory biweekly after sample acquisitions. The canisters will be hand carried from the R7 lab in the GMAP vehicle to (and from) the Verona field sites as part of the weekly GMAP survey deployment. Sample hold times for TO-15/TO-15A analysis are 30 days from canister cleaning to analysis. The 24-hr canisters will be prepared, cleaned, and labeled by ERG and shipped in standard shipping boxes for 6 L canisters. The 1.4 L mini-cans will be prepared, cleaned, and labeled by the EPA ORD CEMM VOC Laboratory and packed in Pelican transport cases along, with a manual pressure gauge. In addition to sample COC documentation, each shipment will include a pre-paid return shipping label to ship from the R7 lab back to ERG (for 24-hr canisters) or to the EPA ORD CEMM VOC Laboratory (for the CGS). Both labs are located in Durham, NC.

Chain of custody requirements for 24-hr and CGS samples follow good laboratory procedures for labeling, recording, and tracking all canisters from preparation and collection through reporting and archiving of concentration data plus all associated meta-data. It will be the responsibility of the individual laboratory personnel to prepare the COCs, canister IDs, and to maintain laboratory logbooks and records that provide a custody record throughout sample preparation and analysis. Canisters will be prepared and packaged for shipment by laboratory personnel in accordance with standard procedures. A shipping COC will be prepared for each deployment batch and will be included with the canisters (Figure B3.1) or equivalent. The laboratory will prepare the top half of the form except for the "Received by" section, which will be filled out by specific EPA field installation/acquisition personnel.

After cleaning the canisters, the laboratory personnel will generate a manila tag that contains the canister identification information specific to each canister. Each canister will have a manila tag in plastic protective covering with a unique canister ID. The tag will be affixed to the canisters, and this information will be recorded in the sampling COC documentation. each 24-hr canister or CGS is installed/acquired, the field technician will measure and record initial canister pressure on the sampling COC for each canister installed. If the canister pressure is >-27 in Hg, the canister will not be used. Field technicians will determine sample ID for each canister sample after acquisition and will record sample IDs on the respective manila tags and sampling COCs. There will be one COC declaration form [Figure B3.1(a)] and one set of COC records [Figure B3.1(b)], (or equivalent form from ERG) associated with each sample batch sent to the field. Sample ID's will adhere to the following:

V-NNNN-MMDDYY-HHMMSS-ZZZ

Where:

V = "V" indicates that the canister is associated with the Verona, MO Project (this QAPP).

NNNNN = unique numerical identifier of the 24-hr canister or CGS tracked by each lab.

MMDDYY = month, day, and year of 24-hr or CGS acquisition, or date of shipping of a field blank

HHMMSS = cell phone local time (military) of the acquisition start time of a 24-hr canister or CGS, with "**999999**" indicating a lab-designated field blank. The 24-hr canister or CGS acquisition end time is contained on the COC [Figure B3(b)] and canister summary tables (Appendix B and Appendix D). The target is to record the start and stop times of the CGS to within 2 seconds of local time to facilitate comparison with other measures. The 24-hr canisters timers with 1 minute time resolution so **SS** = **00** for all.

ZZZ = "SLA", ""SLB", "SLC", "SLF", "SLH", or SLI" for 24-hr canister samples where "L" indicates the location of the sample "1", "2", or "3" for Sites S1, S2, or S3, respectively, as per table B2.1. For the CGS samples **ZZZ** = "001" to "999" corresponding to the incremented GMAP Survey data form which carries the description of the acquisition. The CGS field travel blank is indicated ad "FFF"

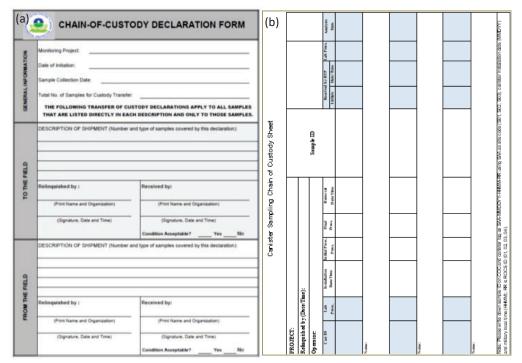


Figure B3.1: (a) EPA chain of custody front summary page and (b) COC form

Any issues or observations related to canister sampling can be recorded in the "Notes" section of the sampling COC and will also be described in applicable QA or data forms. Before returning the canister samples to the laboratories, the field technician will record final field pressures from the manual pressure gauge on the sampling COC. In addition to COC forms of Figure B3.1, the field team lead will track and record canister information in the summary tables in Appendices B and D. Each of the CGSs acquired will also be linked to a specific GMAP data form (Appendix C, table C1) describing the activity. All forms and records will be made into PDF files will be save to the project drives.

B4. Analytical Methods

The laboratory measurement procedures for TO-15/TO-15A analysis of canister samples are described below.⁵ After the canisters have been deployed in the field and shipped back to ERG or the EPA ORD CEMM VOC Laboratory, they will be received, inspected, and COC-documented. The pressures of the canisters will be measured and verified to be within 6 \pm 4 in Hg. If out of specification, the canister data will be flagged for that sample. ERG will analyze samples as per EPA TO-15/TO-15A using proprietary operating procedures which are part of the QA files for this project but are not disseminated as part of this QAPP.⁵

