



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

REGION 4

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12/21/2022

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LSASD Project Number: 18-0317

Mr. Butler:

We have reviewed the following document that you submitted for approval:
Quality Assurance Project Plan for the North Carolina Division of Air Quality Urban Air Toxics (UAT) Network for Collection and Analysis of Volatile Organic Compounds (VOCs) and Carbonyls DAQ-01-008 Revision 0 December 2022.

The quality assurance elements within this QAPP were compared to EPA regulations and current guidance. The stated procedures appear to be clear, sound, and appropriate as written, to the extent they can be evaluated. EPA approval of this document is granted. Approval of this QAPP does not constitute a waiver from any regulatory requirements. NC DAQ remains accountable for ensuring the Urban Air Toxics project adheres to all the applicable requirements and that the data generated are of sufficient quality to be used for the stated objectives. This QAPP should be updated by NC DAQ by August 2023 to be in compliance with the applicable portions of the NATTS TAD R4 as discussed previously.

If you have any questions regarding these comments, please contact Gillian Walshe-Langford at 706-355-8619 or via email at walshelangford.gillian@epa.gov.

Sincerely,

KEITH HARRIS Digitally signed by KEITH HARRIS
Date: 2022.12.21 10:29:43 -05'00'

Keith Harris, Section Supervisor
Quality Assurance Section

Mission: To provide sound Science to our customers through superior environmental evaluation.

Vision: To be a solutions-oriented organization and seen as a leader in sound science through innovation, responsive customer service, and cutting-edge expertise.

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Secretary
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Director



DAQ-01-008

**QUALITY ASSURANCE PROJECT PLAN
FOR THE NORTH CAROLINA DIVISION OF AIR QUALITY
Urban Air Toxics (UAT) Network for the Collection and Analysis of Volatile
Organic Compounds and Carbonyls
Revision 0**

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DISCLAIMER

This quality assurance project plan, or QAPP, covers the North Carolina Department of Environmental Quality (NCDEQ), Division of Air Quality or DAQ Urban Air Toxics (UAT) network for speciated volatile organic compounds (VOC), carbonyls and meteorological parameters. Additionally, this QAPP will be followed by local programs (Forsyth County Office of Environmental Assistance and Protection, Mecklenburg County Air Quality part of the Land Use and Environmental Services Agency, and the Asheville-Buncombe Air Quality Agency (ABAQA). It is the responsibility of the local programs to follow this QAPP and applicable standard operation procedures (SOP) referenced within this document.

Mention of commercial products or trade names should not be interpreted as endorsement.

ACRONYMS AND ABBREVIATIONS

AB	Asheville-Buncombe	ECB	Electronics and Calibration Branch
ABAQA	Asheville-Buncombe Air Quality Agency	EMP	enhanced monitoring plan
ADQ	audit of data quality	EPA	United States Environmental Protection Agency
ADT	average daily traffic	ESMB	extraction solvent method blank
Ag	Agricultural	FB	Field blank
AGL	above ground level	FRO	Fayetteville regional office
AMTIC	Ambient Monitoring Technology Information Center	GC	gas chromatograph
AQS	Air Quality System	hPa	hectopascal, which equals 1 millibar
ASL	analytical support laboratory	HPLC	high performance (pressure) liquid chromatograph
AT	ambient temperature	ICAL	initial calibration
BFB	bromofluorobenzene	ID	Identification
BP	barometric pressure	IDL	instrument detection limit
CAA	Clean Air Act	IDOC	initial demonstration of capability
CAP	corrective action plan	in Hg	inches of mercury
CAR	corrective action report	IP	implementation plan
CBSA	core-based statistical area	IPA	instrument performance audit
CCV	continuing calibration verification standard	IS	internal standard(s)
CDOC	continuing demonstration of capability	ISO	International Organization for Standardization
CDS	chromatography data system	LAB	Laboratory Analysis Branch
CFR	Code of Federal Regulations	LCS	laboratory control sample
COA	certificate of analysis	LCSD	laboratory control sample duplicate
COC	chain of custody	LIMS	Laboratory Information Management System
CTS	collocated transfer station	LST	local standard time (for NC that is Eastern Standard Time)
CV	coefficient of variation	m	meter(s)
DART	Data Analysis and Reporting Tool	MB	method blank
DAS	data acquisition system	MDL	method detection limit
°C	degrees Celsius	µg	microgram(s)
DIT	North Carolina Department of Information Technology	µg/cartridge	micrograms per cartridge
DNPH	2,4-dinitrophenylhydrazine	µg/m ³	micrograms per cubic meter
DQA	data quality assessment		
DQI	data quality indicator		
DQO	data quality objective		
DST	daylight savings time		

MFC	mass flow controller	QA	quality assurance
min	minute(s)	QAIP	quality assurance implementation plan
mL/min	milliliters per minute	QAPP	quality assurance project plan
mm	millimeter(s)	QA/QC	quality assurance/quality control
mmHg	millimeters mercury	QC	quality control
MQO	measurement quality objective	QMP	quality management plan
m/s	meters per second	QS	quality system
MS	mass spectrometry	RCO	Raleigh central office
MUR	Method Update Rule (Section 4.1 of the NATTS TAD Revision 3)	RH	relative humidity
		RPD	relative percent difference
NAAQS	national ambient air quality standard	RRF	relative response factor
NATTS	National Air Toxics Trends Stations	RRO	Raleigh regional office
NC	North Carolina	RSD	relative standard deviation
NCDEQ	North Carolina Department of Environmental Quality	RT	retention time
NCORE	National Core	RTS	retention time standard
ng	nanogram(s)	SB	solvent blank
NIST	National Institute of Standards and Technology	SLT	state, local, or tribal (monitoring organization)
nm	nanometer(s)	SOP	standard operating procedure
NWS	National Weather Service	SSCV	second source calibration verification
OAQPS	Office of Air Quality Planning and Standards	TAD	technical assistance document
OTR	Ozone Transport Region	TSA	technical systems audit
PAMS	photochemical assessment monitoring station	TSS	technical services section (part of the NCDEQ)
pdf	portable document format	UAT	urban air toxics
PM	particulate matter	UHPLC	ultra-high performance (pressure) liquid chromatograph
ppb	part(s) per billion	UPS	United Parcel Service
PPB	Projects and Procedures Branch	US	United States
ppbv	part(s) per billion by volume	USS	United States Ship
ppm	part(s) per million	UV	ultraviolet
PQAO	primary quality assurance organization	VOC	volatile organic compound
psi	pounds per square inch	WARO	Washington regional office
psig	pounds per square inch gauge	WD	wind direction
PT	proficiency test	WiRO	Wilmington regional office
PTFE	polytetrafluoroethylene	WS	wind speed

A. PROJECT MANAGEMENT

The DAQ established a UAT monitoring network in conjunction with the National Air Toxics Trends (NATTS) network designed by the United States Environmental Protection Agency (EPA) in 1994 and to meet the requirements in section 112(k) and Urban Air Toxics in the 1990 Clean Air Act Amendments (CAAA). The origination of the monitoring network was due in part to the EPA's effort to address toxic air pollutant (TAP) emissions in urban areas. This effort is conducted by the DAQ, as well as local environmental programs within the state to assist in the establishment and operation of the DAQ UAT network.

The DAQ UAT network or program is a collaborative effort of the following state and local agencies:

- The NC Department of Environmental Quality (NCDEQ),
 - The NC Division of Air Quality (DAQ),
 - Ambient Monitoring Section (AMS)
 - The Electronics and Calibration Branch (ECB)
 - The Laboratory Analysis Branch (LAB)
 - The Projects and Procedures Branch (PPB)
 - Fayetteville Regional Office (FRO)
 - Raleigh Regional Office (RRO)
 - Washington Regional Office (WARO)
 - Wilmington Regional Office (WiRO)
- The Asheville-Buncombe Air Quality Agency (ABAQA)
- The Forsyth County Office of Environmental Assistance and Protection
- Mecklenburg County Air Quality, a part of the Land Use and Environmental Services Agency

This QAPP describes the DAQ UAT network management, personnel, quality assurance (QA) practices, sampling operations, meteorological data collection, laboratory analyses of field-collected samples, management, auditing, data collection, and data reporting.

A1 Title and Approval

Title: **Quality Assurance Project Plan for the North Carolina Division of Air Quality Urban Air Toxics (UAT) Network for Collection and Analysis of Volatile Organic Compounds (VOCs) and Carbonyls** is hereby recommended for approval and commits the State of North Carolina, Division of Air Quality to follow the elements described within.

DocuSigned by:

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Michael Abraczinskas, Director North Carolina Division of Air Quality Date

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Patrick Butler, Ambient Monitoring Section Chief Date

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Jim Bowyer, LAB Environmental Program Supervisor Date

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Joette Steger, PPB Environmental Program Supervisor Date

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Steven Walters, PPB Chemist II Date

United States Environmental Protection Agency:

EPA Region 4 Designated Approving Official Date

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A3 Distribution List

The analytical support laboratory (ASL) is the LAB which is an independent branch under the North Carolina Division of Air Quality, Ambient Monitoring Section. This facility is located at 4403 Reedy Creek Road, Raleigh, NC 27607. As a result, there is no separate UAT QAPP for the LAB as all requirements for both collection and analysis of the samples are covered in this document. Additionally, all state, local, and tribal (SLT) agencies discussed in this document will adhere to the procedures referenced in this document and procedures described in this document where applicable. Table A3-1 provides the DAQ UAT network distribution list,

Table A3-1. DAQ UAT Network Distribution List

Name/ UAT Position	Organization	Phone	e-mail
Michael Abraczinskas, DAQ Director	NCDEQ DAQ	919-707-8447	michael.abraczinskas@ncdenr.gov
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Table A3-1. DAQ UAT Network Distribution List

Name/ UAT Position	Organization	Phone	e-mail
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A4 Project/Task Organization

The DAQ is a primary quality assurance organization (PQAO) as defined in 40 CFR Part 58, Appendix A, Section 1.2. The DAQ director has organized the ambient monitoring section (AMS) into three main branches: The PPB, the LAB and the ECB, The chief has responsibility for managing these branches in conformance with DAQ policy, The chief delegates the responsibility and authority to develop, organize, and maintain and implement quality programs to the supervisors of each branch, in accordance with the EPA approved NCDEQ quality management plan (QMP).

These supervisors have direct responsibility for assuring data quality. For the DAQ UAT network, the chief will rely on all three AMS branches, and its personnel, for program implementation and QA oversight, including preparation of this QAPP, SOPs, and auditing. The DAQ regional offices and local programs will assist by collecting and shipping UAT samples to the LAB for analysis and providing review of meteorological parameter data where applicable.

Figure A4-1 presents an organization chart of the personnel participating in the DAQ UAT monitoring effort and immediately following is Table A4-1 providing a more detailed description of project personnel roles,

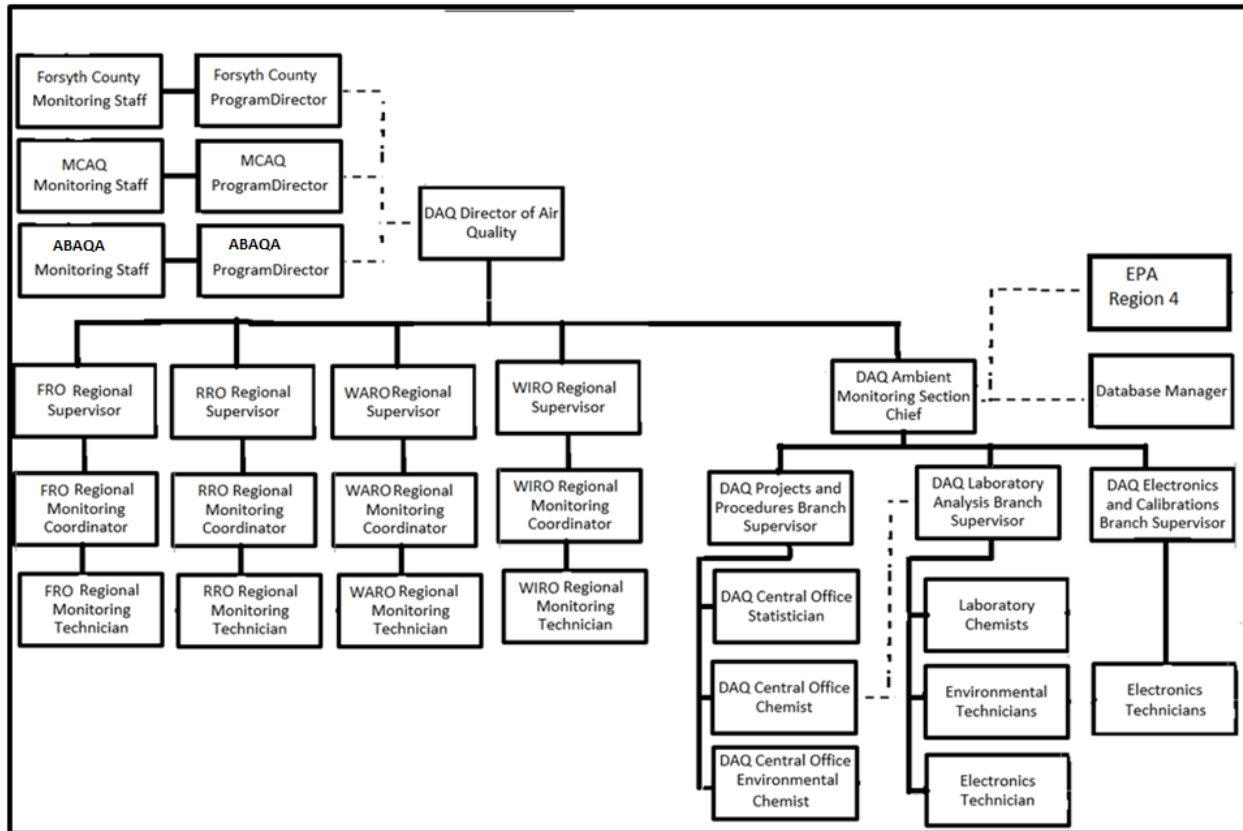


Figure A4-1. DAQ UAT Project Organization Chart

Table A4-1. DAQ UAT Program Roles of Key Project Personnel

Position	Role
DAQ Director	The DAQ director, or director, supervises the chief and the regional office air quality supervisors. The director is responsible for ensuring adequate human and financial resources are available to support DAQ’s UAT monitoring program. The director has ultimate responsibility and final authority on all aspects of the UAT monitoring program. The director also serves as a liaison with other divisions in NCDEQ, with the North Carolina General Assembly, the North Carolina Department of Information Technology, or DIT, and with other regional air-monitoring agency organizations. The DAQ Director signs SOPs and QAPPs indicating final approval.
Local Program Director	The Local Program Directors have direct access to the DAQ director on all matters relating to DAQ’s UAT monitoring program, The local program directors maintain policies within their respective local program offices. They also acquire needed local program monitoring resources, verify implementation of quality programs, and recommend changes when needed in the UAT monitoring program. The local program directors provide input for the design of the UAT network, reviewing and approving the network plan as far as it affects their local program. They also supervise and delineate

Table A4-1. DAQ UAT Program Roles of Key Project Personnel

Position	Role
	duties for the local program monitoring coordinators and local program monitoring technicians.
DAQ Regional Supervisor	The DAQ regional supervisors have direct access to the DAQ director and DAQ AMS chief on all matters relating to DAQ's UAT monitoring program, The regional supervisors maintain division policies at the DAQ regional office level. They also acquire needed regional monitoring resources, verify implementation of quality programs, and recommend changes when needed in the UAT monitoring program. The regional supervisors provide regional input for the design of the UAT network, reviewing and approving the network plan as far as it affects their region. They also supervise and delineate duties for the regional monitoring coordinators and regional monitoring technicians.
DAQ AMS Chief	The DAQ AMS chief, or chief, serves as the QA manager, or QAM, and has direct access to the director on all matters relating to DAQ's UAT monitoring operation, The chief serves as the QAM, maintaining oversight of all QA activities, This position supervises the ambient monitoring staff and serves as the liaison to Region IV monitoring staff. The chief maintains overall responsibility for the UAT monitoring network design and review, subject to the director's approval, The chief approves and distributes division SOPs and QAPPs, The chief serves as the tiebreaker in the event of an impasse on how to handle corrective actions or make a judgment call on data validity. This position develops, administers, and maintains the QMP. When the chief chooses to do so, the chief certifies the air toxics and meteorological data by May 1 every calendar year. This position reviews the quarterly QA reports and the QC summaries to ensure DAQ attains the bias and precision limits. The chief serves as the document custodian by managing the agency's documents and records. The chief tracks corrective actions and determines their success. The chief participates in systems audits. The chief authorizes the installation and discontinuation of monitors within the system. This position also assures the DAQ central office chemists establish and implement QAPPs for each project as applicable, The chief reviews budgets, contracts, grants, and proposals. If the section chief (or designee) is unavailable to perform these duties, the chief will assign someone to fulfill these duties, or if the chief is unable to make that assignment, the director will assign someone to fulfill these duties. The DAQ AMS Chief signs SOPs and QAPPs indicating final approval.

Table A4-1. DAQ UAT Program Roles of Key Project Personnel

Position	Role
Database Manager	Although the database manager does not report directly to the chief, this position has direct access to the chief on all matters relating to DAQ's UAT meteorological database, The database manager maintains the central office data polling station, ensuring it polls meteorological data for each hour of every day. This position ensures the correct transfer of meteorological data to the DAQ Internet-Based Enterprise Application Management (IBEAM) database, the EPA's AirNow-Tech database and the DAQ real-time air quality data webpage. This position participates in technical systems audits (TSAs). The database manager also uploads UAT Air Quality System (AQS) ready text files and meteorological data to the EPA's AQS and serves as the AQS administrator for DAQ. This position also maintains and updates the RCO data polling software and the AQS database when sites and monitors are established or shut down. This position signs SOPs when the primary SOP author is the Database Manager.
LAB Supervisor	The LAB Supervisor manages the LAB chemists, LAB electronics technician, and LAB environmental technicians. This position judges the success of implemented corrective actions. This position is the point of contact for any matter relating to laboratory results, procedures, and laboratory operations. This position also participates in systems audits. This position reports directly to the DAQ AMS chief. The LAB Supervisor signs approved SOPs and QAPPs.
LAB Laboratory Chemists	The laboratory chemists are responsible for the analysis of UAT samples (VOCs and carbonyls). The chemists are responsible for maintaining analysis instruments including analytical support equipment and instrument modules and detectors to ensure functionality and provide accurate and reliable data. Within their specialty, the laboratory chemists process analytical instrument data through the Level 1 data review process and perform Level 2 data reviews on instrument methods with which they are not directly involved. The chemists generate instrument reports, upload data to master spreadsheets, review sampler information forms and chain-of-custody (COC) forms, The chemists generate data review packages and reports for the Level 2 data reviewer and Level 3 data reviewer. The chemists also participate in systems audits. This position reports directly to the LAB supervisor. Laboratory chemists sign SOPs when the primary SOP author is the laboratory chemist
LAB Electronics Technician	The LAB electronics technician reports to the LAB Supervisor and is responsible for installing UAT sampling equipment at the monitoring sites. This technician also maintains and tracks an inventory of replacement spare parts and equipment, including supplies and consumables, to prevent unnecessary downtime. This technician certifies transfer standards or sends them to the vendor for recertification as well as returns any local primary standards to the vendor or EPA for recertification and periodically checks the calibration of backup local primary standards to ensure quality calibrations.