Table B3.1: Target VOC Compound List for ORD Modified TO-15/TO-15A Analysis

ORD GC/MS Target Compounds						
Formaldehyde*	1,1-Dichloroethene	2-Methylheptane				
Acetaldehyde	1,1,2-Trichloro-1,2,2	cis-1,3-Dichloropropene				
Methanol	2,2-Dimethylbutane	3-Methylheptane				
Furan	Acetone	4-Methy-2-Pentanone				
Propanal	Carbon Disulfide	Toluene				
Methacrolein	Isopropyl Alcohol	Octane				
2-Methylfuran	Acetonitrile	trans-1,3-Dichloropropene				
Butanal	3-Chloro-1-Propene	1,1,2-Trichloroethane				
Methyl Vinyl Ketone	2,3-Dimethylbutane	Tetrachloroethene				
3-Methylfuran	Methylene Chloride	2-Hexanone				
Crotonaldehyde	2-Methylpentane	Dibromochloromethane				
Pentanal	Cyclopentane	1,2-Dibromoethane				
Hexanal	Tert-Butanol	Chlorobenzene				
Heptanal	Acrylonitrile	1,1,1,2-Tetrachloroethane				
Benzaldehyde	trans-1,2-Dichloroethene	Ethylbenzene				
Octanal	3-Methylpentane	m/p-Xylene				
m/p/o-Tolualdehyde	Methyl Tert-Butyl Ether	Nonane				
3-Methyl-3-Butene-2-one	1-Hexene	Butyl Acrylate				
2-Ethylfuran	n-Hexane	o-Xylene				
2,5-Dimethylfuran	1,1-Dichloroethane	Styrene				
2-Furaldeyde	Vinyl Acetate	Bromoform				
3-Furaldehyde	2-Chloroprene	a-Pinene				
Benzofuran	Diisopropyl ether	Cumene				
2-Methylbenzofuran	2,4-Dimethylpentane	1,1,2,2-Tetrachloroethane				
3-Methylbenzofuran	Ethyl Tert-Butyl Ether n-Propylben					
Propylene	Methylcyclopentane	Chlorotoluenes				
Propane	cis-1,2-Dichloroethene	m-Ethyltoluene				
Dichlorodifluoromethane	2-Butanone	1-Ethyl-4-Methyl Benzene				
Dichlorotetrafluoroethane	Ethyl Acetate	1,3,5-Trimethylbenzene				
Isobutane	Chloroform	n-Decane				
Chloromethane	Tetrahydrofuran	b-Pinene				
1-Butene	1,1,1-Trichloroethane	1,2,4-Trimethylbenzene				
Vinyl Chloride	2-Methylhexane	Tert-Butyl Benzene				
Butane	Cyclohexane	o-Ethyltoluene				
1,3-Butadiene	2,3-Dimethylpentane	Sec-Butyl Benzene				
trans-2-butene	Carbon Tetrachloride	1,3-Dichlorobenzene				
cis-2-butene	3-Methylhexane	1,4-Dichlorobenzene				
Ethylene oxide	Benzene	1,2,3-Trimethylbenzene				
Bromomethane	1.2-Dichloroethane	o-Cymene				
Chloroethane	Isooctane	1,3-Diethylbenzene				
iso-Pentane	Tert Amyl-Methyl Ether	1,2-Diethylbenzene				
Vinyl Bromide	Heptane	n-Butyl Benzene				
Trichlorofluoromethane	Trichloroethene	1,2-Dichlorobenzene				
1-Pentene	Ethyl acrylate	Undecane				
n-Pentane	Methylcyclohexane	Dodecane				
trans-2-pentene	1,2-Dichloropropane	1,2,4-Trichlorobenzene				
Ethanol	Methyl Methacrylate	Hexachlorobutadiene				
Isoprene	1,4-Dioxane	Naphthalene				
cis-2-pentene	Bromodichloromethane	Maphalalelle				
Acrolein	2,3,4-Trimethylpentane					

For the CGS analysis by the EPA ORD VOC Laboratory, the canisters will be pressurized to 5 psi with humidified zero air. After at least an overnight equilibration period, the pressurized samples will be analyzed for a wider range of VOCs including EtO using the Entech GC/MS system following a modified TO-15/TO-15A analysis method Analytical procedures are detailed in EPA ORD SOP #J-AMCD-AAB-SOP-3916-0 "Standard Operating Procedure for Analysis of Volatile Organic Compounds in Whole Air Samples Using the Entech 7200 Preconcentrator and Agilent 7890A/5975C Gas Chromatograph–Mass Selective Detector" (see Appendix 2 of the referenced SOP). The EPA AMCD VOC Laboratory staff will review the sample analyses and will reduce and track the external standard data to ensure that the instruments are operating within performance specifications.

The Entech GC/MS analytical system located in the EPA ORD CEMM VOC Laboratory in E-288 will be used to perform TO-15/TO-15A analysis to quantify concentrations of ~150 compounds as per standard procedures for CGS canister grab samples. The Entech system consists of the Entech 7016D/7650-M Canister Autosamplers, Entech 7200 Preconcentrator, Agilent 7890B Gas Chromatograph/5977 Mass Selective Detector. The GC/MS system operation generally follows analytical procedures outlined in the SOP J-AMCD-AAB-SOP-3916-0. The Entech 7200 Preconcentrator is operated in Cold Trap Dehydration mode. The GC column that is installed in the Agilent 7890B GC is an Agilent DB-624 Ultra inert (60 m length, 0.32 μ m inner diameter, 1.8 μ m film thickness). The MS is operated in Selected Ion Monitoring (SIM)/Scan mode. Aliquots (nominally 400 mL) of sample are collected from the canister using a canister autosampler (Entech 7650-M) and VOCs are trapped by the preconcentration system (Entech 7200). The VOCs are thermally desorbed from the preconcentration trap in a small volume of high purity helium carrier gas and injected onto the GC column. Target analytes are quantified by MS system in SIM mode. Scan mode MS data are used to identify any coeluting interference compounds not detected in SIM mode.

The peak retention time (RT) and mass spectral pattern in comparison to calibration standards are used to confirm target compound identification. The same quantities of internal standards will be introduced during each analytical run to assess the stability of MS response over time. Internal standard RTs must be within 2 s of average RT from initial calibration and area response must be within 40% of average initial calibration area response. Runs that do not meet these criteria will be flagged, and the initial calibration may be repeated as needed. Quality control checks that are analyzed during each analytical sequence include an instrument blank, lab blank, a replicate sample analysis, and a continuing calibration verification (CCV). The CCV must be within ±30% of expected concentrations. Other quality criteria for these checks are outlined in Section B5. EPA ORD CEMM VOC Laboratory personnel will employ a multipoint calibration of the GC/MS system, using a NIST-traceable TO-15/TO-15A calibration standard following standard record keeping procedures. The calibration procedure will follow all TO-15/TO-15A guidelines.

B5. Quality Control

The quality control procedures for this project are summarized in the Tables of Sections B5.1 through B5.6. Prior to QA testing or data collection, all equipment will be verified by trained staff to be fully operational and properly documented in the project record.

B5.1 24-hr Canister Deployment QA/QC Checks

Table B5.1 summarizes the basic QA/QC checks, their frequency, acceptance criteria, and corrective action for 24-hr canister sample acquisition.

Measurement Parameter	QA/QC Check Procedure	Frequency	Acceptance Criteria	Corrective Action
24-hr canister trigger test	Execute canister timer trigger test to ensure the device is functional	Before field deployment	Canister is triggering automated means	ldentify and fix malfunction or set up issue and replace unit if necessary
24-hr canister leak check	Leak check 24-hr canister system	Before field deployment and in field	<2" Hg change in pressure reading > 2 hr install	Tighten fittings, replace fittings if necessary

Table B5.1: QA/QC checks for	$\cdot 21_{\rm hr}$ and CCS	ovacuated canister	systems and samples
Table DJ. I. QAYQC CHECKS IOF	24-III and COS	evacuated carrister	systems and samples

Measurement Parameter	QA/QC Check Procedure	Frequency	Acceptance Criteria	Corrective Action
24-hr canister sampling system blank certification	Certification of cleanliness 24-hr canister collection system as per lab SOPs	Before field deployment	<mdl concentration="" of="" target<br="">VOCs as compared to reference sample</mdl>	Purge unit with zero air, replace contaminated parts
Proper canister COC documentation (24-hr and CGS)	Verify use proper COC procedures and forms	Each canister acquisition	Documentation verified to be complete after canister acquisition	No corrective action is available for COC documentation error (sample invalid). Conduct training.
Canister field initial pressure check (24-hr and CGS)	Record gauge pressure at time of 24-hr canister install or CGS acquisition	Each 24-hr canister deployed or CGS manually acquired	29 in Hg ± 2 in Hg	If out of tolerance, change to new canister and take original canister out of service and properly document on COC
Canister field final pressure check	Record gauge pressure at removal of 24-hr canister or after CGS acquisition	Each 24-hr canister deployed or CGS manually acquired	6 in Hg ± 4 in Hg	If out of tolerance, make note on COC and notify field team lead, corrective action required to regain sample draw temporal profile

B5.3 Canister analysis QC Checks

The QC parameters related to the canister TO-15/TO-15A lab analysis of 24-hr canister or CGS samples collected for this project are summarized in Table B5.2 below. Additional information on general ERG Laboratory quality assurance practices can be found "Support for the EPA National Monitoring Programs (UATMP, NATTS, CSATAM, PAMS, and NMOC Support), Contract No. EP-D-14-030, ERG-QAPP-0344-7.²²

Table DE 2. OA /OC	ale a due fair 24 lan ageitate	n an CCC as mandas	
Table B5.2: QA/QC	checks for 24-hr caniste	r or CGS samples	(applies to all laboratories)

Measurement Parameter	QA/QC Check Procedure	Frequency	Acceptance Criteria	Corrective Action
Retention time (RT)	Monitor RT of each IS and target compound	All target compounds in each analysis run	RT is \leq 3 s of mean ICAL	Update RTs based on CCV run
Lab blank	Analyze sample filled with humidified zero air	Run with each analysis sequence after CCV	Target concentrations should be the higher of <15 pptv or <mdl< td=""><td>Repeat analysis.; Data will be flagged</td></mdl<>	Repeat analysis.; Data will be flagged
Continuing calibration verification (CCV)	Analyze mid-level calibration sample	Run daily with each analysis sequence after IB and before samples	Target concentrations within ±30% of expected	ICAL will be reanalyzed
Collocated sample	Field sample collected simultaneously next to primary sample using separate sampler	Once biweekly	≤25% precision	Data will be flagged
Replicate analysis	Multiple analyses from same sample	Once per sequence	≤25% precision	Data will be flagged

B5.3 GMAP Survey Daily QA:

For each GMAP deployment day of the GMAP, the operational condition of the equipment will be documented by the procedures and QA form contained in Appendix C (Table C1). The forms will be converted to electronic PDF files for electronic storage on the project folders and the paper forms will be kept in a three-ring binder in R7.

Prior to these daily QA checks, the GMAP vehicle, battery supplies, and equipment must be fully operational (verified by trained personnel) and the Picarro G2920 must be "warmed up" by continuous operation for a minimum of 45 minutes. All equipment used in the GMAP must be documented (i.e., the serial numbers of each instrument in the project record), so that it is traceable to the daily QA forms. The general timestamp off set of the Picarro and the MEMS computer must be known and be part of the project record. The daily GMAP survey QA check includes a single point calibration check (cal-check) of the Picarro G2920, with advanced testing of conducted prior to the field deployment. The checks are required to be completed before data acquisition and it is good practice to perform and document the Picarro calibration check at the close of data acquisition (if feasible). The CH₄ readings away from sources provide a continuous DQI of instrument operational state (1.9 ppmv \pm 0.2 ppmv).

B5.4 GMAP Survey Form:

During all field data collection, a GMAP Survey (GS) Form (Appendix C, Table C2) will be active. A new GS form will be generated whenever there is a change in operations (e.g., switching from mobile route mapping to stationary observation, etc.) and a new MEMS system file name will be generated. The details of the survey, including the start and stop time of data acquisition, the sampling configuration, and the collection of any CGSs acquired will be recorded on the GS form. The GS includes a basic system operation check (green status) and a check of ambient concentrations away from the source. If the data acquisition is downwind of the source, the latter ambient check may not be possible. The forms will be converted to electronic PDF files for electronic storage on the project folders and the paper forms will be kept in a three-ring binder in R7.

B5.5 Summary of GMAP Survey QA checks

Table B5.1 summarizes the GMAP survey QA checks to be performed in this project. QA checks are documented in either the daily QA Form or as part of a GS data form (both found in Appendix C). Checks that are performed in the field rely on the trained operator observing values displayed on the MEMS screen and estimating mean levels. The same QA checks can be performed formally through a 3-minute average of collected data (typically performed after return from the field).

Measurement Parameter	QA/QC Check Procedure	Frequency	Record	Acceptance Criteria	Corrective Action
GMAP survey gear functionality	Appendix C Step C6	Prior to each GMAP survey QA or data run	QA or GS Forms Appendix C	No system errors	Investigate issue and restore functionally
GMAP survey GPS check	Appendix C Step C7	Once per field day	QA form Appendix C	Reasonableness compared to independent values	Investigate issue and repair sample system, or use backup gear
GMAP survey wind monitor checks	Appendix C Steps C8 and C9	Once per field day	QA form Appendix C	Reasonableness compared expected values from fan test	Investigate issue and repair sample system, or use backup gear

Table B5.3: QA/QC Checks for GMAP Survey Systems:

Measurement Parameter	QA/QC Check Procedure	Frequency	Record	Acceptance Criteria	Corrective Action
Picarro ambient operation	Appendix C Step C10	Prior to each GMAP survey QA or data run	QA or GS Forms Appendix C	1.9 ± 0.2 ppm, CH₄ 0.0 ± 0.2 ppm, EtO 30 second visual average	Investigate issue and repair sample system, check calibration
GMAP survey Picarro gas cal- check	Appendix C Steps C11 to C15	Once per field day	QA form Appendix C	+/-20 % EtO, and CH ₄ , (or CO ₂)	Investigate issue and repair sample system, check calibration
GMAP survey timing offset and delay check	Appendix C Steps C11 to C15	Once per field day	QA form Appendix C	Time of MEMS, Picarro, and QA spike gas flow recorded	Investigate issue and conduct training
GMAP survey CGS grab sample comparison	Collocated and time-aligned comparisons	At least once per field day	GS Form Appendix C, CGS COC and summary table	+/-30 % EtO, CH4, and CO ₂ , Depends on level	No corrective action possible since post analysis
GMAP survey to S1 wind data comparison	Execute 15-minute stationary comparison with 3D sonics at Site 1	Monthly	GS Forms Appendix C	±15 deg wind dir. ±20% wind speed	Investigate issue and adjust/repair as necessary

B5.6 Supporting Meteorological and Other Measurements QA/QC Checks

Table B5.4 summarizes the basic QA/QC checks, their frequency, acceptance criteria, and corrective action for supporting meteorological measurements. Additional information on the procedures and QA checks can be found in Appendices E and F and reference therein.