Table A4-1. DAQ UAT Program Roles of Key Project Personnel

Position	Role
	The LAB electronics technician maintains documentation on all transfer standards and local primary standards, This position conducts annual periodic checks, audits and calibrations of air sampling equipment and LAB support equipment, This technician also assists in prescribing corrective actions, participates in systems audits, and recommends changes to the sampling methods, when needed. The LAB Electronics Technician will sign SOPs when the primary SOP author is the LAB Electronics Technician.
LAB Environmental Technicians	The environmental technicians are responsible for shipping and receiving VOC canisters and carbonyl cartridges to and from the laboratory. They are also responsible for cleaning VOC canisters prior to field deployment for the collection of VOCs. The environmental technicians perform UAT field sampling activities. The environmental technicians report directly to the LAB supervisor. LAB environmental technicians will sign SOPs when the primary SOP author is the LAB environmental technician.
PPB Supervisor	The PPB supervisor reports to the DAQ AMS chief. This position supports and assists the DAQ AMS chief in providing oversight of all QA activities and communicates with the QAM to bring attention to QA matters. This supervisor also verifies implementation of all AMS QAPPs and procedures and assists the chief with preparing the annual network plan and 5-year network assessment, The PPB supervisor responds to public records requests and statistical consulting requests, participates in systems audits, ensures training availability and utilization, and approves and implements procedures. The PPB supervisor signs all SOPs and QAPPs indicating final approval.
DAQ Central Office Statistician	The DAQ central office statistician, reports to the PPB Supervisor, provides statistical programming support to the PPB supervisor and other staff of the central and regional offices. The statistician assists the branch supervisor with responding to consulting and data requests, participates in training and certification programs to keep current on technology and interprets data. Each business day the statistician also develops and maintains statistical reports that include tabulations of yesterday's hourly raw meteorological data. The statistician also prepares statistical analysis and summaries of the data, including graphs, for QA and reporting. The statistician participates in systems audits and prepares and delivers data and statistical interpretation of the data to the regional offices and DAQ,
DAQ Central Office Environmental Chemist	The DAQ Central Office Environmental Chemist reports to the PPB supervisor. Duties include conducting quarterly completeness evaluations and performing audits of data quality (ADQs) and generating an ADQ report and submits this report to the PPB supervisor and DAQ central office chemist. This position also performs internal TSAs, This position will identify data quality problems and initiate corrective actions.

Table A4-1. DAQ UAT Program Roles of Key Project Personnel

Position	Role
DAQ Central Office Chemist	<p>The DAQ Central Office Chemist reports to the PPB and LAB supervisors. Duties include assessing the effectiveness of the network system, ensuring timely and appropriate UAT SOP and UAT QAPP updates, and validating VOC and carbonyl data by serving as the level 3 reviewer. This position also verifies all staff performing UAT sampling and analysis methods including data review procedures adhere to approved procedures and perform the required QA/QC activities required by the sampling and analysis methods. This position also maintains QA/QC records and QA/QC summary reports, flags suspect data, and assesses and prepares reports on overall method precision to assess DAQ's ability to achieve the overall UAT monitoring program data quality objective. The chemist transforms validated UAT sampling and analysis data into text files and sends these files to the database manager for reporting to EPA's AQS database. The chemist also prepares data reports using validated UAT sampling and analysis data for other data users. The chemist participates in systems audits, identifies data quality problems, and initiates corrective actions. Also, this position provides UAT sampling and/or analysis training and certification to UAT monitoring program personnel as needed. The chemist responds to audits of data quality (ADQs) reports provided by the DAQ central office environmental chemist. The DAQ central office chemist signs SOPs and QAPPs when the primary SOP or QAPP author is the DAQ central office chemist.</p>
ECB Supervisor	<p>The ECB supervisor has direct access to the chief and has the responsibility and authority to identify quality problems and initiate corrective action; schedule and document instrument performance audits (IPAs) and standard certifications; review and approve QAPPs and SOPs; supervise the ECB electronics technicians; participate in systems audits; and provide and document training and certification of ECB personnel.</p>
ECB Electronics Technician	<p>The ECB electronics technicians report to the ECB Supervisor and are responsible for installing UAT meteorological equipment and helping as needed with installation of UAT sampling equipment at monitoring sites. They maintain and track an inventory of replacement equipment and spare parts, including supplies and consumables, to prevent unnecessary downtime. They calibrate, certify, and track transfer standards or send them to the vendor for recertification, return any "local primary standards" to the vendor or EPA for recertification and periodically check the calibration of backup local primary standards to ensure quality calibrations. They maintain documentation on all transfer standards and local primary standards. They conduct annual audits and calibrations of the meteorological equipment. They also assist in prescribing corrective actions, participate in systems audits and recommend changes, when needed, in the QA/QC program. They perform and document all major maintenance and repair of meteorological equipment as described by SOPs contained in this document,</p>

Table A4-1. DAQ UAT Program Roles of Key Project Personnel

Position	Role
<p>DAQ Regional Ambient Monitoring Coordinators/ Local Program Monitoring Managers</p>	<p>Regional ambient monitoring coordinators and local ambient monitoring coordinators, report directly to their respective regional supervisor or local program supervisor, The coordinators have the overall responsibility of ensuring the implementation of the QA/QC program at the regional level or local program level, They direct the activities of the regional ambient monitoring technicians or local program ambient monitoring technicians, Their responsibilities include: coordinating and reviewing the collection of environmental data; implementing the DAQ QA/QC program within the region; acting as conduits for information to regional monitoring technicians; training other regional ambient monitoring coordinators and regional monitoring technicians in the requirements of the QAPP and SOPs; providing a backup to the regional ambient monitoring technicians; participating in systems audits; recommending changes, when needed, in the QA program; providing regional input on the design and documentation of the monitoring network; performing level 2 data verification activities for UAT meteorological data including the flagging of suspect data; reviewing electronic logbooks, or e-logs, other documentation and the work of the ambient monitoring technicians to ensure they follow the QAPP and associated SOPs; and documenting and assessing corrective actions.</p>
<p>DAQ Regional Ambient Monitoring Technicians and Local Program Monitoring Staff</p>	<p>The regional ambient monitoring technicians report to the regional supervisor. Their duties include ensuring that ambient monitoring programs implement the QA/QC elements of SOPs and QAPPs as well as training new regional coordinators and monitoring technicians in the requirements of the QAPPs and SOPs, They maintain the air toxics monitoring equipment as well as a supply of expendable monitoring items. They participate in training and certification activities, perform all required quality control, or QC, activities to ensure measurement quality objectives, or MQOs, are met as prescribed in the QAPP and SOPs and perform corrective actions to address any activities that do not meet acceptance criteria as prescribed in the QAPP and SOPs, They document deviations from established procedures and methods and report nonconforming conditions and corrective actions to their respective regional coordinator and regional supervisor, They conduct 40 CFR Part 58, Appendix E siting criteria evaluations annually as part of the annual network review process. They participate in systems audits and recommend changes, when needed, in the QA program. They also prepare corrective action reports (CARs), when needed, for the AMS.</p>
<p>Department of Information Technology</p>	<p>The DIT provides security for the ambient monitoring computers. They manage, in cooperation with the regional ambient monitoring and ECB electronics technicians and database manager, the computer located at the monitoring sites as well as the primary server that houses the ENVISTA Air Resources Manager, or ARM, database. Their responsibilities include ensuring the security of the computers and network, updating of the operating</p>

Table A4-1. DAQ UAT Program Roles of Key Project Personnel

Position	Role
	system and other standard software on the computer and ensuring that the technicians maintain adequate access to the computers to perform all necessary monitoring functions.

A5 Problem Definition/Background

In 1999, the EPA Office of Air Quality Planning and Standards (OAQPS) drafted an Air Toxics Monitoring Concept Paper,¹ developed in concert with regional monitoring staff, and which reflected comments from the State and Territorial Air Pollution Program Administrators and Association of Local Air Pollution Control Officials. The paper described the air toxics program and the role of ambient monitoring and presented a strategic monitoring approach for establishing an air-toxics monitoring network. This concept paper stated the objectives of this network as follows:

- Measure pollutants of concern to the air toxics program.
- Use scientifically sound monitoring protocols to ensure consistent data of high quality.
- Collect data to estimate annual average concentrations.
- Complement existing national and State/local monitoring programs.
- Reflect “community-oriented” urban population exposure.
- Represent geographic variability in annual average ambient concentrations.

In July 2004, the EPA OAQPS drafted a document, “National Monitoring Strategy – Air Toxics Component,” to provide a status of the air toxics monitoring program and to provide direction for agencies participating in the national air toxics monitoring program. The document set forth a clear distinction between State and Local scale programs and the national trends-scale program.

The State and Local scale monitoring programs provide a “flexible” approach to address a wide range of TAP issues:

“They are intended to probe potential problem areas throughout the nation that may require subsequent attention with respect to more dedicated monitoring and aggressive emission mitigation strategies. In some instances, these studies will be used to better characterize impacts of diesel emissions, or to define spatial concentration patterns throughout an area that simply is not achievable with a single [National Air Toxics Trends Site] NATTS site. 1”

The DAQ UAT network was a regulatory response, developed with these objectives in mind to focus on urban areas within the State and to work collaboratively with the three local government agencies that regulate air quality programs in their respective jurisdictions. The network complements the TAP programs of each agency and provides a “flexible approach” to address TAP issues in the local areas. The DAQ UAT network provides a framework to conduct more dedicated monitoring to characterize the spatial concentration patterns of specific TAPs

within urban areas. The DAQ UAT network provides the information which allows state and local programs to concentrate on specific problem areas.

The DAQ UAT network consists of seven, currently operating monitoring sites. These sites are in six urban areas across the state with one rural site for comparison, see Table A5-1 below for a list of DAQ UAT sites and the pollutants currently being monitored. Each monitoring site within the network contains equipment designed to collect 24-hour ambient air samples in silica-lined canisters for VOC analysis. Two of the sampling sites contain equipment designed to collect 24-hour ambient air samples using 2,4-dinitrophenylhydrazine (DNPH) cartridges for carbonyl analysis. The DAQ LAB in Raleigh, NC cleans and certifies the silica-lined sampling canisters and analyzes the canisters for VOCs. The DAQ LAB also certifies DNPH cartridges and analyzes sample extracts for Carbonyls.

A5.1 DAQ UAT Site Network

The DAQ director established seven sites for the DAQ UAT network. Six sites are in urban areas and one site is in a rural area. The EPA defines an urban area as a county with either a metropolitan statistical area (MSA) population of at least 250,000 or a county with at least 50% urbanization as defined by the US Census Bureau. The EPA defines a rural area as a county that has less than 50% urbanization as designated by the US Census Bureau. The DAQ may add or remove UAT sites based on the release of the 2020 US Census data or may add or remove sample collection methods as equipment, materials and personnel become available and are adequately trained. All UAT network sites will be released in the DAQ annual network plan which will supersede the UAT sites listed in the QAPP.

The current areas selected for DAQ UAT monitoring in NC are the following: Charlotte, Raleigh, Winston Salem, Wilmington, Greenville, Asheville, and Candor.

The Asheville, Winston-Salem and Charlotte sites are in residential areas relatively close to their downtown business districts. The Raleigh site is in a North Raleigh suburb approximately 7 miles north by northwest from downtown Raleigh. These four sites are on the premises of or near schools. Additionally, the Raleigh-Millbrook site is approximately 18 miles east of the center of the Raleigh-Durham-Chapel Hill combined statistical areas.

The Wilmington site is near the North Carolina Battleship Memorial on the west side of the Cape Fear River on Eagles Island, directly across from the downtown Wilmington area. Eagles Island is mostly wetland marshes located between the city and populated areas of eastern Brunswick County. There are industrial complexes to the north and west of the site and commercial loading docks located on the river to the north and south of the site.

The Greenville site is in an open field behind the Pitt County Soil & Water Conservation building approximately 2 miles north of downtown Greenville, NC in Pitt County.

The Candor site is the designated DAQ UAT background site. This site is on private property rented by the EPA from the Perry family. It borders on the Uwharrie National Forest approximately 2 miles southwest of Candor, NC. The Uwharrie Federal Game Lands are located

to the southeast and northwest of the site. The DAQ UAT sampling site network AQS site ID, site name, site address, latitude and longitude, and the types of sampling conducted are shown in Table A5-1 below.

Table A5-1. DAQ UAT Site Information

Site AQS ID	Site Name	Site Address	Latitude/ Longitude	Sampling Conducted
37-183-0014	Millbrook	3801 Spring Forest Road Raleigh, NC 27616	35. 856258 -78. 574190	VOC, Carbonyls, Meteorology
37-021-0035	Asheville	AB Technical Community College Campus 340 Victoria Rd Asheville, NC 28801	35.572406 -82.558722	VOC
37-067-0022	Winston Salem	1300 block of Hattie Ave, Winston-Salem, NC 27105	36.110950 -80.224424	VOC
37-119-0041	Garinger	Garinger High School 1130 Eastway Dr. Charlotte, NC 28205	35.240129 -80. 785730	VOC
37-129-0010	Eagles Island	USS North Carolina 1 Battleship Drive Wilmington, NC 28401	34.235529 -77. 955865	VOC
37-147-0006	Pitt Ag	403 Government Circle Greenville, NC 27834	35. 641290 -77.360116	VOC
37-123-0001	Candor	112 Perry Drive Candor, NC	35.263170 -79. 836638	VOC, Carbonyls, Meteorology

A5.2 Background

The DAQ regulates 97 TAPs via North Carolina Administrative Code, and 187 hazardous air pollutants (HAPs) via federal Section 112(b) of the 1990 CAAA. Seventy-six TAPs are also HAPs. These pollutants have been associated with a wide variety of adverse health and ecosystem effects. Multiple sources, including major stationary, area, and mobile sources, emit these TAPs and HAPs, resulting in population exposure to these pollutants. While in some cases the public may be exposed to an individual pollutant, more typically people experience exposures to multiple pollutants and from many sources. Potential adverse exposures can result from breathing these pollutants, but exposure can also occur through other routes such as ingestion or skin absorption. The DAQ UAT program does not have a specified end date. The DAQ will upgrade UAT sampling and analysis equipment, including support equipment as new resources and staff become available.

A5.3 DAQ UAT Network List of Chemical Pollutants

Table 1.2-1 of the NATTS Technical Assistance Document (TAD) Revision 3 lists 60 HAPs as analytes of principle interest and assigns tier classes to each analyte of principle interest. Currently, the DAQ UAT monitoring program samples and analyses HAPs using:

- The EPA TAD for the NATTS Network, Revision 3, available on the Ambient Monitoring Technology Information Center (AMTIC) here²:

https://www3.epa.gov/ttn/amtic/files/ambient/airtox/NATTS%20TAD%20Revision%203_FINAL%20October%202016.pdf

- The EPA Compendium Method TO-15, “Determination of Volatile Organic Compounds in Air Collected in Specially-Prepared Canisters and Analyzed by Gas Chromatography / Mass Spectrometry (GC/MS), available on AMTIC here³:

<https://www3.epa.gov/ttnamti1/files/ambient/airtox/to-15r.pdf>

- EPA Compendium Method TO-11A, “Determination of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed by High Performance Liquid Chromatography (HPLC), available on AMTIC here⁴:

<https://www.epa.gov/sites/production/files/2019-11/documents/to-11ar.pdf>

The analytical methods performed by the DAQ LAB will identify and quantify 10 of the 18 Tier I HAPs and 18 Tier II HAPs listed in Table 1.2-1 of the NATTS TAD Revision 3. The remaining 8 Tier I HAPs not analyzed by the DAQ LAB are metals and polycyclic aromatic hydrocarbons (PAH). The DAQ LAB does not currently possess the correct lab equipment or enough laboratory personnel to perform methods IO-3.1, IO-3.5 and TO-13A. NATTS Required sites are not currently located in NC, so DAQ does not have an official plan to expand the current UAT monitoring in NC to include metals and PAHs. However, DAQ is open to expand metals and PAHs monitoring at one urban and one rural site if additional state and/or federal funding becomes available. If additional funding were available today, it would take at least 1-2 years to hire staff, purchase equipment and train staff on the equipment operation and maintenance.

The DAQ LAB analyzes and reports concentration data to AQS for 66 HAPS via method TO-15 and reports concentration data to AQS for 11 HAPS via method TO-11A. Tables A5-2 and A5-3 below list the VOC and Carbonyl compounds analyzed by the DAQ LAB including AQS numbers and current analysis instrument reporting limits (RL). The limits listed in Table A5-2 are the upper and lower reporting limits of both GC/MS systems and the UHPLC system used by DAQ for VOC canister analysis and carbonyl cartridge analysis. VOC and Carbonyl method detection limit (MDL) procedures follow the method update rule (MUR) for MDL determinations as described in Section 4.1 of the NATTS TAD Revision 3.