Measurement Parameter	QA/QC Check Procedure	Frequency	Acceptance Criteria	Corrective Action
3D Sonic Functionality	Appendix E Steps E10 and E11	Once per week	Data present and timing with 10 seconds of actual	Repair or replace unit or adjust datalogger time stamp
3D Sonic Wind Speed, Wind Direction Comparison (if two 3D sonics are co-deployed)	Generate and review a 1-hour co-deployed two-unit QA table retain for records	Before travel to the field, at the start of field deployment, and quarterly	5-minute average wind speed RPD within ± 20% and wind direction within ± 15 deg, for wind speeds > 1.0 m/s	ldentify and fix malfunction or alignment issue and replace unit(s) if necessary
SPod functionality	Generate and review a 1-hour single unit QA table as per Appendix F SOP Section 9.5.1 and retain PDF for records	Before travel to the field, at the start of field deployment, and quarterly	Pass all QA criteria as per Table 9.5.1	Investigate time series and perform repeat test. On second fail, identify and fix malfunction and replace unit if necessary

Table B5.4: QA/QC supporting meteorological measurements

Measurement Parameter	QA/QC Check Procedure	Frequency	Acceptance Criteria	Corrective Action
SPod PID, Wind Speed, Wind Direction, RH, Temp, Pressure (if two SPods are co- deployed)	Generate and review a 1-hour co-deployed two-unit QA table as per Appendix F SOP Section 9.5.2 and retain PDF for records	Before travel to the field, at the start of field deployment, and quarterly	Pass all QA criteria as per Appendix F SPod SOP Table 9.5.1	Ensure co-deployment and like time series (i.e., no calibration occurring) and perform repeat test. On second fail, identify and fix malfunction and replace unit(s) if necessary
SPod PID Cal-check	1 ppm isobutylene cal check as per Appendix F SOP	Before travel to the field, at the start of field deployment, and quarterly	+/-20% of cylinder value	Recalibrate and or replace sensor
Comparison of collocated 3D Sonic and SPod Wind Speed and direction	Generate and review a 1-hour co-deployed two-unit QA table retain for records	Before travel to the field, at the start of field deployment, and quarterly	5-minute average wind speed RPD within ± 20% and wind direction within ± 15 deg, for wind speeds > 1.0 m/s	ldentify and fix malfunction or alignment issue and replace unit(s) if necessary

B6/B7. Instrument/Equipment Calibration, Testing, Inspection, Maintenance

The 24-hr canisters, GMAP survey gear, CGS systems, and associated auxiliary equipment will be tested before field deployment to ensure proper operation. Testing procedures include zero/calibration, leak checks, sample collection triggering checks, and blank verifications. Canisters used in this project will be EtO certified and will be inspected and tested to validate their use for TO-15/TO-15A sampling analysis. These procedures include leak checks and blank certification.

Further information on the ERG laboratory procedures can be found in reference 22. The GC/MS systems used by the EPA VOC Laboratory to conduct CGS analysis will be calibrated with a mix of TO-15/TO-15A and photochemical assessment monitoring stations (PAMS) compounds following guidelines in TO-15/TO-15A and Markes TD/GC/TOFMS SOP #J-AMCD-AAB-SOP-3911-0. Calibration standards used to calibrate the GC/MS system will be prepared by diluting from VOC calibration standards in high-pressure cylinders that are certified with NIST-traceable Certified Reference Material. An Entech 4600A Dynamic Dilutor will be used to prepare working calibration standards at 0.2, 2 ppbv, and 20 ppbv in 6 L Silonite coated cans (SOP CGSAB 134.0 [5]). The calibration range will span from 0 to 20 ppbv and will include at least five effective calibration levels by sampling different volumes ranging from 25 to 800 cc from the three calibration canisters. A linear or quadratic curve fit may be used to achieve the quality control criteria: 1) the calibration fit must have an R2 \geq 0.995, and 2) each calibration level must be within \pm 30% of expected concentration.

B8. Inspection/Acceptance of Supplies and Consumables

For field work, the concentration of gas cylinders and associated gas mixing and zero gas generation equipment used will be certified and calibrated as per standard procedures. The EtO gas standards typically have a track record of verification using multiple measurement approaches. The traceability of gas cylinders and equipment used in the study will be documented in project records.

For VOC Laboratory analysis, the quality of purchased materials (e.g., reagents, gas standards, instrumentation, and equipment) used in the laboratory are specified in the SOPs and protocols. The laboratory purchases reagents with purity requirements that are established within the appropriate SOPs. Compressed gases used in research activities will be procured to the specification defined in the technical SOPs. Field personnel will ensure that incoming canisters and supplies are received in good condition, with COC enclosed. Any anomalies causing the canisters to be unsuitable for sampling will be recorded and immediately reported to Ingrid George at EPA/RTP (contact information, Section B.2) or ERG.

B9. Non-direct Measurements

Information may be provided on a voluntary basis by BCP on process conditions during the period of the field study.

B10. Data Management

B10.1 General Data Management

Data and information generated under this field data acquisition QAPP will be managed the following ways for this project:

- 1. Individuals working in the field will complete (generate) hand-written data forms and COCs included in this QAPP as project documentation deliverables. All notebook entries generated are also project documentation deliverables. The various organizations shall retain original records as per standard business practices.
- 2. These data forms, COCs, and notebook pages will be electronically scanned to make PDF files by the ORD laboratory, ORD or R7 field project leads, or ERG (provided by Jacobs). All parties will individually archive information and provide electronic copies of the information to the EPA ORD and EPA R7 Project data/documentation stewards (E. Thoma and A. Edwards) for archiving on the official project drives and for QA audit preparation. The electronic files will be provided by email as a default.
- 3. The independent and identical ORD and R7 project archive sites will have restricted read/write access and will be located at:
 - C:\Users\ETHOMA\OneDrive Environmental Protection Agency (EPA)\ORD Verona EtO Project 2022
 - R7: C:\Users\aedwar03\OneDrive Environmental Protection Agency (EPA)\R7 Verona EtO Project 2022
- 4. The ORD file structure for project documentation will be:
 - ORD Verona EtO Project 2022
 - Documentation
 - o Raw Data
 - Processed Data
 - o Analysis
- 5. The R7 file structure for project documentation will be:
 - R7 Verona ETO Project 2022
 - \circ Documentation
 - o Raw Data
 - Processed Data
 - o Analysis

- 6. Any data or information provided by BCP will be converted to PDF or saved in native electronic file format and delivered to the project file for archiving. These procedures will change if confidential information control is invoked by BCP regarding certain process information (to be separately stored as confidential business information).
- 7. All data generated are project deliverables. Raw data from Picarro instruments, GMAP MEMS, 3D sonic anemometers, SPods, and other field and laboratory results will be archived on the project drives.
- 8. It is the responsibility of the individual groups to back up data each field day to help prevent data loss in the event of equipment failure.
- 9. Additional sub-folders related to the organization of documentation, raw data, processed data, analysis, reporting may be added to the ORD R7 project but are not described in this QAPP.