Table A5-2. DAQ UAT VOC Compound List and Reporting Limits

Compound and AQS # (Bold = NATTS Core I and Proficiency Test [PT] Compounds)	Lower Reporting Limit (ppb)	Upper Reporting Limit (ppb)
1,1,1-Trichloroethane 43814	0.2	10.0
1,1,2,2-Tetrachloroethane 43818	0.2	10.0
1,1,2-Trichloroethane 43820	0.2	10.0
1,1-Dichloroethane 43813	0.2	10.0

Table A5-2. DAQ UAT VOC Compound List and Reporting Limits

Compound and AQS # (Bold = NATTS Core I and Proficiency Test [PT] Compounds)	Lower Reporting Limit (ppb)	Upper Reporting Limit (ppb)
1,1-Dichloroethene 43826	0.2	10.0
1,2,3-Trimethylbenzene 45225	0.2	10.0
1,2,4-Trichlorobenzene 45810	0.2	10.0
1,2,4-Trimethylbenzene 45208	0.2	10.0
1,2-Dibromoethane 43843	0.2	10.0
1,2-Dichlorobenzene 45805	0.2	10.0
1,2-Dichloroethane 43815	0.2	10.0
1,2-Dichloropropane 43829	0.2	10.0
1,3,5-Trimethyl Benzene 45207	0.2	10.0
1,3-Butadiene 43218	0.2	10.0
1,3-dichlorobenzene 45806	0.2	10.0
1,4-dichlorobenzene 45807	0.2	10.0
1,4-Dioxane 46201	0.2	10.0
2-Pentanone 43562	0.2	10.0
3-Hexanone 43557	0.2	10.0
3-Pentanone 43553	0.2	10.0
Acetonitrile 43702	0.2	10.0
Acrolein 43505	0.2	10.0
Benzene 45201	0.2	10.0
Benzyl chloride 45809	0.2	10.0
Bromodichloromethane 43828	0.2	10.0
Bromoform 43806	0.2	10.0
Bromomethane 43819	0.2	10.0
Carbon disulfide 42153	0.2	10.0
Carbon Tetrachloride 43804	0.2	10.0
chlorobenzene 45801	0.2	10.0
Chloroethane 43812	0.2	10.0
Chloroform 43803	0.2	10.0
Chloromethane 43801	0.2	10.0
Cis-1,3-dichloropropene 43831	0.2	10.0
Cyclohexane 43248	0.2	10.0
Cyclopentane 43242	0.2	10.0
Ethylbenzene 45203	0.2	10.0
Freon 11 43811	0.2	10.0
Freon 113 43821	0.2	10.0
Freon 114 43208	0.2	10.0
Freon 12 43823	0.2	10.0
Freon 22 43359	0.2	10.0

Table A5-2. DAQ UAT VOC Compound List and Reporting Limits

Compound and AQS # (Bold = NATTS Core I and Proficiency Test [PT] Compounds)	Lower Reporting Limit (ppb)	Upper Reporting Limit (ppb)
Hexane 43231	0.2	10.0
Iodomethane 43808	0.2	10.0
Isobutene 43270	0.2	10.0
Isoprene 43243	0.2	10.0
m,p-xylene 45109	0.2	10.0
Methacrolein 43515	0.2	10.0
Methyl Butyl Ketone 43559	0.2	10.0
Methyl Ethyl Ketone 43552	0.2	10.0
Methyl Isobutyl Ketone 43560	0.2	10.0
Methyl Tert Butyl Ether 43372	0.2	10.0
Methyl Vinyl Ketone 43558	0.2	10.0
Methylene Chloride 43802	0.2	10.0
n-Pentane 43220	0.2	10.0
o-Xylene 45204	0.2	10.0
Propanal 43504	0.2	10.0
Propylene 43205	0.2	10.0
Styrene 45220	0.2	10.0
Tetrachloroethylene 43817	0.2	10.0
Toluene 45202	0.2	10.0
Trans-1,2-Dichloroethene 43838	0.2	10.0
Trans-1,3-dichloropropene 43830	0.2	10.0
Trichloroethylene 43824	0.2	10.0
Vinyl Acetate 43447	0.2	10.0
Vinyl Chloride 43860	0.2	10.0

Table A5-3. DAQ UAT Carbonyl Compound List and Reporting Limits

Compound and AQS Number (Bold = NATTS Core I and PT Sample Compounds)	Lower Reporting Limit (ppbv)	Upper Reporting Limit (ppbv)
Formaldehyde 43502	0.028	8.481
Acetaldehyde 43503	0.019	5.782
Propionaldehyde 43504	0.015	4.385
Crotonaldehyde 43528	0.036	3.634
2-Butanone (MEK) 43552	0.035	3.532
Methacrolein 43515	0.036	3.634
Butyraldehyde 43510	0.035	3.532
Benzaldehyde 45501	0.024	2.400
Valeraldehyde 43518	0.030	2.957
m-Tolualdehyde 45508	0.021	2.120

Table A5-2. DAQ UAT VOC Compound List and Reporting Limits

Compound and AQS # (Bold = NATTS Core I and Proficiency Test [PT] Compounds)	Lower Reporting Limit (ppb)	Upper Reporting Limit (ppb)
Hexaldehyde 43517	0.025	2.543

A6 Project Task/Description

This section provides a summary of the description of work, equipment procurement activities, field activities, laboratory activities, and project assessment techniques.

A6.1 Description of Work

The DAQ will operate and maintain the sampling and analysis instruments, including support equipment, needed to make meteorological and chemical measurements for the DAQ UAT network. The measurement parameters and the make and model of the instruments used to measure them are listed in Table A6-1.

Table A6-1. Measurement parameters and Instruments used in the DAQ UAT Network

Measurement Parameter	Instrument Model and Method
VOCs	<p>VOC sampling: Xontech 911A canister sampler collecting 24-hour samples – Collection per EPA Compendium Method TO-15.</p> <p>VOC chemical analysis system I: (Markes-Agilent GC) includes the Agilent 7890B GC and 5977B Agilent MS detector with a Markes International CIA Advantage-Xr canister autosampler, Markes International Kori-Xr water condenser, and Markes International Unity-Xr thermal desorber – Analysis per EPA Compendium Method TO-15.</p> <p>VOC chemical analysis system II: (Markes-Agilent GC) includes the same configuration as System I but the Agilent MS detector for system II is the Agilent 5977A – Analysis per EPA Compendium Method TO-15.</p>
Carbonyls	<p>Carbonyl sampling: ATEC 2200 cartridge sampler collecting 24-hour samples – Collection per EPA Compendium Method TO-11A.</p> <p>Carbonyl analysis: Thermo Ultimate 3000 ultra-high performance liquid chromatograph (UHPLC), and ultraviolet (UV) detection – Analysis per EPA Compendium Method TO-11A.</p>
Ambient Temperature (AT)	MetOne AIO2 All-in-One resistance type sensor.
Wind Direction (WD)	MetOne AIO2 All-in-One ultra-sonic anemometer.
Wind Speed (WS)	
Barometric Pressure (BP)	MetOne AIO2 All-in-One sensor piezoresistive silicon sensor.

Measurement Parameter	Instrument Model and Method
Relative Humidity (RH)	MetOne AIO2 All-in-One sensor capacitive/solid state sensor.

A6.2 Equipment Procurement Activities

All supplies, materials, instrumentation, and support equipment used in the DAQ UAT network will be tested by DAQ prior to field and laboratory use to ensure compliance with manufacturer specifications, the NATTS TAD (where applicable), EPA Compendium Methods TO-15 and TO-11A (where applicable), and EPA's Volume IV QA Handbook on Meteorological Measurements.

Analysis instrument calibration standards, check standards, and internal standards (IS) will contain a certificate of analysis (COA) that is National Institute of Standards and Technology (NIST)-traceable. Flow and pressure standards used to calibrate and verify sampling equipment will be NIST-traceable.

Additional equipment procurement activities are described in more detail in the following SOPs:

- DAQ-03-001.1 Xontech 911A Urban Air Toxics VOC Sampler, ECB Responsibilities
- DAQ-03-002.1 ATEC 2200 Urban Air Toxics Carbonyl Sampler, ECB Responsibilities
- DAQ-03-003.2 Markes/Agilent GC-MS Analysis of VOC in Ambient Air Collected in 6-L Canisters, Operator Responsibilities
- DAQ-03-004.2 Thermo Ultimate 3000 UHPLC-UV-MS (UAT and PAMS Carbonyls Analysis), Operator Responsibilities
- DAQ-03-005.1 Entech 3100A Canister Cleaner, ECB Responsibilities
- DAQ-03-006.1 Entech 4700 Precision Diluter, ECB Responsibilities
- DAQ-07-003.1 MetOne AIO2 All-in-One Weather Sensor, ECB Responsibilities

A6.3 Field Activities

Field activities for the DAQ UAT network include site installation of equipment, operation of the sampling equipment, shipping and receiving of sampling materials, filling out sampler information and COC forms, and recording comments of field observations. Field activities typically include five phases: blank sample media receipt, pre-sampling, sampling, post-sampling, and sampled media shipments to the analysis laboratory.

Summaries of field activities are logged in bound site logbooks located at each UAT site or in electronic logbooks stored on site computers and loggers. All field data parameters are recorded on sampler information and COC forms. All logbook and form entries are made with indelible ink including the current date and initials of the person performing the activity and a summary of the activity being performed.

The DAQ UAT network field activities are described in more detail in Sections 3, 4, 5, and 6 of the following SOPs:

- DAQ-03-001.1 Xontech 911A Urban Air Toxics VOC Sampler, ECB Responsibilities
- DAQ-03-001.2 (old SOP# 2.51.2) Xontech 911A VOC Canister Sampler, Operator Responsibilities
- DAQ-03-002.1 ATEC 2200 Urban Air Toxics Carbonyl Sampler, ECB Responsibilities
- DAQ-03-002.2 ATEC 2200 Urban Air Toxics Carbonyl Sampler, Operator Responsibilities
- DAQ-07-003.1 MetOne AIO2 All-in-One Weather Sensor, ECB Responsibilities
- DAQ-07-003.2 MetOne AIO2 All-in-One Weather Sensor, Operator Responsibilities

A6.4 Laboratory Activities

Laboratory activities supporting the DAQ UAT network include the preparation of sampler information forms, sample media COC forms, analysis of field collected samples, cleaning, certifying, and preparing sampling media and equipment for field use, data entry, and level 1 and level 2 reviews of field and laboratory data.

Summaries of laboratory sample analysis, sample extractions, calibration and QA/QC standard preparations, and general laboratory instrument maintenance activities are logged in laboratory logbooks. These logbooks are assigned to a designated piece of equipment or specific location in the laboratory (i. e, the canister cleaning system logbook is next to the instrument in the canister cleaning laboratory room and the extraction laboratory logbook is located in the extractions laboratory room).

All logbook entries are made with indelible ink including the current date and initials of person performing the laboratory activity.

Laboratory activities are described in more detail in Sections 3, 5, and 6 of the following SOPs:

- DAQ-03-001.1 Xontech 911A UAT VOC Sampler, ECB Responsibilities
- DAQ-03-002.1 ATEC 2200 UAT Carbonyl Sampler, ECB Responsibilities
- DAQ-03-003.2 Markes-Agilent GC-MS VOC Canister Analysis, Operator Responsibilities
- DAQ-03-004.2 Thermo Ultimate 3000 UHPLC-UV-MS UAT and PAMS Carbonyl Analysis, Operator Responsibilities
- DAQ-03-005.1 Entech 3100A Canister Cleaning System, ECB Responsibilities
- DAQ-03-005.2 Entech 3100A Canister Cleaning System, Operator Responsibilities
- DAQ-03-006.1 Entech 4700 Precision Static Dilution System, ECB Responsibilities
- DAQ-03-006.2 Entech 4700 Precision Static Dilution System, Operator Responsibilities

A6.5 Project Assessment Techniques

The DAQ will assess the performance of the UAT network activities by conducting independent assessments detailed in Section C1.1 of this document.

A7 Quality Objectives and Criteria

The primary objective of the DAQ UAT Network is to detect long term trends in air toxics concentrations across the state of NC which includes the ability to detect a statistically significant increase or decrease in successive 3-year annual average VOC and Carbonyl concentrations. The DAQ UAT network will adhere to the requirements described in this document and the NATTS TAD Revision 3. The DAQ UAT network will provide data of known quality for use by the DAQ, EPA, SLT, modelers and scientists.

A7.1 Data Quality Objectives

Data quality objectives (DQOs) are qualitative and quantitative statements derived from the DQO Planning Process that clarify the purpose of a study, define the most appropriate type of information to collect, determine the most appropriate conditions under which to collect that information, and specify tolerable levels of potential decision errors. DQOs define the quality of and the acceptable levels of uncertainty in the measurements and their associated uncertainty that can be tolerated to make decisions regarding the measurements. Stated another way, DQOs are statements describing “how good” the measurements need to be to provide data to control decision risk(s) to meet the project outcomes within a known certain level of confidence and to ensure that collected data are of sufficient quantity and quality to be fit for the stated purpose to objectively assess the risk in the decisions to be made. The NATTS Required Site Network has already developed a single DQO using the seven step DQO planning process.

Additional information on the NATTS DQO planning process can be found on AMTIC at the following link:

<https://www3.epa.gov/ttnamti1/files/ambient/airtox/nattdqo20130613.pdf>

The single, main DQO derived from the DQO planning process and quoted in the NATTS TAD Revision 3 states:

- ***“to be able to detect a 15% difference (trend) between two successive 3-year annual mean concentrations (rolling averages) within acceptable levels of decision error”.***

The DAQ UAT network will adopt the DQO described in the NATTS TAD Revision 3. The DAQ intends to collect VOC and Carbonyl data of known quantity and quality to achieve the DQO stated above.

Secondary monitoring objectives for the DAQ UAT network are listed below:

- *To be able to detect trends in speciated VOCs and Carbonyl concentrations between urban and rural environments and*
- *To be able to detect differences between background and samples collected at particular locations on special occasions when fence-line or emergency response monitoring is performed.*

A7.2 Data Quality Indicators

The data quality indicators (DQIs) of representativeness, completeness, precision, bias, and sensitivity are the characteristics describing how good the data must be to meet the DQO. The DQIs are characterized by prescribing an associated MQO for each DQI that details the specific criteria to be met. These DQIs and associated MQOs are detailed further in Sections A7.3.1 through A7.3.5,

A7.3 Measurement Quality Objectives

The MQOs for each of the DQIs are shown in Table A7-1.

Table A7-1. DAQ UAT DQIs and Associated MQOs					
Method or Parameter	DQI				
Chemical Measurements	Representativeness (Sampling Frequency)	Bias (%)	Precision (%)	Sensitivity ^b (Detection Limit, ppbv)	Completeness (%)
TO-15 Speciated VOCs	1-in-6-day sampling frequency for 24-hour periods (midnight to midnight local standard time [LST]) following the EPA national sampling schedule	≤ 25	≤ 15 ^a	Acrolein ≤ 0.039 Benzene ≤ 0.041 1,3-Butadiene ≤ 0.050 Carbon Tetrachloride ≤ 0.027 Chloroform ≤ 0.10 Tetrachloroethylene ≤ 0.025 Trichloroethylene ≤ 0.037 Vinyl Chloride ≤ 0.043	≥ 85
TO-11A Carbonyls	1-in-6-day sampling frequency for 24-hour periods (midnight to midnight LST) following the EPA national sampling schedule	≤ 25	≤ 15 ^a	Formaldehyde ≤ 0.065 Acetaldehyde ≤ 0.25	≥ 85
Ambient Temperature	Continuous 10-second sampling rates with stored 1-minute and 1-hour time-based averages for AT, RH, BP and 1-minute and 1-hour vector summation averages (WS and WD)	± 0.5°C ^c	± 0.25 ^c	≤ 0.1 °C	≥ 75
Relative Humidity		± 5.0% ^c	± 2.5% ^c	≤ 0.5% RH	
Barometric Pressure		± 2.0 hPa ^c	± 1.0 hPa ^c	≤ 0.1 hPa	
Wind Speed		± 1.0 m/s ^c	± 0.5 m/s ^c	≤ 0.1 m/s	
Wind Direction		± 10° ^c	± 10° ^c	≤ 1 degree	

^a measured as the coefficient of variation of the relative percent differences (RPDs) across sample sizes greater than 2, as applicable, all duplicate/collocated field-collected canisters and cartridges. See Sections 2.5.1 and 2.5.2 of the NATTS 2011-2012 NATTS Quality Assurance Annual Report available here:

<https://www3.epa.gov/ttnamti1/files/ambient/airtox/NATTS20112012QAARfinal.pdf>

^b See Table 4.1-1 in the NATTS TAD Revision 3.

^c Bias and Precision for meteorology is determined using the collocated transfer station (CTS) method by comparing the site sensor against a separately calibrated audit sensor, designated the audit sensor. To be consider a valid CTS pair, the hourly averaged wind speed must be ≥ 1.0 m/s. Also, a minimum of 48 CTS pairs are required for valid bias and precision calculations and the 48 CTS pairs must be collected over at least two diurnal cycles. When all criteria are met, the CTS audit pair is used for bias and precision measurements. See SOP DAQ-07-003.1 for additional CTS method information.

A7.3.1 Representativeness

Temporal representativeness and spatial representativeness are described further in this section.

A7.3.1.1 Temporal Representativeness

To adequately characterize the annual average concentrations of VOC and Carbonyl compounds, sampling frequency will occur on a 1-in-6-day schedule during the calendar year. Additionally, to adequately characterize daily average concentrations of VOC and Carbonyl compounds sampling durations will occur over 24 ± 1 -hour periods from midnight-to-midnight LST. VOC and Carbonyl sampling frequencies will provide approximately 60 to 61 samples per calendar year. The DAQ will follow the EPA national sampling calendar for 1-in-6-day sampling. The national schedule is available at the following link on AMTIC:

[Sampling Schedule Calendar | US EPA](#)

A7.3.1.2 Spatial Representativeness – Chemical Measurement Probe Siting Criteria

Sampling inlet probes and equipment must comply with the siting criteria in 40 CFR Part 58, Appendix E to ensure the collected atmosphere is representative of the ambient air in the geographic area of the site. If there are any issues with meeting the requirements, DAQ will describe the siting criteria concerns in the annual network plan. See Volume 1 of the DAQ network plan at the following link for siting criteria issues for the UAT:

<https://deq.nc.gov/about/divisions/air-quality/air-quality-data/annual-network-plan/annual-monitoring-network-plan-for-north-carolina-air-quality>.

The probe must be at least 1 meter (m) vertically or horizontally away from any supporting structure, walls, parapets, penthouses, etc., and away from dusty or dirty areas. Inlet probes must have unrestricted airflow in a continuous 270-degree arc and the predominant wind direction must be included in this arc. To the extent feasible, inlet probes must not be located on the side of a building. However, if such is unavoidable, then the inlet must be located on the windward side of the building or wall relative to the prevailing wind direction and must have unrestricted airflow in an arc of at least 180 degrees. The probes at all UAT monitoring sites extend at least 1 m above the roof of the building.

Inlet Probe Heights: Inlet probes must be placed at the following heights:

UAT VOCs	2 to 15 m above ground level (AGL)
UAT carbonyls	2 to 15 m AGL

Obstructions: The inlet probe must be minimally twice the distance from the potential obstruction as the potential obstruction extends above the inlet probe. For example, if a wall extends 2 m above the inlet probe, the inlet probe must be 4 m or more from the wall.

Spacing from Trees: Trees can provide surfaces for ozone or nitrogen dioxide adsorption or reactions and may prevent the accurate measurement of UAT and VOC compounds when of a sufficient height and leaf canopy density to interfere with airflow. To avoid such interferences, inlet probes must be minimally 10 m from the dripline of the nearest tree.

Spacing from Roadways: Mobile sources represent a significant source of VOCs and Carbonyls; therefore, it is important to ensure that monitoring site inlet probes are sufficiently displaced from roadways where they can be unduly impacted by motor vehicle emissions. Minimum separation distances for monitor inlet probes from roadways assume DAQ UAT sites are neighborhood scale and therefore must comply with Table E-1 of 40 CFR Part 58, Appendix E, reproduced below in Table A7-2. Note that these minimum separation distances must also be maintained from other motor vehicle traffic areas such as parking garages and parking lots.

Table A7-2. Minimum Monitor Separation Distance from Roadways

Roadway average daily traffic (ADT), vehicles per day	Minimum distance for sites existing before 18 Dec 2006 ^a (m)	Minimum distance for new sites ^a (m)
≤ 1,000	10	10
10,000	10	20
15,000	20	30
20,000	30	40
40,000	50	60
70,000	100	100
≥ 110,000	250	250

^a Distance from the edge of the nearest traffic lane, The distance for intermediate traffic counts will be interpolated from the table values based on the actual traffic count.

A7.3.1.3 Spatial Representativeness - Meteorology

Wind Speed and Wind Direction: The standard height for surface layer wind measurements is 10 m AGL, The location of the site for the wind measurements must ensure that the horizontal distance to obstructions (e.g., buildings, trees) is at least 10 times the height of the obstruction, An obstruction may be man-made (e.g., a building) or natural (a tree). A wind instrument must

be securely mounted on a mast on the tower that will not twist, rotate, or sway. Sensor height and its height above the obstructions, as well as the character of nearby obstructions are documented in the DAQ Network Plan document (link in section A7.3.1.2 above).

An open lattice tower is the recommended structure for monitoring of meteorological measurements at the 10-m level. In the case of wind measurements, certain precautions are necessary to ensure that the measurements are not significantly affected by turbulence in the immediate wake of the meteorological tower. To avoid such tower effects, the wind sensor will be mounted on a mast a distance at least one tower width above the top of the tower, or if the tower is higher than 10 m, on a boom projecting horizontally from the tower. In the latter case, the boom will extend a distance at least twice the diameter/diagonal of the tower from the nearest point on the tower. The boom will project into the direction which provides the least distortion for the most important wind direction (i.e., into the prevailing wind).

Ambient Temperature and RH: The standard height for surface layer AT and RH measurements is 2 m AGL. Higher mounting is permitted; if a tower is used, the temperature sensor will be mounted on a boom which extends at least one tower width/diameter from the tower. The measurement will be made over a uniform plot of open, level ground at least 9 m in diameter centered on the sensor. The surface will be covered with non-irrigated or non-watered short grass or, in areas which lack a vegetation cover, natural earth. Concrete, asphalt, and oil-soaked surfaces and other similar surfaces must be avoided to the extent possible. The sensor will be at least 30 m horizontally from any such paved area. If these siting criteria (open ground and distance from paved surfaces) cannot be achieved, it will be identified in site characterization documentation. Other areas to avoid include extraneous energy sources (subway entrances, rooftops, electrical transmission equipment), large industrial heat sources, steep slopes, hollows, high vegetation, swamps, snow drifts, standing water, tunnels, drainage culverts, and air exhausts. The distance to obstructions for accurate temperature measurements will be at least four times the obstruction height. The DAQ will use the AIO2 sensor for RH and AT measurements and will mount the sensor at 10 m AGL.

Barometric Pressure: BP instruments will be in a ventilated shelter and ideally should be mounted about 2 m AGL. The height of the station above mean sea level and the height of the pressure sensor AGL will be documented in the site characterization records. The DAQ will use the AIO2 sensor for BP measurements and will mount the sensor at 10 m AGL.

A7.3.2 Completeness

Generation of a dataset sufficient to characterize the annual concentrations of VOC and Carbonyl compounds requires that a minimum number of the intended measurements be valid.

Completeness is defined as the percentage of the number of valid data values compared to the number of values intended to be collected. The MQOs for completeness are specified for each parameter in Table A7-1.

For continuous meteorological measurements reported as the hourly average, uncollected or invalidated measurement results are lost, and cannot be made up. Forty-five minutes will be

considered a valid hour and 18 hours a valid day. The completeness MQO for VOC and carbonyl measurements listed in Table A7-1 will be calculated every calendar quarter as the total valid samples out of the samples possible. If a VOC or carbonyl sample day is missed, an appropriate null code will be reported to AQS for the missed sample run date. To the extent possible, the DAQ will schedule a make-up sample to be collected as soon as practical according to the make-up sampling policy described below.

VOC and Carbonyls Make-up Sample Policy: For invalidated or missed VOC or carbonyl sampling events, a make-up sampling event will be conducted. A replacement VOC or carbonyls sample will be collected for the same duration as the missed sample. Make-up samples will be collected according to the following:

1. Before the next scheduled sampling date, if possible, best practice.
2. Within 30 days of the missed collection date, with preference given that the rescheduled date occurs on a weekday or weekend day to match that of the missed sample date.
3. If the missed sample occurs within 30 days of the end of the calendar year or end of calendar quarter, the makeup sample must occur before the end of the calendar year or quarter.

A7.3.3 Precision

Precision is a measure of agreement among repeated measurements of the same property under identical, or substantially similar, conditions. The lack of precision (imprecision) represents the random component of error. The VOC and carbonyl precision MQOs are listed in Table A7-1.

Overall Precision for Speciated VOCs and Carbonyls: Overall precision is assessed by calculating the coefficient of variation (CV) of the RPDs between collocated sample collection pairs. The formula for calculating CV is shown in Equation 1 and applied only when the number (n) of sample pairs is >2 .

Equation 1:

$$CV = \sqrt{\frac{\sum_i^n \left[\frac{(p-r)}{0.5 * (p+r)} \right]^2}{2n}}$$

p = primary data

r = replicate, repeated or collocated data

n = # of pairs

Collocated VOC and carbonyl samples are collected at the Millbrook UAT site on a 1-in-6-day schedule, yielding approximately 60 to 61 pairs of primary and collocated samples each calendar year.

Approximately, 14% of all VOC canister samples and 50% of all carbonyl cartridge samples collected by the DAQ will be collocated sample pairs. The DAQ intends to collect collocated samples using two separate samplers and two separate inlet sampling probes. The MQO for VOC and Carbonyl precision is listed in Table A7-1.

Relative percent differences that are calculated from concentrations that are either invalidated or qualified due to sampling or analysis issues will not be included in CV calculations.

The DAQ UAT network MQO for VOC and Carbonyl precision is based on an evaluation of at least two primary and collocated sample pairs, preferably an entire calendar years' worth of primary and collocated sample pairs.

The CV of the RPDs for bold font compounds listed in Tables A5-2 and A5-3 must be $\leq 15\%$. The CV is determined using Equation 1 listed above.

Precision for Meteorology Measurements: Precision assessments for meteorological measurements are addressed in SOP# DAQ-07-003.1 MetOne AIO2 All-in-One Met Sensor, ECB Responsibilities. The DAQ performs the collocated transfer station (CTS) method to evaluate precision in real-time and to perform functionality checks of new and recently calibrated meteorological sensors. The precision MQO for meteorological measurements are listed in Table A7-1.

A7.3.4 Bias

Bias, the systematic (nonrandom) deviation of a measurement from a known or accepted value, is minimized by using calibrated instruments and equipment, by checking that instruments remain calibrated over time, and by minimizing sources of background contamination.

All instruments must be suitably calibrated before UAT sample collection or analysis begins. Their calibration must be periodically demonstrated to remain valid by comparison with a known traceable certified reference standard or instrument. For VOC and carbonyl measurements, once calibration is established for an instrument, the calibration is to be immediately verified against a known traceable certified standard, typically a second source standard or at minimum the same source but a different lot number than the one used for instrument calibration.

Laboratory bias is mainly controlled through laboratory analysis of double-blind, proficiency test (PT) samples (spiked VOC sample canisters and spiked carbonyl cartridges) provided twice per year by the EPA. The MQO for bias is described in Table A7-1.

Laboratory bias is also controlled by establishing a multi-point calibration curve with subsequent analysis of a check standard and periodically thereafter.

Sampling instrument bias is controlled by a combination of checks. These checks include zero bias certifications, mass flow controller (MFC) calibrations, and flow verification checks. Carbonyl sampling and VOC canister sampling flow rate bias is controlled to within $\pm 10\%$ of

the design flow rate. If post-sample flow rate verifications indicate flow rates outside this criterion, all chemical parameters detected in the sample analysis results are flagged with a “W” qualifier flag prior to reporting.

Bias for Meteorology Measurements: Bias assessments for meteorological measurements are evaluated using the CTS method. The CTS method provides bias evaluations in real-time. The bias MQOs for meteorological measurements are listed in Table A7-1.

A7.3.5 Sensitivity

Sensitivity must be established for each of the chemical measurements (VOCs and carbonyls) by experimentally determining the MDL. The MDLs are determined for each measurement method as described in section 4.1 of the NATTS TAD Revision 3. MDLs will be determined annually, typically at the beginning of the calendar year, and should not exceed the MDL values listed in Table 4.1-1 in the NATTS TAD Revision 3 or in Table A7-1 in this document. MDLs are determined by the analysis of at least seven separate method spike samples and seven separate method blank samples. The MDL spike samples must target a nominal spiked concentration level that is below the lowest reportable limit. See tables A5-2 (VOC parameters) and A5-3 (carbonyl parameters) in this document for the lowest reportable limits.

The VOC MDL must be determined using all types of canisters deployed for routine field sampling and must include at least three different preparation batches, include canisters from at least three different cleaning batches and must include analysis results from at least three different analysis batches. The preparation batches cannot occur on consecutive days. The cleaning batches cannot occur on consecutive days. The analysis batches cannot occur on consecutive days. Since DAQ uses two GCMS instruments for VOC canister analysis, the MDL will be established, individually, using both systems. In other words, system I and system II will have their own, calculated MDL value unique to the system being used for analysis of VOC canister samples.

The Carbonyl MDL must be determined using the same cartridges deployed for routine field sampling and the MDL must include at least three different preparation batches, three different extraction batches, and three different analysis batches. The preparation batches, extraction batches, and analysis batches cannot occur on consecutive days.

A valid MDL meets the acceptance criteria established in section 4.1 of the NATTS TAD Revision 3.

If a valid MDL cannot be determined according to acceptance criteria established in section 4.1 of the NATTS TAD Revision 3, an analysis instrument detection limit (IDL) must be performed, so that analysis instrument sensitivity can be established first, to better understand and/or adjust the MDL spiking level. The IDL does not replace the MDL, nor does the IDL get reported to the EPA AQS with the concentration data. The IDL is not used to apply MD and SQ qualifier flags to the data for values detected near the MDL. Only valid, MDLs achieved using approved EPA guidance that also meet the acceptance criteria for determining a valid MDL, are reported to EPA

with the concentration data. The IDL values may be reported with concentration data in sample reports to external customers, but values are for informational purposes only and are not used to qualify detected concentration values near the MDL value. The IDLs are not meant to replace the MDL but instead are used to guide the analyst to adjust the spiking level so that a valid MDL, per guidance in the NATTS TAD Revision 3, can be achieved.

The analysis IDL is determined by analyzing a low-level spiked sample at least seven consecutive times, calculating the standard deviation of the measured values, and multiplying the standard deviation by the appropriate student-t value based on a 99% confidence interval.

Meteorology instruments will meet the resolution specifications listed in Table A7-1. Sensitivity for meteorology instrument measurements is fundamentally different than for chemical measurement instruments for which the lowest concentration differentiable from background is useful. For ambient meteorology measurements, sensitivity is better understood as resolution, or the ability to differentiate between two similar measurements, since the conditions to be quantified are not challenging to detect in the same way that low concentrations of a target chemical analyte are. For example, the ability to discern between temperatures of 24.2 degrees Celsius (°C) and 24.6°C is important; however, it is not important to be able to measure the lowest temperature possible since such is not a concern for ambient monitoring.

A8 Special Training/Certifications

Individuals conducting ambient measurements resulting in data generation (sampler operators, laboratory instrument analysts), data verification and validation, and audits/assessments must possess the skills and education or experience to perform activities for which they are responsible. Specific requirements are described in the following sections and in DAQ SOP DAQ-15-003 Standard Operating Procedures for Training Ambient Monitoring Staff and Documenting and Tracking Training (currently under development). Management, by way of the interim and final Valuing Individual Performance reviews which occur in January and July each year, must verify that staff are competent to conduct all such activities. DAQ will detail in SOP DAQ-15-003 the requirements and certifications for staff carrying out the duties described in Section A6.2. Individuals operating instruments, performing data transformations, and conducting oversight (such as QA and management personnel) must minimally have read and documented attestation of compliance with the appropriate quality system (QS) documents. Training can consist of attendance at seminars, courses provided by instrument vendors, online training courses, training videos, and time spent working with instruments with the intent to become familiar and learn the instruments and associated software.

DAQ staff must comply with all applicable QS requirements and will attest in their training records that they have read and will comply with pertinent QS documents, such as the DAQ UAT QAPP and SOPs describing the duties for which they are responsible (refer to Section A9).

Staff will review and, as necessary, revise QS documents, perform maintenance on equipment, seek training to maintain skills and proficiency, and must demonstrate continuing proficiency to execute the activities for which they are responsible.

A8.1 Sampler Operator Training

Sampler operators require special training to operate, maintain, and troubleshoot instruments and support equipment needed to make UAT measurements. Each site operator will possess the appropriate skills and education to perform their assigned tasks. At the discretion of the DAQ, instrument vendors or experienced staff train new site operators on how to set up and operate VOC sampler, carbonyl samplers, and meteorological sensors. At the discretion of DAQ, site operators will receive training materials and will attend training sessions and online training webinars provided by instrument vendors, EPA, and/or experts. Any such training will be documented (such as program completion certificates, course attendance records, etc.) and maintained in the staff training records. Management will document their approval of the staff member's competency to perform their assigned tasks as part of the interim and final Valuing Individual Performance reviews that occur in January and July of each year. When management assigns or hires new staff, the staff member's competency to perform their assigned tasks must be documented via an initial demonstration of capability (IDOC) process. The IDOC must be completed before data collection activities may begin. A member of the QA unit will observe the site operator performing the procedures as described in the applicable SOP as part of the approval process. Annually thereafter a member of the QA team will observe site operators performing the procedures to complete a continuing demonstration of capability (CDOC). The DAQ training forms are included in SOP# DAQ-15-003.

The level of training required for conducting VOC and carbonyl sampling and operating meteorological sensors is less rigorous than for operation of laboratory analysis instrumentation. Site operators will need to be familiar with the instrument operation including troubleshooting, software menu navigation, data retrieval, maintenance, and calibration verification routines. Operation of meteorological instruments require site operators to be familiar with instrument operation, maintenance, and typical data outputs. Meteorological instruments require little intervention aside from regular inspection for proper operation and lack of interferences (e.g., presence of bird or insect nests) and occasional maintenance for cleaning or alignment. Maintenance requirements are listed in Table B6-1.

Once site operators are trained and approved by management to perform their assigned tasks, they may train other staff members to perform similar tasks. Training new site operators will involve a three-step process consisting of:

1. The trainee observing a trained staff member performing the task,
2. The trainee performing the task under the supervision and assistance of the trained staff member, and
3. The trainee performing the task independently under observation of the trained staff member.

As the DAQ UAT network matures and evolves, procedures and equipment are expected to be updated and refined. Site operators will seek opportunities for continuing education and refinement of their skills to maintain competency in their assigned tasks. At the discretion of

DAQ management and local and tribal agencies under the PQA of DAQ; UAT project staff will attend quarterly NATTS Required Site Network calls and/or webinars hosted by the EPA and EPA contractors during which training on technical issues and questions may be covered and individuals may pose questions to the group and seek assistance in instrument start up and troubleshooting.

A8.2 Auditor Training

DAQ quality assurance staff performing assessments (described in Section C) will not need to be proficient in operating UAT instruments; however, they will be familiar with the equipment and procedures employed to generate measurement data and with software and procedures with which data are reviewed, verified, and validated. Auditors will read and understand the QS documents, minimally consisting of the DAQ UAT QAPP and SOPs governing the processes to be assessed and will complete written attestation signifying compliance with the QS (an example form is provided in Appendix D).

EPA has developed an audit checklist for NATTS Required Sites. The DAQ intends to utilize these checklists and update questions to meet DAQ needs. Shakedown audit and internal TSA checklists, including auditing procedures are described in more detail in SOP# DAQ-15-004 Shakedown Audits and Internal TSAs, currently under development with an anticipated completion date of August 2023. DAQ staff performing audits need not be intimately familiar with the operations of the instruments and software functions for generating, evaluating, and validating measurement data; however, such staff must be able to follow the described procedures and determine whether the activities as carried out comply with the established procedures described in the QS documents. Auditors will maintain documentation for attendance of training sessions (e.g., training classes, webinars, vendor training) and for materials reviewed (e.g., audit checklists, instrument manuals, and training videos).