C. ASSESSMENTS AND OVERSIGHT

C1. Assessments and Response Actions

The 24-hr canisters and the GMAP Mobile Survey and CGS will be conducted by ORD and R7 personnel. The Jacobs TO Lead (Figure A.4.1) is primarily responsible for project site and equipment set up and for the management and documentation of ERG lab analysis. A R7-appointed QA official independent from the project will perform an assessment near the start of the campaign to ensure the following from both measurement teams:

- Safe work procedures and COVID-19 protocols are being followed
- Equipment is operational
- QA procedures are being followed
- Proper documentation forms and COCs are available and being used
- All equipment has been time-synchronized as specified
- All gas standard certifications and equipment calibrations are documented
- Laboratory analysis is meeting QA acceptance criteria

The assessment by the R7 QA official will be conducted by direct observation of the measurement teams, checking the above procedures are being followed. A copy of the R7 audit report will be provided to the to the ORD QA Manager. In addition, due to the designation of QA Category A for EtO measurements, the ORD QA Manager will perform an audit of data quality (ADQ) on the reported data. An ADQ traces a randomly selected percentage of reported data back to the raw form and ensures calculation and transcriptions were done correctly. The audit will be completed prior to the publication/release of any reports or manuscripts.

C2. Reports to Management

EPA management will be informed of progress through regular updates. For Jacobs, there is no formal (end of project report) required for this study. Jacobs and the EPA/ORD/VOC Laboratory and field team leads will deliver the reduced data sets, raw data files, and all QA information with copies of field notes to the project drive for compilation into a final data set. The production of the project database with associated data dictionary will be performed by the EPA documentation stewards. This database will consist of a collection of individual reduced datasets from each of the NGEM devices. Each NGEM dataset will contain data that meet the QA acceptance criteria for the individual techniques, along with key metadata that will allow the results acquired with the various techniques to be compared (e.g., measurement location and time). This database will form the basis for the EPA scientific data management

plan for this project (not described in this QAPP). Additionally, data will be managed in accordance with EPA R7's data management policy. Publications produced using data acquired in this project will be based on data contained in the primary project database.

D. DATA VALIDATION AND USABILITY

D1/D2. Data Review, Verification, and Validation/Verification and Validation Methods

While in-field, the ORD and R7 field team leads will assess operations and documentation. All persons participating in this project will adhere to the procedural requirements of the QAPP and safety plans including criteria to accept, reject, or qualify project data. Proper sample collection technique will be verified by pilot-level surveillance audits as summarized in Table D1.1. Data packages will be verified by the analyst and reviewed by a second person for transcription errors, calculation errors, and data completeness. The second reviewer will produce an electronic copy of the data reviewed, highlight the material confirmed, and electronically sign that copy. The reviews will be documented in the project file.

In-process data validation includes reviews by EPA personnel of data reduction and storage activities to ensure that utilized prototype procedures are being followed and modified or adjusted, if required. Surveillance audits will be performed at the initiation of a sampling or analysis activity to ensure proper data collection and adherence to the procedures described in this QAPP. Data validation and auditing activities are described in Table D1.1. If modifications of procedures need to be made, the project's EPA technical lead or co-leads will authorize changes or deviations in the operation of the project. Deviations will be documented, and these will be disseminated by the project team to those on the QAPP distribution list.

All manually entered data and information will be independently verified against the source data for accurate transcription of values and units. Any data that are calculated (e.g., summary statistics for the numerical data) will also be verified for accurate transcription of values from the studies and accurate equation setup in Excel. Electronic data transfers of data will be verified to ensure completeness and accuracy of data transfers and to identify potential systematic errors. Verification will require a random sampling of data elements from the source data, at a minimum 5% of the raw data, until the integrity of the data export\import process is demonstrated.

Type of Audit	Frequency	Details	Documentation
Surveillance audit of 24-hr canister deployment	Conducted during the first day of sampling	Audit performed by R7 QA official. This validation will verify physical set up and timer configuration of the samplers	Documented in R7 project notebook and then as a memo to the project record.
Surveillance audit of GMAP survey system installation and QA Tests	Conducted during the first day of sampling	Audit performed by R7 QA official. This validation will verify physical set up of GMAP, cal- checks, and documentation	Documented in R7 project notebook and then as a memo to the project record.
Surveillance audit CGS sampling	Conducted during the first day of sampling	Audit performed by R7 QA official. This validation will verify proper operation and documentation of CGS acquisitions	Documented in R7 project notebook and then as a memo to the project record.
Surveillance audit of 3D Sonics and SPods	Conducted during the first day of sampling	Audit performed by R7 QA official. This validation will verify proper operation and documentation of these systems.	Documented in R7 project notebook and then as a memo to the project record.
Surveillance audit of CGS laboratory analyses	Conducted during analysis of the first set of samples	EPA ORD VOC Lab lead or designee	Performance of this audit is documented in VOC Lab lead or designee notebook then as a memo to the project record.
Audit of lab data quality	Conducted after the first set of data has been analyzed and processed	EPA ORD VOC Lab lead or designee	Performance of this audit is documented in VOC Lab lead or designee notebook then as a memo to the project record.

Table D1.1: Data Validation and Auditing

D3. Analysis and Reconciliation with User Requirements

The ORD technical lead will review the reported data to verify that QC checks have been documented as described in the project QAPP, that acceptance criteria have been met, and that data has been qualified appropriately. The acceptance of individual data will involve multiple levels of screening. For example, if an CGS sample is determined by the ORD CEMM VOC Laboratory lead to be invalid, that sample will be excluded from project synthesis analysis. As another example, if upwind GMAP Picarro data are found in analysis to be reporting unreasonable results for a known QA parameter (e.g., CH4 = 0.01 ppm), these data are flagged as invalid until the assignable cause/repair is performed. These reviews will be documented in the EPA ORD laboratory notebooks of the ORD and R7 data stewards. Synthesis level screening includes the combination of atmospheric data and concentration measurements and is performed in post analysis. For example, a stationary measurement that is intended to be performed downwind of the source but was actually performed upwind of the source. The data are not invalid but are not source informative. These types of data limitations will be documented in the research notebook or directly on field data sheets when discovered.

The technical leads will use the results of the data review, verification, and validation process to assess whether the data quality meets the project requirements and thereby the user requirements. If there are data quality issues that may impact their use, the impact will be evaluated by the technical lead and limitations of the data will be documented in any publications or reports. The technical lead may seek assistance from QA staff as needed.

The following procedures will assess data usability to meet project objectives:

- 1. Picarro calibrations and cal-checks will be performed as per approved QAPP.
- 2. Picarro and other instrument raw data will undergo 100% QA screening to filter out invalid points. Any missing data will be flagged and documented.
- 3. As available, valid data above detection limit from collocated devices will be compared in a procedure to ascertain the similarity of results.
- 4. Canister data will be validated with QA flags applied as per laboratory procedures documented in applicable SOPs.
- 5. With assistance of project team, conclusions with regard to the use of the data will be developed and communicated as part of project reporting.