A8.3 Laboratory Analyst Training

Once the LAB analyst has read the relevant QAPP and SOPs and documented the completion and intention of compliance with them, the staff member must demonstrate proficiency prior to conducting analyses to generate UAT network data. Individuals conducting laboratory extraction and analysis for carbonyls will have demonstrated proficiency by conducting an IDOC prior to performing the applicable laboratory activities. The IDOC will consist of preparing a set of at least four cartridge spike samples and performing the extraction, calibration, and analysis procedures under observation of a member of QA staff, management (direct supervisor, or similar), or other trained analyst familiar with the procedure. The observer will ensure that the procedures were performed properly and review the analysis results to ensure that each laboratory control sample (LCS) meets spike recovery acceptance criteria ($\pm 15\%$ of nominal).

Individuals conducting laboratory analysis of VOC canisters will have demonstrated proficiency by conducting an IDOC prior to performing the applicable laboratory activities. The IDOC will consist of preparing a set of at least four separate canister spike samples and performing the

calibration and analysis procedures under observation of a member of the QA staff, management (direct supervisor, or similar), or other trained analyst familiar with the procedure. The observer will ensure that the procedures were performed properly and review the analysis results to ensure that canister spike results meet acceptance criteria ($\pm 30\%$ of nominal).

The observer will document the acceptable performance and laboratory management will approve the analyst to independently perform the analysis by approval signature on the IDOC (checklist, approval form, or similar).

Once the IDOC is completed, the analyst will demonstrate continued proficiency with the method on an annual basis by performing a CDOC. The CDOC will be met by the analyst achieving recovery within the method bias specification ($\pm 25\%$ of nominal) for all bold font compounds listed in Tables A5-2 and A5-3. The CDOC sample (spiked canister or cartridge sample) can be prepared by the Level 2 reviewer, Level 3 reviewer, or member of the internal UAT TSA audit team or the CDOC can be met by meeting PT sample bias requirements for spiked compounds.

A9 Documentation and Records

DAQ will establish and maintain document control procedures for the timely preparation, review, revision, approval, issuance, use, retirement, and archival of documents and records. A dedicated document and records custodian would be a tremendous asset; however, such a position is not likely to be created due to a lack of funding within DAQ. Therefore, DAQ has established that the individual staff member that generates the original document and/or record is responsible for the placement, maintenance, and archival of their respective document and records. Electronic records are stored on a secure internal DAQ network drive that is backed up daily by DAQ IT staff. Paper records, such as COC forms, are stored in a secure file cabinet at the analysis laboratory or are scanned electronically and stored on the secure internal DAQ network drives. The categories and types of records and documents that are applicable to the DAQ UAT Program are presented in Table A9-1.

Additional DAQ document management practices and procedures are described in more detail in SOPs DAQ-14-001 SOP on Preparation of SOPs, DAQ-14-003 Document Retention Procedure and DAQ-14-002.5 SOP and QAPP Tracking Database.

Documentation and records generated and maintained include:

1. DAQ UAT QAPP
2. UAT SOPs and QA Memos
3. Sample collection records in electronic and written format
4. Sample analysis records in electronic and written format
5. Logbooks and data sheets in electronic and written format
6. Training records
7. Instrument and equipment calibration information

8. Quality assurance documentation (for example, outcomes of TSAs, IPAs, and ADQs; and corrective action plans [CAPs] and reports) in electronic and written format
9. Documentation, records, and reports that support data review, validation, and certification activities

Table A9-1. Pertinent Documents and Records for UAT

Categories	Record/Document Types
Management and Organization	Personnel qualifications and training Quality management plan Document control policy/procedure Records retention and archival policies
Site Information	Site characterization file Site maps/photographs Annual siting reevaluation
Environmental Data Operations (Field and Lab)	QA Project Plan(s) (QAPPs) Standard operating procedures (SOPs) QA Memos IDOC and CDOC records Field and laboratory notebooks Sample handling and management, including holding time/storage/number of samples to be collected, etc., Instrument inspection/maintenance records
Raw Data	Original data (routine and QC) Sample collection forms Chain of custody forms Electronic instrument data (raw, processed, and reprocessed) Certificates of analysis for standards materials Calibration certificates for transfer standards Original observations as recorded in field and laboratory notebooks Instrument calibrations
Data Management	Validation of data collection, transformation, and reduction algorithms Data management plans/flowcharts Transformed and reduced data Data review, verification, and validation documentation
Data Reporting	AQS data submission summary reports AQS data verification reports
Quality Assurance	Control charts Calibration data, MDL/IDL data etc. Audit reports for: IPAs, TSAs, ADQs CARs and supporting documentation Network reviews

Recorded data, whether hand recorded in ink on paper or through electronic entry or captured through a computer system, will be maintained such that the activities can be reconstructed. DAQ uses a combination of SOPs that describe how to execute routine procedures, including, but not limited to, instrument operation, maintenance, sample collection, and analysis for each of the UAT measurement methods, data verification/validation/reporting, corrective action, training, and data management. As applicable, each SOP will include information on equipment and instruments required, calibration, quality control activities and acceptance criteria, calculations, and typical corrective actions for routine non-conformances. Where activities involve a potential physical hazard, safety precautions will be addressed.

DAQ will maintain a system (such as a controlled electronic document in an access-controlled network folder, internal website, or similar) that will list the most current version of QS documentation containing the information given in Table A9-1. Superseded versions of controlled QS documents must be inaccessible such that only the most up-to-date procedures are performed. All previous versions of QS documents will be archived and maintained to ensure that measurement data are traceable to the policies and procedures in place at the time the data were generated, transformed, or reduced, and reported.

As the UAT site network matures, the QS documents will require revision to accommodate lessons learned and best practices. Revisions to the QS documents will be handled in a manner that ensures only current approved procedures are available. To ensure that DAQ and EPA Region IV staff are aware of the changes if a revision to the document cannot be completed and approved in a timely manner, a quality bulletin (refer to Appendix A) or similar memorandum will be distributed to the UAT stakeholders as described in Section A1.2 to announce the changes and indicate when the changes are effective.

A9.1 Recording of Data

Activities conducted to generate reported measurements will be documented in sufficient detail such that the measurements reported to AQS are traceable (i.e., an independent assessor can trace a reported value back through collection of the data, transformation of the data, and the certified standards used to calibrate the instruments). Instrument operators, data validators, and QA personnel will record data within bound logbooks, on dedicated forms, or within electronic logs, as appropriate per instructions detailed in DAQ UAT program SOPs. Please see Appendix E in this document for a complete list of DAQ UAT program SOPs. The control of these documents is described in more detail in SOP#s DAQ-14-001 SOP on Preparation of SOPs, DAQ-14-003 Document Retention Procedure and DAQ-14-002.5 SOP and QAPP Tracking Database.

A9.1.1 Paper Records

Documentation requirements for the UAT network will follow general good scientific data recording practices. Observations will be recorded in sufficient detail to reconstruct the activities and such that original data records are maintained and not obliterated or erased when corrections or changes are made,

Measurements, observations, and activities will be recorded promptly in indelible ink and will be attributable to the individual making the entry by signature or initials and include the date the entry was made. Corrections must be by single line strikeout and must be dated and initialed. Bound logbooks with consecutively numbered pages or forms specific to the intended use (e.g., chain of custody form, field sample collection form, flow verification form, etc.) will be utilized to ensure the requisite information is captured and recorded. Such forms will be controlled documents.

A9.1.2 Electronic Records

Original raw data acquired by electronic systems (e.g., instrument acquired raw area counts for a GC/MS analysis of a canister sample), data transformed or reduced within electronic systems (e.g., adjusting integration parameters for carbonyls analysis by HPLC, or data reduced within an electronic spreadsheet), and data recorded within electronic logbooks (such as is available in some data acquisition systems) will be maintained so activities may be reconstructed and calculations or transformations independently verified. Data recorded, transformed, or reduced in electronic systems will be attributable to the individual recording or evaluating the data and will indicate the date on which the activity was performed (and recorded, if different). If so equipped, audit trails will be enabled on software systems to ensure modifications to electronic records are recorded and that the original data are not overwritten.

A9.2 Chain-of-Custody Records

Samples collected for analysis that are packaged and transported to another location will be accompanied by a COC form that documents how such media are handled and tracks the integrity of the collection media through the various stages of transportation and receipt. COC procedures will be described in SOPs specific to the media type and the approved COC form will be a controlled document within the DAQ or LAB document control system. Completed COC forms (or a copy thereof) will be retained by the LAB as part of the official analytical record. DAQ COC procedures are covered in the following SOPs:

- DAQ-03-001.2 (old SOP 2.51.2) Xonteck 911A UAT VOC Sampler Operator Responsibilities
- DAQ-03-002.2 ATEC 2200 UAT Carbonyl Sampler Operator Responsibilities
- DAQ-03-003.2 Markes-Agilent GC-MS VOC Canister Analysis Operator Responsibilities
- SOP# DAQ-03-004.2 Thermo Ultimate 3000 UHPL-UVMS UAT and PAMS Carbonyl Analysis Operator Responsibilities.

COC procedures and requirements are detailed in Section B3.1.1 and B3.2.1. An example COC form specific to UAT carbonyls samples is included in Appendix B. An example of a COC form specific to UAT VOC samples is included in Appendix C.

A9.3 QA/QC Records

In addition to documenting routine operations, QA and QC activities must also be appropriately documented. Such QA/QC activities include:

- Instrument maintenance, calibration, and calibration verification
- Standards certification, recertification, or calibration
- IPAs
- TSAs
- ADQs
- Supplies and equipment acceptance testing
- Corrective actions
- Data verification and validation

The outcomes of these QA/QC-related activities must be recorded on site logbook, laboratory logbook, hard copy forms, in electronic spreadsheets, electronic portable document format (pdf) files, in data management software systems, or by another appropriate means as defined in the DAQ-controlled document (e.g., QMP, QAPP, or SOP) governing the activity. Documentation methods include logbooks, spreadsheets, worksheets, and data management systems, whether electronic or hard copy.

Records for some of the QA/QC activities described above may only be available as hard copies. Where possible, these hard copy records will be scanned so that electronic versions can be filed and maintained with associated electronic air monitoring records.

A9.4 Records Archival and Retention

Records described in Sections A9.1 through A9.3 will be retained minimally for three years as per the statute of limitations codified in 2 CFR 200.334 and further clarified in Section 5.0 of the EPA QA Handbook. This statute states that records will be maintained for a minimum of three years from the date the grantee submits the final expenditure report unless otherwise noted or if the records involve a legal action. The DAQ will retain all air records collected in support of the air toxics program for a minimum of six complete calendar years from the date of collection as required in the NATTS TAD Revision 3. However, if any litigation, claim, negotiation, audit, or other action involving the records has been started before the expiration of the six-year period, DAQ will retain the records until completion of the action and resolution of all issues that arise from it or until the end of the regular six-year period, whichever is later.

UAT Network QAPPs and supporting SOPs will be archived for minimally 10 years following the date that they are superseded. Electronic data such as databases, raw and processed electronic instrument data, electronic logbooks, etc., will be backed up minimally monthly to a physically separate storage device (separate hard drive, server, or similar). Archived electronic data will be stored in a manner such that they are protected from inadvertent alteration (e.g., password protected, access limited). Once archived, the archived data are reviewed or tested minimally

annually to ensure complete records are maintained and data have not been corrupted. DAQ stores electronic records within the data management systems located at the UAT sites, or Envidas, the RCO, or Envista ARM, and on network servers in the LAB, ECB, regional offices and RCO. The DIT backs up data and records stored on the network server in the LAB, ECB, regional offices and RCO nightly and stores these back-ups off-site. The database manager regularly backs up the Envista ARM database to SharePoint.

A9.5 Sample Retention

The UAT measurement methods involve the collection of samples onto discrete media except for meteorology measurements. Therefore, sample retention applies only to VOC and carbonyl samples. Once carbonyl samples are extracted, the spent cartridge is no longer useful and can be discarded. To afford reanalysis in the event there are problems with the analysis, sample extracts will be maintained in refrigerated storage until the analysis data is validated and approved or the 30-day extract holding time has been exceeded. Expired extracts are of little value; however, in the event expired extracts are analyzed, results reported from such expired extracts require qualification as "QX" when reported to AQS. Extracts will not be archived and will be disposed properly according to hazardous waste procedures established by the laboratory.

VOC sampling media can be cleaned and reused after recertification that the VOC canister is clean. Sampled VOC canisters have a shelf life of 30 days from the date sample was collected to the date of analysis by GC-MS. VOC canister samples analyzed past the 30-day holding time require all parameters to be qualified QX when reported to AQS.

B. DATA GENERATION AND ACQUISITION

B1 Sampling Process Design

All sampling and analytical instruments and support equipment used for the UAT network are vendor supplied and were designed specifically for their prescribed use. The equipment meets the design and the specifications described in the EPA compendium methods TO-15 and TO-11A and the NATTS TAD Revision 3. The objective of the UAT sampling process design is to collect VOC and Carbonyl concentration data of known quality to achieve the primary DQO. See Volume 1 of the DAQ network plan at the following link for the DAQ implementation plan (IP) and the requested waivers for the UAT network:

<https://deq.nc.gov/about/divisions/air-quality/air-quality-data/annual-network-plan/annual-monitoring-network-plan-for-north-carolina-air-quality>.

The following parameters will be measured at UAT sites (meteorological parameters are only measured at the background site and the PAMS/NCore site). See table A5-1 in the QAPP for individual VOC and carbonyl parameters monitored at each UAT site.

- **VOCs**
- **carbonyls**
- **meteorological parameters:**
 - **ambient temperature**
 - **vector-averaged wind direction**
 - **vector-averaged wind speed**
 - **barometric pressure**
 - **relative humidity**

B1.1 Sample Collection Schedule

VOC and carbonyl sampling conducted at UAT sites will follow the 1-in-6-day EPA national sampling schedule. Additional sampling collection schedule information is shown below in Table B1-1.

Continuous instrument measurements (meteorology) will operate continually to measure ambient conditions except during QC checks or maintenance. Note that meteorology instruments do not typically require ongoing daily QC checks.

Table B1-1. UAT Site Sampling Schedule by Parameter

Parameter	Sampling Duration and Frequency	Value Reported
VOCs (TO-15)	24-hour on 1-in-6-day schedule	24-hr average
Carbonyls (TO-11A)	24-hour on 1-in-6-day schedule	24-hr average
Meteorological Parameters	Continuously, daily	Hourly average

The time reported for the sample collection is to be the LST at the start of sample collection or the start of the averaged hour, not adjusted for daylight savings time (DST). Hourly averaging periods will include the beginning of the hour through the end of minute 59 of the hour. For example, the hourly average represented for 9:00 AM covers 09:00:00 through 09:59:59.

B1.1.1 Carbonyl Sampling by TO-11A

Carbonyls samples will be collected every sixth day per the national sampling calendar available at the following link on AMTIC:

[Sampling Schedule Calendar | US EPA](#)

Carbonyl samples will be collected for 24 hours \pm 1 hour, starting at approximately midnight and ending at approximately midnight (next day) according to LST.

In cases where samples are invalidated due to a field sampling issue, a make-up carbonyl sample should be scheduled as described per the make-up policy in Section A7.3.2.

B1.1.2 VOC Sampling by TO-15

VOC canister samples will be collected for 24 \pm 1 hours starting at midnight and ending at 23:59 the same day or midnight (next day) according to LST.

In cases where samples are invalidated due to a field collection issue, a make-up VOC canister sample should be scheduled as described per the make-up policy in Section A7.3.2.

B1.1.3 Continuous Measurement Methods

Data collection for continuous meteorological methods will include minimally 45 minutes of data collection during the respective hour to be valid. Hours with fewer than 45 minutes of data collection will be invalidated.

B1.2 Quality Control Measurements

QC samples are collected and/or analyzed for VOCs and carbonyls and may be positive controls or negative controls. Positive controls consist of a sample with a known amount of target analyte for challenging the measurement method (instrument), such as continuing calibration verification standards (CCVs), span checks, secondary source calibration verification (SSCV) standards, and LCS spikes. Negative controls challenge the measurement method to demonstrate the instrument response remains sufficiently low in the absence of the target analyte; negative controls include zero air blanks, solvent blanks, and field QC blank samples such as field blanks (FBs) and trip blanks. Both positive and negative controls are prepared and analyzed to demonstrate that the measurement system remains in control on an ongoing basis; that is, that the measurement system is acceptably calibrated, and that interferences and contamination are acceptably low.

QC parameters and associated acceptance criteria are detailed in Section B5 and in Tables B5-1, B5-2, B5-3, and B5-4 for carbonyls field sample collection, VOC field sample collection, carbonyls laboratory analysis, and VOCs laboratory analysis respectively.

DAQ and the LAB will track QC sample performance using Microsoft excel spreadsheets and macros that automatically flag or highlight the out-of-control QC parameter. Inspection of these spreadsheets allows the identification of trends or drifts in the performance of the overall measurement method and can provide a focused effort to improve sampling procedures or analysis procedures and provide justification for adjusting acceptance criteria limits for some QC parameters.

Please see the “recommended corrective action” for each QC parameter listed in tables B5-1, B5-2, B5-3, B5-4, and B5-5.

B2 Sampling and Measurement Methods

This section describes the sampling instruments, procedures for collecting samples, identifies the sampling methods and equipment including sample preservation requirements, and specific method and instrument performance requirements such as maximum allowable sample pickup times for VOC canisters and carbonyl cartridges, Also described are actions to take when a failure in the sampling or measurement system occurs, who is responsible for corrective action, and how corrective action will be documented.

Table B2-1 provides the makes and models of equipment used for the sample collection and analysis of VOC and carbonyls.

Table B2-1. Measurement parameters and Instruments used in the DAQ UAT Network

Measurement Parameter	Instrument Model and Method	AQS Method Code
VOCs	<p>VOC sampling: Xontech 911A canister sampler collecting 24-hour samples – Collection per EPA Compendium Method TO-15</p> <p>VOC chemical analysis system I: (Markes-Agilent GC) includes the Agilent 7890B GC and 5977B Agilent MS detector with a Markes International CIA Advantage-Xr canister autosampler, Markes International Kori-Xr water condenser, and Markes International Unity-Xr thermal desorber – Analysis per EPA Compendium Method TO-15.</p> <p>VOC chemical analysis system II: (Markes-Agilent GC) includes the same configuration as System I but the Agilent MS detector for system II is the Agilent 5977A – Analysis per EPA Compendium Method TO-15</p>	150

Table B2-1. Measurement parameters and Instruments used in the DAQ UAT Network

Measurement Parameter	Instrument Model and Method	AQS Method Code
Carbonyls	<p>Carbonyl sampling: ATEC 2200 cartridge sampler collecting 24-hour samples – Collection per EPA Compendium Method TO-11A</p> <p>Carbonyl analysis: Thermo Ultimate 3000 ultra-high performance liquid chromatograph (UHPLC), and ultraviolet (UV) detection – Analysis per EPA Compendium Method TO-11A</p>	202
Ambient Temperature	MetOne AIO2 All-in-One resistance type sensor	069
Wind Direction	MetOne AIO2 All-in-One ultra-sonic anemometer	020
Wind Speed		
Barometric Pressure	MetOne AIO2 All-in-One sensor piezoresistive silicon sensor	069
Relative Humidity	MetOne AIO2 All-in-One sensor capacitive/solid state sensor	

B2.1 Chemical Parameter Sampling Method

This section describes ambient air sample field collection methods for VOC canisters and carbonyl cartridges. All parameters listed in tables A5-2 and A5-3 will be reported to AQS. Ambient air samples will be collected through individual sampling unit inlet probes. The materials comprising, the siting of, and the configuration of the inlet probe will comply with 40 CFR Part 58, Appendix E and Section A7.3.1.2 of this QAPP to ensure the sampled atmosphere is representative of the ambient air in the geographic area intended to be represented by the site.

Briefly, the inlet probe(s) will be constructed of borosilicate glass or chromatographic grade stainless steel. Additional guidance for inlet probe siting is included in Section 2.4 of the NATTS TAD Revision 3. Note that Teflon[®] is not recommended for VOC sampling inlet pathways.

B2.1.1 Carbonyls by TO-11A

Sampling methods for the collection of carbonyl compounds are described in SOP# DAQ-03-002.2 ATEC 2200 UAT Carbonyl Sampler Operator Responsibilities. The analysis of carbonyl compounds by TO-11A are described in SOP# DAQ-03-004.2 Thermo Ultimate 3000 UHPLC-UV-MS UAT and PAMS Carbonyl Analysis Operator Responsibilities. The target carbonyl compounds are shown in Table B2-2. For this method, ambient air is pulled by a vacuum pump through an ozone denuder to remove ozone. The sampled air scrubbed of ozone is then passed through a silica gel sorbent cartridge impregnated with DNPH where carbonyls in the air stream react with DNPH to form hydrazone derivatives. These hydrazones are maintained within the sorbent bed until extraction at the analysis laboratory. Carbonyl sampling for the UAT program involves collecting 24-hour samples on a 1-in-6-day schedule as described in Table B1-2. It is

preferable that samples are retrieved as soon as possible after the end of collection; however, cartridges must be retrieved within 72 hours of sample completion. Samples must be stored and transported cold ($\leq 4^{\circ}\text{C}$) and protected from light. An example of a UAT and PAMS Carbonyls Sample Information Form can be found in Appendix B of this document.

The UHPLC system used for carbonyl analysis contains two detectors (UV and MS). The MS detector results are not currently reported by DAQ to EPA's AQS database.

More information regarding carbonyl sampling and analysis methods can be found in section 4.3 of the NATTS TAD Revision 3.

B2.1.2 VOCs by TO-15

Sampling methods for the collection of VOC compounds in 6-Liter canisters are described in SOP# DAQ-03-001.2 Xonteck 911A UAT VOC Sampler Operator Responsibilities. The analysis of VOC compounds by TO-15 are described in SOP# DAQ-03-003.2 Markes-Agilent GC-MS UAT VOC Canister Analysis Operator Responsibilities. The target VOC compounds are shown in bold in Table A5-2. For this method, ambient air is pulled through a diaphragm pump, passing through a flow orifice and heated flow controller into an evacuated 6-Liter Silica-lined canister. The DAQ performs super ambient pressurized canister sampling, targeting approximately 13.5psig in the canister after sampling at 8 mL/min for 24 hours. The canister vacuum at sample start must be ≥ 28 inches of mercury (in Hg) vacuum, The VOC canister sampler flow rate limits are 7.2-8.8 mL/min, which is $\pm 10\%$ of design flow rate of 8.0 mL/min. The expected canister pressure range at the end of the sampling event is 9.6-17.6psig. This pressure range is derived using the equation in section 8.3.2.1 of EPA's compendium method TO-15 document. Using the minimum allowable flow rate (7.2mL/min) and minimum allowable duration (23hrs), the expected canister pressure is 9.6psig. Using the maximum flow rate (8.8mL/min) and maximum allowable duration (25hrs), the expected canister pressure is 17.6 psig. For a canister sample to be considered valid, the post-sampling flow rate verification and final canister pressure must meet acceptable limits.

The DAQ LAB uses two Markes-Agilent GC-MS systems for the measurement of VOCs in 6-L canisters. The systems are identified as System I and System II. Each system has a unique MDL value. The summary files generated by both systems are identified by the analyst as 'system I' or "system II." System I is the primary GC/MS system and the VOC concentration results obtained from this system are reported to AQS. Please see Table B5-2 for System I and System II configurations. Both systems collect and pre-concentrate VOCs from sampled canisters and separate the VOCs for identification and quantification via mass selective detection.

System II VOC results are reported to AQS if System I is under repair or non-operational. Both systems are configured with similar support modules and operated by the same instrument control software. Both systems use the same separation columns; front end sampling and moisture management systems; and the same column oven programs. Both systems are calibrated using the same calibration standard mix and calibrated using the same nominal calibration levels. Additionally, both systems are verified using the same nominal check standard

level. Differences between system I and system II concentrations are evident when very low VOC concentrations are detected in the canister samples (<0.2ppb). MDL samples (MDL spikes and MDL blanks) are analyzed on each system, individually. Each system MDL is calculated independently from the other system. The DAQ laboratory does not pool all MDL sample analysis results from both systems into one MDL value, representing the overall method, should both systems be used. Currently, the VOC MDL values are not reported to EPA AQS along with the reported VOC concentrations until a valid MDL is achieved, following guidance and acceptance criteria in section 4.1 of the NATTS TAD Revision 3.

Additional details on canister analysis methods, including technical guidance regarding moisture management, are provided in Section 4.2 of the NATTS TAD Revision 3.

B2.2 Meteorology

Meteorology measurements will include the parameters listed in Table B2-3.

These measurement methods will meet the criteria specified in Table 0-1 of *Quality Assurance Handbook for Air Pollution Measurement Systems, Volume IV - Meteorological Measurements* (EPA-454/B-08-002) available at the following link:

[Volume IV Meteorological Measurements](#)

Results will be measured continuously and reported as the hourly average. Meteorological data collection and processing procedures are described in more detail in the following SOPs:

- DAQ-07-003.1 MetOne AIO2 All-in-One Met Sensor ECB Responsibilities, and
- DAQ-07-003.2 MetOne AIO2 All-in-One Met Sensor Operator Responsibilities.

Table B2-3. Meteorological Parameters

Parameter	AQS Parameter Code	Duration	AQS Duration Code	Example Reported Unit ^a	AQS Unit Code ^a
Ambient Temperature	62101	hourly average	1	°C	017
Relative Humidity	62201	hourly average	1	% relative humidity	019
Barometric Pressure	64101	hourly average	1	millibar (hPa)	016
Wind Speed - Resultant	61103	hourly average	1	m/s	011
Wind Direction - Resultant	61104	hourly average	1	degrees compass	014

Table B2-3. Meteorological Parameters

Parameter	AQS Parameter Code	Duration	AQS Duration Code	Example Reported Unit ^a	AQS Unit Code ^a
Sigma-Theta Horizontal Wind Direction Deviation	61106	hourly average	1	degrees compass	014

^a Listed units are one of several standard units accepted by AQS for the given parameter, DAQs may report measurement data in any standard unit accepted by AQS.

B3 Sample Handling and Custody

Sample handling and custody requirements apply to VOC canister and carbonyls sample collection, handling, and analysis. Meteorological measurements are performed in-situ and therefore do not require sample handling and custody procedures to be followed.

Sample custody procedures are required to avoid misplacement of samples or confusion of one sample with another, and to provide documentation to assist in identification and resolution of instances where sample identity or integrity is called into question. A sample is in custody if it is in one's actual physical possession or stored in a secured area restricted to authorized personnel.

VOC sample handling and custody procedures are described in more detail in SOP# DAQ-03-001.2 (SOP 2.51.2) Xonteck 911A VOC Canister Sampler Operator Responsibilities and SOP# DAQ-03-003.2 Markes-Agilent GC-MS VOC Canister Analysis Operator Responsibilities.

Carbonyl sample handling and custody procedures are described in more detail in SOP# DAQ-03-002.2 ATEC 2200 UAT Carbonyl Sampler Operator Responsibilities and SOP# DAQ-03-004.2 Thermo Ultimate 3000 UHPLC-UV-MS UAT and PAMS Carbonyl Analysis Operator Responsibilities.

B3.1 VOCs by TO-15

Certified clean and evacuated canisters are shipped via state courier service or commercial courier service at ambient temperature by the LAB staff to the regional office staff or local program staff performing VOC canister sampling or hand-delivered by LAB staff to the regional office staff or local program staff performing VOC canister sampling.

All shipping and receiving of unsampled and sampled canisters are done under ambient conditions. Sample refrigeration is not required for VOC canisters.

B3.1.1 Canister Chain of Custody

Unsampled, evacuated, and certified clean sample canisters originate at the LAB. Each canister that has been assigned a field sampling site is sealed with a valve cover and the valve cover is

sealed with a COC tag. These canisters are also assigned a COC form that also acts as a sample information form with space to record canister numbers, sample numbers, sampling sites, sample dates, canister pressures before and after sampling, leak checks, sampler flow rates before and after sampling, and general comments regarding sample collection observations.

The VOC canister COC form records transfers of sample canister custody by way of breaking and sealing the COC tags and recording the initials and dates and times of breaking the COC tag and dates and times of sealing the COC tag. All sample canister transfers are recorded on the COC form. An example of the VOC COC form is found in Appendix C of this document.

Unsampled, evacuated, and certified clean canisters that have not been assigned a sample location or COC form may be stored inside the laboratory building without valve covers and valve cover COC seals.

Sampled canisters are shipped from the regional office staff or local program office staff to the LAB via state courier service or commercial courier service or hand delivered by the regional office or local program staff to LAB staff. All sampled canisters used for UAT VOC sampling are sealed with a valve cover and the valve cover is sealed with a COC tag before leaving the sampling site. Sampled canister pressures are recorded by the site operator by way of the 911A sampler pressure gauge. The sampled canister pressure is verified by the laboratory staff using a different, certified pressure gauge than the one used on the 911A sampler.

Laboratory sample custodians, or designated individuals responsible for assuring sample custody, will ensure that sample custody documentation is complete. Site operators will be contacted, as appropriate, to complete missing information. VOC canister COC documentation will be maintained in accordance with Section A9.

B3.2 Carbonyls by TO-11A

DNPH cartridges are shipped at ambient temperature by the manufacturer, currently Waters. Upon receipt by the LAB, the cartridges are stored in a monitored refrigerator dedicated to blank carbonyl cartridge sample storage. The cartridges are received individually sealed in an opaque foil pouch, in boxes of 20 cartridges, containing a COA of background formaldehyde, acetaldehyde, and acetone contamination in micrograms per cartridge ($\mu\text{g}/\text{cartridge}$). To maintain cartridge integrity and limit potential contamination, the sealed foil cartridge storage pouch will not be opened until the cartridge is to be used in the field or laboratory. Additionally:

- Cartridges will only be handled with gloved hands (chemicals from hand sanitizers, lotions, etc., can contaminate sample cartridges).
- Cartridges will be labeled in such a manner to uniquely identify the cartridge, i.e., to permit the identification of the sampling date, time, and whether it is a primary sample or field QC sample (precision sample [such as collocated or duplicate], FB, or trip blank).
- Cartridge storage areas will be free of carbonyls. Climate-controlled storage units will be used for storage of solvents or carbonyl-containing solutions or standards.

Upon retrieval, each field-collected cartridge must be sealed in its individual foil pouch, and placed immediately in refrigerated storage (e.g., refrigerator onsite or cooler with ice packs). Collection details will be documented appropriately on the sample collection form (whether hard copy or electronic) and sample storage information will be recorded on the COC form or similar form or database (such as a laboratory information management system [LIMS]). To ensure that samples arrive at the laboratory under refrigeration, samples will be hand-carried or shipped by overnight courier/shipper. Experience has shown that extended shipping times will result in samples arriving at the laboratory at elevated temperatures ($> 4^{\circ}\text{C}$).

B3.2.1 Carbonyl Cartridge Chain of Custody

Blank, unsampled cartridge media originates at the LAB. Each cartridge, whether an ambient sample or field QC sample (such as a FB) will be listed on the COC form documenting the transfer of the sample cartridges from their origin, receipt by field operators including sample media inspection, sample collection, and transport to and receipt by the analysis laboratory. The following information must minimally be recorded on the COC form (an example form is included in Appendix D):

- Origin of cartridges (e.g., analysis laboratory or field office)
- Transfer of cartridges between individuals – dates, times, and signatures of individuals relinquishing and receiving cartridges
 - Relinquishing cartridges to site operator (either by handoff or shipment by courier)
 - Receipt of cartridges by site operator
 - Relinquishing of sampled cartridges by site operator following retrieval (for handoff to analysis laboratory or shipment with courier)
Note: Shipping couriers are not expected to sign COC forms. The individual relinquishing the samples to the shipper/courier will indicate relinquishment to the shipper/courier on the COC form. Custody is presumed to be with the courier until received at the laboratory.
 - Receipt of field-collected cartridges by analysis laboratory
- Unique identifier(s) for each sample, sample collection date(s), and site(s) location information
- Storage of cartridges at each point during transfer between individuals, including during shipment
 - Storage of field-collected cartridges at the monitoring site, if applicable (e.g., stored at $\leq 4^{\circ}\text{C}$ in onsite refrigerator, etc.)
 - Shipping conditions (e.g., on ice packs) and associated information for tracking or evaluating the shipping conditions - such as thermometers placed in a shipping cooler
 - Upon receipt at the laboratory – document thermometer used for measuring temperature as received and location for storage within laboratory (e.g., uniquely identified refrigerator)

Laboratory sample custodians, or designated individuals responsible for assuring sample custody, will ensure that sample custody documentation is complete. Site operators will be contacted, as appropriate, to complete missing information. COC documentation will be maintained in accordance with Section A9.

B4 Analytical Methods

The analytical methods for the determination of Carbonyl and VOC concentrations are covered in this QAPP. Additional analytical method information can be found in compendium methods TO-11A and TO-15 and sections 4.1, 4.2, and 4.3 of the NATTS TAD Revision 3.

B4.1 Carbonyls by TO-11A

Samples collected for carbonyls analysis (refer to Section B2.1.2) will be extracted and analyzed per EPA Compendium Method TO-11A and will meet the performance specifications listed in Table B5-4. The DAQ will follow SOP# DAQ-03-004.2, which describes the procedures for cartridge handling, sampler information forms, cartridge COC forms, solvent extraction of derivatized carbonyl-hydrazones collected on the DNPH cartridge samples, analysis of these extracts by UHPLC with UV detection, analysis data processing, QC parameters, QC acceptance criteria, review of sampling and analysis data, and verification of sampling and analysis data.

Ambient air and QC samples must be extracted for analysis within 14 days of collection. Extracts are then analyzed by HPLC or UHPLC with UV detection at 360 nanometers (nm) within 30 days of extraction and the carbonyl concentrations in the ambient air sample calculated from the measured concentrations in the sample extracts and the volume of air sampled onto the cartridge.

B4.2 VOCs by TO-15

GC-MS systems will be used for the analysis of VOCs collected in 6L canisters. The GC-MS systems collect and pre-concentrate VOCs from a sampled canister and subsequently separate and quantify the VOCs by mass selective detection. DAQ will follow SOP # DAQ-03-003.2 which describes procedures for canister handling, canister shipping, canister receiving, canister COC forms, analysis of VOCs collected in the canister by GC-MS, analysis data processing, QC parameters, QC acceptance criteria, review of sampling and analysis data, and verification of sampling and analysis data.

Ambient air and QC samples must be analyzed within 30 days of collection. Evacuated and certified clean canisters have a maximum holding time of 30 days prior to sample collection.

B5 Quality Control

QC is the overall system of technical activities that measures the performance of an ongoing process against established standards and to verify that such performance meets the QC

acceptance criteria established by the data user or stakeholder. In the case of the UAT Network, QC activities ensure that the quality objectives and criteria for measurement data, as discussed in Section A7, are maintained so that the primary UAT DQO can ultimately be met. QC checks and procedures will be performed at a frequency sufficient to ensure data of adequate quality are obtained while minimizing loss of data when non-conformances occur.

B5.1 Quality Control for Field Activities

QC for field activities relate to carbonyls sample collection, VOC canister sample collection, and meteorological parameters.

B5.1.1 Quality Control for Carbonyls Sample Collection

Carbonyls sample collection QC includes the performance of quality checks on the sampling instrument to ensure the instrument is not imparting a positive bias (i.e., contaminating) to the collected samples, the instrument flow control is accurate, and the instrument clock is accurate. Carbonyl field QC samples include, as described in Table B5-1 and in SOP# DAQ-03-002.2, FBs and trip blanks, which characterize the level of contamination attributable to sample handling and transportation, and duplicate and/or collocated samples, which characterize the precision between samples collected from the same air mass.

For flow controller calibration verification and clock accuracy, corrective action will be taken immediately when non-conformances are observed. When clock setting deviations are noted, the clock should be reset and noted on the sample collection records. For example, if the carbonyls sampler clock shows 11:06 a.m. when the time is 10:59 a.m., the operator should reset the clock to 10:59 a.m. and note the time adjustment in the sample collection records. For the positive bias challenge (as described in Section A7.3.4), compliance with acceptance criteria must be attained prior to deploying the sampling instrument for sample collection. A positive bias challenge is recommended if instrument contamination is suspected (such as would be indicated by poor precision for duplicate or collocated samples or if unusually elevated concentrations are reported). The need for follow up corrective action for FB, trip blank, or collocated or duplicate sampling criteria failures will not be apparent until analysis results are completed. A root-cause analysis will be performed as soon as possible for field QC sample non-conformances, and efficacy of corrective actions will be evaluated by collection of follow-up field QC samples.