F. References

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- 5. Note: EPA Method TO-15A is not yet fully implemented by EPA/ORD/CEMM, ERG, or contractor laboratories for EtO at this time given its relatively recent publication date. The work performed under this QAPP meets the standards of TO-15 with methods improvements in some areas towards TO-15A. The procedures used in this project are referred uniformly as TO-15/TO-15A. Modification from TO-15 or TO15A will be documented in laboratory and project records.
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Appendix A: Training Documentation

The following is a list of training leads for this project, followed by a training documentation form that is required to be completed for newly trained individuals (less than 6 months of task experience). EPA ORD and other laboratory long-term personnel training status are separately documented. Field and laboratory safety training are not covered in this QAPP.

Training leads for this project:

- EPA ORD CEMM VOC Laboratory operations: Ingrid George
- ERG laboratory operations: Julie Swift
- 24-hr canister field procedures: Ingrid George
- GMAP survey operation with Picarro 2920: Ali Gitipour
- CGS field procedures: Ali Gitipour
- 3D sonic anemometer procedures: Eben Thoma
- SPod procedures: Megan McDonald

- 1. Name/signature of person being trained: ______
- 2. Name/signature of person trainer/evaluator: ______
- 3. Date of training and evaluation: _____
- 4. QAPP procedure trained (circle letter, one form per procedure trained/tested):
 - a. 24-hr canister deployment, timer, COC documentation, and shipping/receiving
 - b. GMAP survey operation
 - c. CGS acquisition, COC documentation, and shipping/receiving
 - d. 3D sonic anemometer procedures
 - e. SPod fenceline sensor procedures
- 5. Describe the training conducted

6. Describe the training evaluation procedure

Appendix B: 24-hr Canister Field Procedure

The 24-hr canister field set up, sample acquisition, and documentation procedures includes the following steps to be executed by trained personnel with knowledge of field equipment and procedures.^{7,8} The 24-hr canister field procedures assume that the deployment sites S1, S2, and S3 have secure site infrastructure already in place and are accessible. This procedure assumes that the canisters and timer-based canister acquisition systems have been previously EtO-certified and leak checked, so that the only potential leak point that needs to be rechecked is the canister to timer connection at install. Complete following steps (<u>B1</u> through <u>B19</u>) for each deployment and pickup cycle.

<u>B1:</u> Receive shipping case containing new 24-hr canisters and inspect contents against COC, ensure working pressure gage and required hand tools are part of the field kit, and transport to field site.

<u>B2:</u> At S1, gain access to the 24-hr canisters through the security fence. If previous canisters were deployed and acquired, remove one canister from the sampling rig, identify this canister on the post-acquisition COC and verify sample ID.

<u>B3:</u> Check the timer for the canister that was just removed and ensure that it was triggered as per sampling plan. Verify that the date and time encoded in the canister sampling ID and the COC at installation agree with each other and the data provided by the timer inspection. If the sample ID and date and time are not correct, add canister acquisition time information to the COC and note QA issue.

<u>B4:</u> Connect the manual pressure gauge to the canister and briefly open and close valve to measure and record the final field pressure of the 24-hr canister on the COC. The final pressure should be 6 in Hg \pm 4 in Hg. Add notes to COC as needed and contact field team lead if out of tolerance.

<u>B6</u>: Ensure valve is closed and remove pressure gauge.

<u>B7</u>: Put canister in shipping box.

<u>B8:</u> Repeat Steps B2 through B7 for the other acquired canisters at S1, S2, and S3, and for the field travel blank and make any required notes on COC. Pick up of acquired canisters is now complete.

-----Deploy new 24-hr canisters -----

<u>B9:</u> At S1, make any required changes to the 24-hr canister timers and document these changes in field project records.

<u>B10:</u> Remove a new canister from the shipping box and ensure the canister sample tag sample ID and COC sample ID match. Complete the ID on the COC and sample tag to indicate the data and time of planned canister acquisition and the type of sample.

<u>B11:</u> Connect the manual pressure gauge to the canister and briefly open and close valve to measure and record the final field pressure of the 24-hr canister on the COC. The final pressure should be 29 in Hg \pm 2 in Hg. Add notes to COC as needed and contact field team lead if out of tolerance.

<u>B11:</u> Connect to the timer.

<u>B12:</u> Repeat Steps <u>B9</u> through <u>B11</u> for the other at S1, S2, and S3.

<u>B13:</u> Deploy the field travel blank and move QA samples between sites as per plan.

<u>B14:</u> Confirm that all paired timers are configured to create simultaneous acquisitions at each stie as per sampling plan and complete deployment sections of COC.

<u>B15:</u> Secure sites, new canisters are now prepared for acquisition.

<u>B16</u>: Access electronic project record file folder and open "Verona 24-hr Canister Master Table.xlsx". For the acquired canisters that have been retrieved from the field, complete the following entries of the 24-hr Canister Master Table:

- 24-hr Can Sample ID
- Acquisition Date (mm/dd/yy)
- Acquisition Start (hr:min)
- Acquisition Stop (hr:min)
- Field Notebook and Page #
- Location Acquired (S1, S2, or S3)

<u>B17</u> Perform 100% inspection of COC forms, field notes, and 24-hr Canister Summary table to ensure they are complete, accurate, and possess consistent information.

<u>B18</u>: Package and ship canisters and COC to ERG.

<u>B19</u>: Complete the remaining fields of the 24-hr Canister Summary table when information is available from the Laboratory.

24-hr Can Sample ID	Acquisition Date (mm/dd/yy)	Acquisition Start (hr:min)	Acqusition Stop (hr:min)	Field A Flag? Notebook and Pield QA Flag? Page#	Field QA Flag? (Y/N)	Location Acquired (S1, S2, or S3)	Lab Analysis ID	Lab QA Flag?
-V-								
۷-								
۷-								
۷-								
۲-								
۷-								,
۷-								
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۲-								

Table B1: 24-hr Canister Summary Table

Appendix C: GMAP Survey QA and Data Forms

Prior to these daily QA checks, the GMAP vehicle, battery supplies, and equipment must be fully operational (verified by trained personnel) and the Picarro G2920 must be "warmed up" by continuous operation for a minimum of 45 minutes. All equipment used in the GMAP must documented (i.e., the serial numbers of each instrument in the project record), so that it is traceable to the daily QA forms. The general timestamp off set of the Picarro and the MEMS computer must be known and be part of the project record. The daily GMAP survey QA check includes a single point calibration check (cal-check) of the Picarro G2920, with advanced testing of conducted prior to the field deployment.

The QA equipment needed to conduct the GMAP survey daily QA procedure includes calibrated Alicat MFCs and MFS, true North handheld compass (or knowledge of "North", from Google Earth[™] imagery and ground-visible landmarks), handheld battery-operated fan, handheld GPS or (or knowledge of current GPS coordinates, from Google Earth[™] imagery and ground-visible landmarks). The Picarro cal-check gas standard (default 100 ppbv EtO, 9 ppm CH₄, in N₂) must be positioned within 10 m of the GMAP vehicle and placed downwind, with two-stage regulator installed. A ¼″ stainless-steel Swagelok[™] Tee and 3 additional 10 m lengths high density polyethylene tubing (P/N 50375K41, McMaster-Carr, Atlanta, GA), 6.4 mm outer diameter, 3.2 mm inner diameter are required for gas standard supply and a 10 m length of ½″ diameter piece of flexible tubing for the Picarro pump exhaust.