Table B5-1. Carbonyls Field Quality Control Parameters

QC Parameter	Detail	Required Frequency	Acceptance Criteria	Recommended Corrective Action
Positive Bias Challenge (sampler bias check)	Sequential collection of two 24-hour humidified samples of zero-air to investigate contamination contributed by the sampler. The first sample is the “reference” sample, and the second sample is the “positive bias check” sample.	Prior to installation and every 365 days thereafter or when corrective action requires performance of another positive bias challenge.	All target compounds must be < 0.2ppbv greater than the concentration detected in the reference sample.	If Tier I core compounds fail criteria, attempt another positive bias sample collection. If contamination is confirmed for Tier I core compounds or if non-Tier I core compounds fail, the sampler may be used but failing compounds detected in the samples collected using the sampler must be qualifier flagged “SB” prior to reporting data to AQS.
Mass Flow Controller (MFC) Calibration	Establishment of the MFC slope and intercept by comparison to a flow transfer standard.	Prior to installation of new (never used for field sampling) sampler at a monitoring site and every 365 days thereafter or when flow verification checks fail criteria.	Sampler flow rate must be within $\pm 10\%$ of design flow rate.	Recalibrate MFC. If problem persists, investigate for leaks, blockage in flow path, etc. May require replacement of MFC or other instrument parts.

Table B5-1. Carbonyls Field Quality Control Parameters

QC Parameter	Detail	Required Frequency	Acceptance Criteria	Recommended Corrective Action
MFC Calibration Verification	Verify sampling flow at the sampling flow setting.	Immediately following MFC calibration and before and after each sampling event.	Sampler Flow Rate must be within $\pm 10\%$ of design flow rate.	Verify with a different flow standard. If failing condition persists, recalibrate flow controller and verify within proper specification. If sampler fails pre or post sampling flow verifications and is used to collect a sample, apply qualifier flag "W" to all carbonyls detected in the sample prior to reporting data to AQS.
Clock Accuracy	Verify clock accuracy against a known accurate time standard.	Each sampling event.	Within ± 5 minutes of the true reference time not corrected for daylight savings time (DST).	Reset sampler clock to match reference time not corrected for DST.
Field Blank	Blank cartridge installed in a sampling channel for five to ten minutes.	Once per month during the calendar year.	Measured mass per cartridge ($\mu\text{g}/\text{cartridge}$): - Acetaldehyde ≤ 0.40 - Formaldehyde ≤ 0.30 - Acetone ≤ 0.75 - Sum of other compounds ≤ 7.0	Investigate sources of contamination in handling and transport, Apply qualifier flag "FB" to all detected carbonyls in all field samples collected since the last passing FB sample prior to reporting data to AQS or if required, update data already reported to AQS.

Table B5-1. Carbonyls Field Quality Control Parameters

QC Parameter	Detail	Required Frequency	Acceptance Criteria	Recommended Corrective Action
Trip Blank	blank cartridge accompanying collected samples to and from the field site.	Not routinely collected. Used for corrective action purposes only when three consecutive FB results do not pass the acceptance criteria.	Measured mass per cartridge ($\mu\text{g}/\text{cartridge}$): - Acetaldehyde ≤ 0.10 - Formaldehyde ≤ 0.15 - Acetone ≤ 0.30 - Other individual compounds ≤ 0.10	Investigate sources of contamination in handling and transport. Apply qualifier flag "TB" to all detected carbonyls in all samples transported with the failing trip blank sample prior to reporting data to AQS.
Sample Retrieval	samples are retrieved, capped, protected from light, and stored at $\leq 4^{\circ}\text{C}$.	each sampling event.	within 72 hours of end of sampling period.	Apply qualifier flag "HT" to associated samples prior to reporting data to AQS.

B5.1.2 Quality Control for VOC Canister Sample Collection

VOC canister sample collection QC includes the performance of quality checks on the sampler and canisters to ensure they are not imparting a positive bias (i.e., contaminating) to the collected samples. Additionally, the sampler flow control is verified accurate, and the instrument clock is verified accurate. VOC canister field QC samples are described in Table B5-2 and in SOPs DAQ-03-001.2 and DAQ-03-003.2. Field QC samples include duplicate and/or collocated samples, which characterize the precision between samples collected from the same air mass.

For variable flow controller verification and clock accuracy, corrective action will be taken immediately when non-conformances are observed. When clock setting deviations are noted, the clock should be reset and noted on the sample collection records. For example, if the VOC canister sampler digital timer clock shows 11:06 a.m. when the time is 10:59 a.m., the operator should reset the clock to 10:59 a.m. and note the time adjustment in the sample collection records. For the sampler and canister positive bias challenge (as described in Section A7.3.4), compliance with acceptance criteria must be attained for all Tier I Core VOC compounds prior to deploying the sampling instrument or canisters to the field for sample collection. Sampling media and samplers indicating unacceptable levels of background contamination may still be used in the field but the failing parameters that are also detected in the field samples will be appropriately flagged prior to reporting. A positive bias challenge is recommended if instrument contamination is suspected (such as would be indicated by poor precision for duplicate or collocated samples or if unusually elevated concentrations are reported). The need for follow up

corrective action for collocated or duplicate sampling criteria failures will not be apparent until analysis results are completed. A root-cause analysis will be performed as soon as possible for field QC sample non-conformances, and efficacy of corrective actions will be evaluated by collection of follow-up field QC samples where applicable.

Current canister samplers used by the DAQ are not capable of purging the inlet sample line with a minimum of 10 air exchanges prior to sample collection. Therefore, DAQ will make every effort to make VOC sampler inlet lines as short as possible to minimize the amount of stagnant air sampled into the canister.

Table B5-2. VOC Canister Field Quality Control Parameters

QC Parameter	Detail	Required Frequency	Acceptance Criteria	Recommended Corrective Action
Clean Canister Batch Certification Sample	Analysis of one or two designated canisters in a cleaning batch that collects a representative sample from all canisters cleaned in the batch of canisters.	Every cleaning batch of 9-12 canisters: 2 canisters are chosen as the batch certification canisters. Every cleaning batch of 8 or less canisters: 1 canister is chosen as the batch certification canister. In all cases, a representative sample is pulled from all cleaned canisters into the certification canister(s).	VOC concentrations should be < 0.2 parts per billion (ppb) in all batch certification canisters or < 3x MDL, whichever is lower	If contaminated batch of canisters are used to collect field samples, the VOCs detected in the field samples that also fail clean canister criteria are qualifier flagged "CC" prior to reporting data to AQS.

Table B5-2. VOC Canister Field Quality Control Parameters

QC Parameter	Detail	Required Frequency	Acceptance Criteria	Recommended Corrective Action
Canister Viability (certified clean sample canisters)	Maximum holding time allowable for certified clean and evacuated canisters	All canisters used for routine sample collection will be evaluated	The difference between the canister sample date and canister cleaning date must be ≤ 30 days	If clean canisters used for routine sampling are used past the initial 30 day hold time, apply qualifier flag "QX" to all detected VOCs prior to reporting data to AQS.
Sampler Clock Accuracy	Verify clock accuracy against a known accurate time standard	Each sampling event	Within ± 5 minutes of true reference time not adjusted for DST	Reset sampler clock to match reference time not adjusted for DST,
Canister Starting Pressure Verification	Verification of canister pressure prior to use for routine sampling or QC sample or standard preparation	All canisters, prior to shipping unsampled canisters from the laboratory to the field site and during canister installation	Vacuum ≥ 28 inches of Hg vacuum as determined with a NIST traceable pressure gauge or transducer	If pre-sampling canister vacuum does not meet requirement the canister should not be used. If the canister is used for sample collection, apply qualifier flag "QX" to all detected VOCs prior to reporting data to AQS.

Table B5-2. VOC Canister Field Quality Control Parameters

QC Parameter	Detail	Required Frequency	Acceptance Criteria	Recommended Corrective Action
Sampler Leak Check	Leak checking of canister connection to the sampler	Prior to all sample collection	Leak rate must be ≤ 0.2 psi over ~5-minute period	For a full synopsis of the recommended corrective action, See SOP# DAQ-03-001.2. If the leak check fails and the canister is used for sampling and collects a pressurized sample, apply qualifier flag "QX" to all detected VOCs prior to reporting data to AQS.
Sampling Frequency	How often a VOC canister sample should be collected	One sample every 6 days according to the EPA National Monitoring Schedule	Samples should be collected on the scheduled sample dates	If the scheduled sample is missed, apply an appropriate null code to all VOCs for the missed sample prior to reporting data to AQS. A make-up sample should be scheduled according to the sample make-up policy.

Table B5-2. VOC Canister Field Quality Control Parameters

QC Parameter	Detail	Required Frequency	Acceptance Criteria	Recommended Corrective Action
Sampling Period	How long a canister sample is collected during a routine sampling event	With all field collected samples	24 ± 1 hour starting and ending at approximately midnight LST as indicated by the canister sampler timer program	If a collected sample is analyzed but does not meet sampling period criteria, schedule a make-up sample according to the make-up sample policy. If a make-up sample is not collected, apply qualifier flag “QX” to all detected VOCs in the sample prior to reporting data to AQS,
Sampled Canister Pressure	Post sampling canister pressure verification	With all field collected samples immediately after sampling by the sampler pressure gauge and when received by the laboratory and again immediately prior to analysis by GC-MS	Must be between 9.6-17.6 psig as indicated by the sampler pressure gauge and laboratory receipt pressure reading to be considered a valid 24hr sample collection. Also, just prior to injection the canister pressure must be > 0.2psi as indicated in the analysis instrument files.	If a collected sample is analyzed but does not meet final pressure criteria, schedule a make-up sample according to the make-up sample policy. If make-up sample is not possible, apply qualifier flag “QX” to all detected VOCs in the sample prior to reporting data to AQS.

Table B5-2. VOC Canister Field Quality Control Parameters

QC Parameter	Detail	Required Frequency	Acceptance Criteria	Recommended Corrective Action
Sampler Positive Bias Challenge (zero air challenge)	Collection of a 24-hour sample of humidified zero-air to investigate contamination contributed by the sampler.	Prior to installation at monitoring site and every 365 days thereafter or when corrective action requires performance of another positive bias challenge	All compounds must be < 0.2ppb or < 3x MDL, whichever is lower.	Another positive bias challenge is performed. If a contaminated sampler is used to collect field samples, qualify all detected VOCs "SB" in the field samples that also failed the sampler positive bias challenge prior to reporting data to AQS.
Variable Flow Controller Verification	Verify sampling flow at the sampling flow setting	During sampler certification and before and after each sample event.	Sampler flow rate must be within $\pm 10\%$ of the design flow.	For pre-sample flow checks, simply adjust sampler flow to meet criteria. If the post-sample flow check fails criteria, apply qualifier flag "W" to all detected VOCs prior to reporting data to AQS.

B5.1.3 Quality Control for Meteorology

Meteorological instruments require minimal intervention and maintenance once configured and calibrated. Meteorology parameters will be measured minimally at the Garinger and Millbrook UAT sites (urban) and the Candor UAT site (rural). The DAQ may install additional meteorological sensors at other UAT sites as supplies become available and staff are trained. QC procedures for meteorology measurements consist of the initial calibration and annual calibration checks. SOP# DAQ-07-003.1 MetOne AIO2 All-in-one Met Sensor, ECB Responsibilities describes the annual quality control check using a CTS method. The CTS method measures bias and precision in real-time. The limits for bias and precision are listed in SOP# DAQ-07-003.1.

B5.2 Quality Control for Laboratory Activities

QC for laboratory activities applies to carbonyl cartridge samples and VOC canister samples. Meteorological parameters do not have a laboratory component.

B5.2.1 Quality Control Carbonyls Laboratory Analysis

Laboratory QC procedures for carbonyls analysis includes the shipment of blank sample media to the field, receipt of sampled media at the laboratory, extraction and analysis of sample media, level 1 data review, and level 2 data review. Table B5-3 describes the laboratory QC evaluation, frequency of the evaluation, criteria the evaluation must meet, and recommended corrective actions. Additional details on the procedures performed by the laboratory can be found in DAQ SOP # DAQ-03-004.2 Thermo Ultimate 3000 UHPLC-UV-MS UAT and PAMS Carbonyl Analysis Operator Responsibilities. Laboratory QC samples consist of extraction batch QC (extraction solvent method blanks [ESMB] and DNPH media method blanks [MB] and known standard spikes – LCS/LCSD) and analysis batch QC samples including solvent blanks (SB), SSCV standards, continuing CCV, MDL blanks, MDL spikes, and replicate analysis of an extract. Other QC processes include establishing HPLC instrument calibration and adhering to proper cartridge storage conditions and holding times,

Table B5-3. Quality Control for Carbonyls Laboratory Analysis

QC Parameter	Detail	Required Frequency	Acceptance Criteria	Recommended Corrective Action
Solvent Blank (SB) “ACN-blank”	Analysis of acetonitrile solvent to demonstrate the HPLC is sufficiently clean	Prior to ICAL, prior to first daily CCV, and after each CCV when additional samples are to be analyzed	Target analyte concentrations \leq MDL _{spk}	Apply qualifier flag “LB” to the detected carbonyls in the field sample extracts analyzed in the same analysis batch as the failing solvent blank prior to reporting data to AQS.

Table B5-3. Quality Control for Carbonyls Laboratory Analysis

QC Parameter	Detail	Required Frequency	Acceptance Criteria	Recommended Corrective Action
UHPLC Initial Calibration (ICAL)	Analysis of at least five different calibration standard levels covering the concentration range of interest	Prior to sample extract analysis, after calibration verification failures of formaldehyde and acetaldehyde or after changing instrument components or maintenance which impacts calibration response	R ² (UHPLC instrument software calculates value as a percent) > 99.9%, recovery of each calibration curve standard level within ± 20% of nominal, absolute value of intercept divided by slope must be ≤ MDL	Prepare new ICAL curve levels and reanalyze or remove one calibration point and recalculate. If failing condition is confirmed and sample extracts are analyzed apply null code "AT" to the failing carbonyl in all sample extracts analyzed in sequence prior to reporting data to AQS,
Second Source Calibration Verification (SSCV) and Continuing Calibration Verification (CCV) a.k.a, "HL-QA"	Analysis of a known standard prepared from a stock solution sourced from a vendor independent of the primary calibration standard or same vendor stock but a different lot number than the primary calibration standard.	Immediately following ICAL, prior to sample extract analysis and every 10 th sample extract injection and at the conclusion of an analysis sequence	Target carbonyl concentrations within ± 15% of nominal	Prepare new HL-QA and/or ICAL and reanalyze sample extracts. If associated samples cannot be reanalyzed or if failing conditions are confirmed, apply null code "ST" to failing carbonyl in all sample extracts analyzed since last passing HL-QA prior to reporting data to AQS.

Table B5-3. Quality Control for Carbonyls Laboratory Analysis

QC Parameter	Detail	Required Frequency	Acceptance Criteria	Recommended Corrective Action
Retention Times (RT)	RT measured by the UHPLC used to identify a known target carbonyl compound	Every sample analysis	Carbonyl RTs must be within ± 2 standard deviations of the mean ICAL RT calculated using the RTs measured in the calibration curve levels	Carbonyls detected in samples that fail retention criteria cannot be positively identified and are reported as "0.000" ppbv and qualified "ND" prior to reporting data to AQS.
Holding Times	Maximum duration from sample date to sample extraction date. Maximum duration from sample extraction date to sample extract analysis date	all field-collected and laboratory QC cartridges	Extraction date – Sample date must be ≤ 14 days Analysis date – extraction date must be ≤ 30 days	Apply qualifier flag "HT" to all carbonyls detected in samples that fail one or both holding time requirements prior to reporting data to AQS
DNPH Lot Blank Analysis	Extraction and analysis of a representative amount of each lot of DNPH cartridge media to demonstrate acceptably low background	with each new lot of DNPH cartridge media – 3 cartridges per lot or 1%, whichever is larger	Formaldehyde $\leq 0.03 \mu\text{g/mL}$; Acetaldehyde $\leq 0.02 \mu\text{g/mL}$; Acetone $\leq 0.06 \mu\text{g/mL}$; and all others $\leq 0.02 \mu\text{g/mL}$ to pass	Contact cartridge manufacturer for guidance on replacing cartridge media. If media is used to collect samples, apply qualifier flag "LB" to failing carbonyls that are also detected in the sample extracts prior to reporting data to AQS

Table B5-3. Quality Control for Carbonyls Laboratory Analysis

QC Parameter	Detail	Required Frequency	Acceptance Criteria	Recommended Corrective Action
Extraction Solvent Method Blank	Aliquot of extraction solvent carried through the entire extraction process but without eluting solvent through an unsampled cartridge.	No required frequency. Used to investigate excessive carbonyl contamination that has not been attributed to cartridge or solvent contamination	target analyte concentrations must be \leq MDL _{spk}	Thoroughly clean volumetric glassware and extraction manifold and perform another extraction solvent method blank. If confirmed, obtain new lot numbers of extraction material, and perform test again. Apply null code "MB" to failing carbonyls prior to reporting co-extracted samples to AQS.
Method Blank (MB) a.k.a. "Cartridge Blank"	Blank cartridge from the lot of co-extracted field-collected samples – extracted to assess cleanliness of media and reagents	one per extraction batch of 20 or fewer field-collected samples	target analyte concentrations must be \leq MDL	Apply qualifier flag "LB" to failing carbonyls also detected in the co-extracted samples prior to reporting data to AQS.
Laboratory Control Sample (LCS) a.k.a. "Cartridge Spike"	Unsampled cartridge spiked with a known amount of target analytes (nominal concentration = lower third of the calibration curve range)	One per extraction batch of 20 or fewer field-collected samples	Formaldehyde recovery \pm 20 of nominal, all other target analytes recovery \pm 30% of nominal	Apply qualifier flag "QX" to failing carbonyls also detected in the samples co-analyzed with the cartridge spike prior to reporting data to AQS.