This procedure requires completion of the Daily GMAP QA form found directly in Appendices C. The form matches the procedures outlined below. Complete following steps (C1 through C16) prior to each field deployment and as necessary to check operation.

<u>C1:</u> Record the QA Form ID, QA-**NNN** where "**NNN**" is sequentially- incremented QA trial number (e.g., 01, 02, etc. associated with the three-month deployment for Verona and any other QA activity). The operator must sign the form.

C2: Record Date and Start Time for the QA test (Record End Time when QA is complete).

<u>C3:</u> Record serial numbers of the mass flow sensor (MFS) and mass flow controller (MFC) to be used in the Picarro cal-check.

<u>C4:</u> Record information on the gas standards to used.

<u>C5:</u> Position the GMAP vehicle away from upwind emission sources in a safe stationary location with the front of the vehicle pointed due North. Turn the engine off and verify that all the GMAP instruments (e.g., Picarro, AiMar, and 3D sonic, if used) are status "green" in MEMS. Ensure that the GPS is set to "AirMar" and not "hemisphere" (default configuration). Put a check mark in the form to indicate that the step is complete.

<u>C6:</u> Start the MEMS stationary file and record file name and storage location. Confirm data is streaming in MEMS for Picarro EtO, CH_4 , and CO_2 , and AirMar GPS, wind speed, wind direction, temperature, and atmospheric pressure (system is recording). Put a check mark in the form to indicate that the step is complete.

<u>C7:</u> Confirm that the AirMAR GPS reading is reasonably close to the independently known GPS coordinates where ethe QA test is being conducted. As an example, the potential GMAP location G7 of Figure A6.2.1 is an easily discernable location at the northeast corner of S. 2nd street and E. Ella Street with an approximate Google EarthTM GPS coordinate of 36°57'38.34"N, 93°47'42.46"W. A reasonable GPS check would be a result of 36°57'38.XX"N, 93°47'42.XX"W, where XX is any two digits. Put a check mark in the form to indicate that the step is complete.

<u>*C8*</u>: There are two ways to execute this test. If the ambient wind is steady and is emanating from a direction of clear fetch (open area), note the direction using the using a bird feather on string and confirm that the wind monitor is indicating the proper direction to within \pm 20 deg and confirm that the wind speed is reasonable compared to forecasted values for the area. If the ambient wind is calm, use a handheld fan (e.g, RYOBI ONE+ 18V Cordless 4 in Model #PCF02KN, Home Depot) placed 1 m from AirMar to apply simulated wind from due South for 1 minute and confirm wind direction and auto North functionality of AirMar is reasonable (i.e., 180 deg \pm 20 deg). The simulated wind speed should be approximately 2 m/s and should go to zero when the fan is turned off (under calm conditions). Carefully record the start time of the fan test and verify the reasonableness of the result. Put a check mark in the form to indicate that the step is complete.

<u>C9:</u> If a stationary 3D sonic is used with MEMS, repeat <u>C.8</u> for the tripod-mounted 3D Sonic anemometer that has been rotated to point North. Put a check mark in the form to indicate that the step is complete.

<u>C10</u>: Visually observe the readings in MEMS for ~30 seconds and record the approximate mean ambient baseline EtO, CH₄, and CO₂ readings. If EtO = 0.0 ppbv \pm 0.3 ppbv, and CH₄ = 1.9 ppm \pm 0.2 ppmv, and CO₂ = 400 ppmv \pm 30 ppmv the values are within tolerance, move to next step, otherwise consult field team lead.

<u>C11:</u> Uncoil the 10 m Picarro sampling line from the roof of the GMAP vehicle and connect it to the operating MFS and record the Picarro flow rate. The flow rate of the instrument should be 225 sccm \pm 50 sccm. Using the measured Picarro flow rate, calculate the QA spike flow rate by dividing the Picarro flow rate by 10 (e.g., Picarro flow rate = 220 sccm, QA spike flow rate = 220/10 = 22 sccm), record.

<u>C12:</u> Disconnect the sampling line from the MFS and perform the following Picarro cal-check steps:

• Ensure that the GMAP vehicle and personnel are upwind of the QA gas standard in a wellventilated position prior to gas release to avoid unnecessary exposure. Put a check mark in the form to indicate that the step is complete.

• Ensure that the exhaust of the Picarro pump is ventilated outside of the vehicle (use additional tubing) and is venting in a downwind direction so that the EtO from the QA gas challenge does not fill the vehicle or unnecessarily expose personnel (refer to field safety plan).

- Place the inlet of the uncoiled 10 m GMAP sampling line on a tripod and position it away from and downwind of the GMAP vehicle.
- Connect a ¼" stainless-steel Swagelok™ Tee to the GMAP sampling line inlet located on the tripod (if a Tee is not already present).
- Connect one of the Tee inlets to the QA gas supply line and **make sure that the third inlet of Tee remains open to ambient air (do not block Picarro flow).**
- Connect the other end of the QA gas supply line to the output of the MFC.
- Connect the final QA line to the two-stage regulator (set at 30 psi) attached to the QA gas standard.
- Set MFC flow rate to the QA spike flow rate (do not start the flow)
- Verify the cal-check setup and safety conditions in the QA form

<u>C13</u>: Record the exact local cell phone time (target within 2 seconds) of the of the start of the QA spike flow and continue gas flow for 5 minutes total. The accurate start time of gas flow is used to establish timing offsets between the MEMS and the Picarro and the delay in registering plumes while in motion.

<u>C14</u>: During the final three minutes of QA spike gas flow, visually observe the readings in MEMS for ~30 seconds and record the approximate mean EtO, CH_4 , and CO_2 readings displayed on the QA form. A more precise value may be obtained from the average of Picarro's response to the final three minutes of QA gas flow to pre-flow values using MEMS recorded data, but typically the observed value from the MEMS is sufficient for in-field verification of operation. Make sure to stop the gas flow once the readings have been recorded.

<u>C15</u>: Subtract the values recorded in step C<u>.10</u>. from the values recorded under QA spike gas flow recorded in step C<u>.14</u>: and record as "delta values" in the QA form. The delta values for EtO, CH₄ and CO₂ should be within the QA tolerance values of EtO = 8.0 ppbv \pm 2.0 ppbv, and CH₄ = 0.9 ppmv \pm 0.2 ppmv, and CO₂ = 0.0 ppm \pm 30 ppmv. If within tolerance, move to next step, otherwise consult field team lead. Note that the EtO and CH₄ nominal value can differ from 8.0 ppbv depending on the actual cylinder concentration and age.

<u>C16</u>: Stop MEMS file recording, record End Time of GMAP Daily QA test at the top of the form, return GMAP back to physical sampling configuration and properly store QA gear and gas cylinders.

Step C1	QA Form ID: QA <u>-</u>	Operator Signature:	
Step C2	Date:	_Start Time:	_End Time:
Step C3	S/Ns of MFS and MFC Used :_		
Step C4	Gas Standards Used:		
Step C5	GMAP Postioned N?	_GMAP Engine off?	GMAP Inst. Green?
Step C6	GMAP MEMS File Name and	Location	_System Recording?
Step C7, Step C8	GPS Reasonable?	Fan Test Start	_Wind Reasonable?
Step C9	If 3D-sonic is installed	Fan Test Start	_Wind Reasonable?
Step C10	EtO (0.0 ± 0.2 ppb):	_CH _{4 (} 1.9 ± 0.2 ppm)	_CO ₂ (400 ± 30 ppm)
Step C11	Measured Flow Rate:	Calc. Spike Flo	w Rate:
Step C12, Step C13	Cal Setup and Safety Verified	?Gas Flow Start	Time:
Step C14	QA EtO:	_QA CH₄:	_QA CO ₂ :
Step C15	Delta EtO:	_Delta CH₄:	Delta CO ₂ :
Delta QA	tolerence: EtO = 8.0 ± 2.0 ppt	o, CH4 = 0.9 ± 0.2 ppmv, and 0	CO2 = 0.0 ±30 ppmv.
B5.3.16	MEMS field stopped, End Tir	ne recorded, GMAP config ret	ored?
Notes:			

Table C2: GMAP Survey Data Form

GS Data Form ID: GS	Opera	tor Signature:
Date:	_Start Time:	_End Time:
Full Map:	_Transect:	_Stationary:
MEMS File:	Picarro File:	Status Green?:
Upwind Ambient EtO:	_Upwind Ambient CH ₄ :	_ Upwind Ambient CO ₂ :
Describe Trial:		
If EC was acquired, record EC	information here, in EC summ	ary table, and COC or (N/A)
Record End Time for Mobile	Test on Line 2	

Appendix D: CGS Field Acquisition and Record Procedures

The CGS field acquisition and record procedures included the following steps to be executed by trained personnel. The CGS procedures assume that the canister grab sample is acquired in conjunction with a fully documented GMAP mobile survey stationary data acquisition trial.

<u>D1</u>. Receive shipping case containing clean and evacuated CGS canisters and transport to the field site.

<u>D2:</u> Prepare to acquire a CGS by first ensuring the collocated GMAP stationary location data acquisition trial is properly operating and documented. Use the active GS data form (Appendix C table C2) to describe the CGS acquisition and location.

<u>D3:</u> Remove a CGS from shipping container and identify the unique canister ID and location on COC.

<u>D4:</u> Install pressure gage on CGS quick connect and measure and record initial pressure on COC.

<u>D5:</u> If the pressure is >-27" Hg, the canister is invalid, note on COC and choose another canister.

D6: Remove the manual pressure gage.

D7: Install the CGS manual sampling rig.

D8: Hold the canister within 1 m from GMAP inlet in free-flowing air (do not block with body).

D9: Use MEMS computer timestamp as the clock.

<u>D10</u>: Open the valve for 30 seconds then close and record the exact start and stop times in the COC and GS data form.

D11: Remove the CGS sampling rig.

D12: Install pressure gage on CGS quick connect and measure and record final pressure on COC.

<u>D13</u>: Complete the COC sample ID and record the full ID on the GS data form (describe as needed).

<u>D14</u>: Access electronic project record file folder and open "Verona CGS SummaryTable.xlsx" and complete the following entries of the CGS summary table.

- CGS Sample ID
- CGS Date (mm/dd/yy)
- CGS Start (hr:min:sec)
- CGS Stop (hr:min:sec)
- GS Form ID
- Field QA Flag? (Y/N)

<u>D15:</u> Perform 100% inspection of COC forms, GS data forms, and CGS summary table to ensure they are complete, accurate, and possess consistent information.

<u>D16:</u> Package and ship canisters and COC to EPA ORD CEMM VOC Lab.

<u>D17</u>: Complete the remaining fields of the CGS canister summary table when information is available from the Laboratory.

CGS Sample ID	CGS Date (mm/dd/yy)	CGS Start (hr:min:sec)	CGS Stop (hr:min:sec)	GS Form ID	Field QA Flag? (Y/N)	Location Acquired	Lab Analysis ID	Lab QA Flag? (Y/N)
۷-				GS-				
۷-				GS-				
۷-				GS-				
۷-				GS-				
۷-				GS-				
۷-				GS-				
۷-				GS-				
۷-				GS-				
۷-				GS-				
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Table D1: CGS Summary Table

Appendix E: 3D Sonic Procedure

Reference the following equipment manuals contained on the project drives for the RM Young 81000V 3D sonics, Acumen data loggers, solar power/battery systems. The physical fixturing and instrument set up will be configured and tested by Jacobs's Technology technical personnel prior to deployment to the field. This project will set up two 3D sonic systems at S1 on the SPod deployment pallet (reference Figure B1.4). Execute the following steps to set up and operate the units.

<u>E1:</u> Set up SPod pallet, solar panels, and battery systems.

<u>E2:</u> Carefully remove 3-D sonics from the transport boxes and attach to the SPod pallet at approximately 3 m above ground level.

E3: Slightly loosen pole clamps and rotate the sonics until properly pointing towards true North.

<u>E4:</u> Tighten pole clamps and take photos documenting alignment for the project record.

E5: Connect Acumen dataloggers to 3D sonics.

E6: Install SD cards into Acumen dataloggers.

E7: Connect power of 3D sonics and Acumen dataloggers to solar panel/battery supply.

<u>E8</u>: Record the local cell phone time of power on.

<u>E9:</u> Record 5 minutes of data.

<u>E10:</u> Using hand-held fan, conduct fan test by holding fan 1 m from each sonic for 30 seconds so as to create a simulated wind from due South. Carefully record the start and stop times time of the tests in project field notebooks.

<u>E11:</u> Power off Acumen, remove SD card and read in flied computer. Confirm data is being recorded and document any timestamp offset in project field notes. Reinstall SD card, restart datalogger.

E12: Repeat Step E11 for other Acumen data logger.

<u>E13:</u> If the time stamps between the two 3D sonics do not agree with each other and with local cell phone time to within 10 sec, take corrective action to synchronize the units.

<u>*E14:*</u> During each weekly visit, ensure the rotation of the 3D sonics haven't changed by comparing to original field photos.

E15: During each weekly visit, repeat E10 through E13.

<u>E16:</u> Ensure 3D sonic data is backed-up weekly.

Appendix F: SPod Procedures

Reference Sensit SPod Fenceline Sensor and Canister Grab Sample System Deployment and Operation, J-AMCD-SFSB-SOP-4380-2 (ref). Complete all procedures and QA forms contained in the SPod SOP and document in project records.