Table B5-3. Quality Control for Carbonyls Laboratory Analysis

QC Parameter	Detail	Required Frequency	Acceptance Criteria	Recommended Corrective Action
Laboratory Control Sample Duplicate (LCSD) a.k.a. "Cartridge Spike Duplicate"	Duplicate blank cartridge spiked with a known amount of target analytes (nominal concentration = lower third of the calibration curve range and same concentration level as the LCS.	One per extraction batch of 20 or fewer field-collected samples	Formaldehyde recovery $\pm 20\%$ of nominal, all other target analytes recovery $\pm 30\%$ of nominal. RPD between the LCS and LCSD must be $\pm 20\%$	Apply qualifier flag "QX" to failing carbonyls also detected in the samples co-analyzed with the cartridge spike duplicate prior to reporting data to AQS.
Replicate Analysis (Duplicate injection)	Repeat analysis of a routine sample extract	One replicate analysis of a field sample to represent 20 or fewer samples analyzed in the sequence. A sequence with 21 samples requires two replicate analysis pairs. A sequence with 41 samples requires three replicate analysis pairs. This repeats for every 20 or fewer field samples analyzed in the sequence.	RPD $\leq 10\%$ when at least one carbonyl is $\geq 0.1 \mu\text{g/mL}$	Reanalyze extracts to confirm disparate results. If confirmed, apply qualifier flag "4" to failing carbonyls also detected in samples co-analyzed with the replicate analysis prior to reporting data to AQS
Sampled cartridge receipt temperature	The measured temperature of the sampled cartridges received by the laboratory	Every sampled cartridge received by the laboratory	Sampled cartridge temperature must be $\leq 4^\circ\text{C}$	Apply qualifier flag "TT" to all detected carbonyls prior to reporting data to AQS

Table B5-3. Quality Control for Carbonyls Laboratory Analysis

QC Parameter	Detail	Required Frequency	Acceptance Criteria	Recommended Corrective Action
Collocated Sample Collection and Analysis	Collection and analysis of a separate sample cartridge collected concurrently with a primary 24-hour sample through an independent inlet probe and sampler.	Collocated samples are collected with every routine sample.	RPD \leq 20% of the associated primary cartridge for compounds \geq 0.5 $\mu\text{g}/\text{cartridge}$	Apply qualifier flag "3" to failing carbonyls detected in the primary and collocated sample extracts prior to reporting data to AQS.
Method Detection Limit (MDL)	Analysis of at least seven spikes and seven blank cartridges prepared over at least 3 non-consecutive extraction batches and analyzed over at least 3 analysis sequences	Performed according to the method update rule (MUR) described in section 4.1 of NATTS TAD. Once per calendar year or whenever changes to the instrument affect instrument sensitivity	Formaldehyde and Acetaldehyde must meet MDL listed in Section 3 of the most recent NATTS workplan template. https://www3.epa.gov/ttnamti1/files/ambient/airtox/nattsworkplantemplate.pdf	If MDL fails criteria investigate the MDL spiking level and perform MDL again. Also, consult the MUR in Section 4.1 of the NATTS TAD Revision 3.
Proficiency Testing	Blind sample submitted to each laboratory to evaluate laboratory bias	Twice per calendar year or on frequency determined by EPA	Each target compound within \pm 25% of the assigned target value	For a full synopsis on the routine corrective action for PT sample failures, see SOP DAQ-03-004.5

B5.2.2 Quality Control VOC Canister Laboratory Analysis

Laboratory QC procedures for VOC canister analysis includes the shipment of blank sample media to the field, receipt of sampled media at the laboratory, analysis of sample media, level 1 data review, and level 2 data review. Table B5-4 describes the laboratory QC evaluations for VOC canister analysis, frequency of the evaluation, criteria the evaluation must meet, and recommended corrective actions. Additional details on the procedures performed by the laboratory can be found in DAQ SOP # DAQ-03-003.2 Markes-Agilent GC-MS UAT VOC

Canister Analysis Operator Responsibilities. Laboratory QC samples consist of instrument blanks, bromofluorobenzene (BFB) tune checks, laboratory blanks, method blanks, MDL blanks, MDL spikes, CCV standards, and replicate analysis samples. Other QC processes include establishing GC-MS instrument calibration and verifying the calibration with a second source standard or at minimum, a standard from the same source but a different lot number than the standard used for GC-MS calibration. Additional QC processes are verifying and adhering to proper cleaned canister and sampled canister holding times.

Table B5-4. Quality Control for VOC Canister Laboratory Analysis

QC Parameter	Detail	Required Frequency	Acceptance Criteria	Recommended Corrective Action
BFB Tune Check	Verify detector meets method tuning criteria.	Prior to ICAL or first LCS certification sample analysis, and every 24 hours of analysis thereafter (for quadrupole MS only)	Must meet abundance criteria in SOP# DAQ-03-003.2	Repeat BFB tune. If failing condition continues, contact instrument manufacturer for guidance
Multi-point calibration (ICAL)	Analysis of a minimum of five calibration levels covering the calibration range of interest	Initially and minimally every three months thereafter, following failed BFB tune check, failed SSCV or CCV, or when changes to the instrument affect calibration response	Average relative response factor (RRF) $\leq 30\%$ relative standard deviation (RSD) and each calibration level must be within $\pm 30\%$ of nominal. For linear regression (with linear or quadratic fit), $r \geq 0.995$ and each calibration level must be within $\pm 30\%$ of nominal	Review and adjust integration and adjust if possible. If Tier I Core and PT compounds do not meet criteria, prepare new ICAL curve levels. If re-analysis not possible, null failing compounds "AT" for all samples analyzed using the calibration curve prior to reporting data to AQS.

Table B5-4. Quality Control for VOC Canister Laboratory Analysis

QC Parameter	Detail	Required Frequency	Acceptance Criteria	Recommended Corrective Action
Secondary Source Calibration Verification (SSCV)	Analysis of a secondary source of standard at the mid-range of the calibration curve to verify ICAL accuracy.	Immediately after the ICAL and in the same sequence as the ICAL. The SSCV is also analyzed at least once in the middle of sequences containing 20 or fewer field samples.	Target analyte concentrations within $\pm 30\%$ of nominal or RRF within $\pm 30\%$ of the mean ICAL RRF	If reanalysis or manual integrations do not correct failing condition, apply null code "ST" to failing VOCs for all samples co-analyzed with the failing SSCV prior to reporting data to AQS.
Continuing Calibration Verification (CCV) and Laboratory Control Sample (LCS)	Analysis of a known standard made from primary standard mix (same mix used for GC-MS calibration) at the mid-range of the calibration curve to verify ongoing instrument calibration accuracy and precision	Analyzed at the beginning and end of sequences containing 20 or fewer field samples.	Target analyte concentrations within $\pm 30\%$ of nominal. The RPD of the two LCS/CCV injections analyzed at the beginning and end of a sequence containing at least one field sample must be $\pm 25\%$.	If reanalysis or manual integrations do not correct failing condition, apply qualifier flag "SP" to failing VOC detected in all samples co-analyzed with the LCS/CCV nominal failure or apply null code "AX" to failing VOC for all samples co-analyzed with the LCS/CCV RPD precision failure.
Internal Standard Response	Deuterated or non-naturally occurring compounds added to each injection onto the instrument	Analyzed with all injections to monitor instrument response and assess matrix effects	Area response for each IS within $\pm 40\%$ of the mean ICAL IS response	Apply qualifier flag "MX" to all VOCs detected in the sample injection prior to reporting data to AQS.

Table B5-4. Quality Control for VOC Canister Laboratory Analysis

QC Parameter	Detail	Required Frequency	Acceptance Criteria	Recommended Corrective Action
Method Blank	Certified clean, evacuated sample canister filled with humidified diluent gas pulled from the dilution system	One injection with every analysis batch containing 20 or fewer field-collected samples	Each target VOC concentration must be < 0.2 ppb or < 3x MDL, whichever is lower	If reanalysis or manual integrations do not correct the failing condition, apply qualifier flag "LB" to the failing VOC detected in the field samples co-analyzed with the method blank canister prior to reporting data to AQS.
Pre-concentrator leak check	Pressurizing or evacuating each canister connection to the pre-concentrator to verify as leak-free prior to analysis	Every injection just before the pre-concentrator pulls an aliquot of sample from the canister for analysis	< 0.2 psi change/minute or manufacturer specifications	Reanalyze canister sample. If reanalysis is not possible, apply null code "AR" to all VOCs prior to reporting data to AQS. Schedule a make-up sample according to the make-up sample policy
Retention Time (RT)	RT of each target analyte and IS	Evaluated with each analysis run	Each target VOC must be within ± 0.5 minutes of its mean ICAL RT. Each IS RT must be within ± 0.33 minutes of its mean ICAL RT.	Check system integration and manually adjust integration if possible. For target VOCs: If adjustment cannot be made, apply null code "BH" to failing target VOCs prior to reporting data to AQS. For IS: If adjustment cannot be made apply qualifier flag "MX" to VOCs detected in sample prior to reporting data to AQS.

Table B5-4. Quality Control for VOC Canister Laboratory Analysis

QC Parameter	Detail	Required Frequency	Acceptance Criteria	Recommended Corrective Action
Target VOC identification	Qualitative identification of each target VOC in all samples and standards injected on the GC instrument	Evaluated with each injection and for each VOC parameter	<p>RT within prescribed window.</p> <p>Ion abundances of the primary quantitation ion within 30% of ICAL mean.</p> <p>Peak apexes co-maximized (within one scan for quadrupole MS).</p>	Detected VOC parameters in the samples that do not meet all compound identification criteria will be reported to AQS as “0.000” ppb concentrations and flagged “ND” prior to AQS upload. Detected VOC parameters that are quantified (provide a concentration in pbb) and fall outside RT criteria must be null coded “BH” prior to reporting data to AQS.
Replicate Analysis	A single additional analysis of a field collected sample	Once with every analysis sequence	Precision \leq 25% RPD.	If reanalysis or manual integrations do not correct the failing condition, apply qualifier flag “4” to failing VOC detected in the sample selected for replicate analysis prior to reporting data to AQS.
Collocated Sample Collection and Analysis	Collection and analysis of a separate sample canister collected concurrently with a primary 24-hour sample through an independent inlet probe and sampler.	Collocated samples are collected with every routine sample at one monitoring site.	RPD must be $\leq \pm 25\%$ for all detected VOCs.	If reanalysis or manual integration does not correct failing condition, apply qualifier flag “3” to failing VOC detected in the primary and collocated sample prior to reporting data to AQS.

Table B5-4. Quality Control for VOC Canister Laboratory Analysis

QC Parameter	Detail	Required Frequency	Acceptance Criteria	Recommended Corrective Action
Method Detection Limit	Statistical assessment of blank and low-level spiked canisters (field sample canisters and standard prep canisters) to determine an overall MDL representative of the entire sample collection and analysis process	Determined initially and minimally annually thereafter and when analysis instrument changes alter instrument sensitivity	Acrolein, Benzene, 1,3-Butadiene, Carbon Tetrachloride, Chloroform, Tetra-chloroethylene, Trichloroethylene and Vinyl Chloride must meet MDL listed in Section 3 of the most recent NATTS workplan template. https://www3.epa.gov/ttnamti1/files/ambient/airtox/nattsworkplantemplate.pdf	If MDL fails criteria investigate the MDL spiking level and perform MDL again. Also, consult the MUR in Section 4.1 of the NATTS TAD Revision 3.
Proficiency Testing	Blind sample submitted to each laboratory to evaluate laboratory bias	Twice per calendar year or on frequency determined by EPA	Each target compound within $\pm 25\%$ of the assigned target value	For a full synopsis on the routine corrective action for PT sample failures, see SOP DAQ-03-003.5

B6 Instrument/Equipment Acceptance, Testing, Inspection, and Maintenance

Instrumentation used to conduct UAT measurements or to calibrate UAT equipment will be maintained in accordance with the manufacturer's guidelines regarding routine maintenance of the specific instrument/equipment. Inspection and maintenance procedures will be followed as described in the approved instrument SOPs. Routine instrument maintenance activities and their prescribed frequencies are shown in Table B6-1.

B6.1 Instrument Acquisition

All sampling, analysis, and support equipment have been purchased and are currently being used for UAT field collections and sample analysis. New monitoring equipment will be selected and

purchased to ensure sufficient time to receive, inspect, install, calibrate, and become familiar with the operation of the instruments.

B6.2 New Instrument Acceptance Testing and Shakedown

The instruments and support equipment for UAT monitoring are complex and typically require a testing, conditioning, and shakedown period to ensure that instrument operation is stable and that monitors are suitably free of contamination and ready for the collection and analysis of the trace levels of pollutants in ambient air. Once equipment is received and inspected and proper operation is verified, instruments require calibration and independent verification of the calibration.

B6.2.1 Initial Instrument Acceptance Testing

Once new equipment is purchased and received, the equipment will be inspected within one month of receipt (earlier if possible) to ensure the equipment is in good condition and all the necessary components required for installation are included. Vendors will be contacted immediately when issues are discovered during this initial inspection. Instruments will be installed in the monitoring shelter or laboratory (by the vendor, site operator, or other qualified individual or 3rd party provider of such services), as appropriate, and DAQ will condition the instruments and ensure their proper functionality, which may include:

- Checking and documenting the diagnostics of the instrument, looking for error messages or warnings;
- Ensuring that parameters such as sample flow rate, pressure, temperatures, etc., are within specifications per instrument manuals; and
- Performing leak checks on the instrument.

Once proper instrument operation has been confirmed, LAB chemists and LAB electronics technicians will calibrate and/or verify the calibration of the instruments, as appropriate, as part of the instrument shakedown which typically occurs inside the laboratory building. There are known aspects of instrument and support equipment operation which require several days to weeks to complete including, but are not limited to, the purging and conditioning of VOC canisters; passivation and conditioning of calibration standard gas regulators, lines, and calibrators; and flow calibration of carbonyls sampling instruments and flow verifications of the VOC sampling instruments.

B6.2.2 Annual Instrument Acceptance Testing

The DAQ will operate all or some of the instruments year-round and perform ongoing acceptance testing to verify instruments are operating as designed. For example, samplers used to collect VOC and carbonyl samples will be tested for positive bias (cleanliness) prior to site installation, every 365 days thereafter, and again whenever corrective action requires additional

positive bias testing to be conducted such as when three or more primary and collocated sample pairs fails precision criteria (RPD must be within $\pm 25\%$) for target compounds detected in sufficient quantities.

B6.3 Equipment Inspections

In general, the following routine inspections will be conducted:

- Monitoring shelters, sample inlets, and equipment facilities (such as pump or compressor housings) should be inspected during each site visit and must be inspected monthly to ensure conditions do not adversely affect sample collection, instrument operation or data integrity.
- Data collected in-situ, such as meteorological parameters, are reviewed each business day to inspect for trends or signs of problems. Data trends that indicate a need for further inspection include issues such as identical (“frozen”) numbers for several consecutive hours or erratic spikes or dips in the measured concentration values.
- Sampling equipment will be inspected during site visits to ensure instruments are in appropriate working order. Site visit checklist are available for the AIO2 sensors. Carbonyl and VOC sampling instrument inspections will be noted in the site logbook and/or noted on the sample information forms and COC forms.

B6.4 Instrument Maintenance

Preventive maintenance minimizes instrument downtime and associated data loss. Routine preventive maintenance will be conducted in accordance with the manufacturer’s operation manuals and applicable maintenance bulletins, or updates issued by the manufacturer and according to procedures and frequencies described in the approved UAT instrument SOPs. UAT instrument and support equipment maintenance activities will be performed per the frequency detailed in Table B6-1.

The DAQ will maintain an appropriate supply of critical spare parts and ensure tools are available prior to conducting routine maintenance. Components known to fail or require frequent replacement should be readily available to address unforeseen events. A list of these supplies will be detailed in the specific equipment SOPs.

Table B6-1. Routine Instrument Maintenance Activities

Instrument	Maintenance Activity	Frequency
Markes-Agilent GC-MS	Maintenance activities are prescribed in SOP# DAQ-03-003.2. They include replacing pre-concentrator trap(s), servicing the Kori-XR, and Unity-XR instrument components.	Performed annually once per calendar year

Table B6-1. Routine Instrument Maintenance Activities

Instrument	Maintenance Activity	Frequency
UHPLC for carbonyls analysis	Maintenance activities are prescribed in SOP# DAQ-03-004.2. Such activities include servicing pumps, replacing guard columns, replacing solvent frits, injector needles, etc.	As prescribed in this QAPP and the SOP. Instrument preventative maintenance performed annually; replacement of consumables performed as needed
Xonteck 911A VOC canister sampler	Maintenance activities are prescribed in SOP# DAQ-03-001.1. They include cleaning internal flow path components, replacing the particulate filter, performing positive bias challenge, and flow controller verification.	Performed annually once per calendar year
ATEC 2200 Carbonyls sampler	Maintenance activities are prescribed in SOP# DAQ-03-002.1. They include recharging/replacing the ozone denuder, replacing the particulate filter, performing positive bias challenge, and MFC calibration.	Performed annually once per calendar year
Entech 3100A VOC Canister Cleaner	Maintenance activities are prescribed in SOP# DAQ-03-005.1.	See SOP for frequency
Entech 4700 Precision Diluter	Maintenance activities are prescribed in SOP# DAQ-03-006.1	See SOP for frequency

Once per calendar year, or whenever there are systemic failures of precision and bias, the DAQ will complete maintenance on the instruments and support equipment necessary for UAT measurements. The DAQ will replace worn items as needed, verify proper operation, and calibrate instruments such that the instruments are readied for collecting and reporting UAT measurements.

UAT site operators will perform basic checks during each site visit which include visually examining the instruments at the site and verifying communication with the data acquisition system (DAS) where applicable. Operators should pay particular attention to instruments outdoors, such as meteorology instruments. A visual inspection will include verifying that instrument temperature shields are present, free of damage, and not blocked (such as with a bird nest, insect nest, etc.). In general, site operators should compare current meteorological readings to nearby National Weather Service (NWS) site conditions or other reliable nearby readings.

B7 Instrument/Equipment Calibration and Frequency

Calibration is defined as the comparison of a measurement standard, instrument, or item with a standard or instrument of higher accuracy to detect and quantify inaccuracies and to report or eliminate those inaccuracies by adjustment. Instruments and devices employed at UAT sites will be calibrated prior to use and according to the schedule/frequency described within this section, which are duplicated in the NATTS TAD Revision 3 and instrument SOPs. Note that calibration checks which may involve verification of calibration at one or more different levels ensure the calibration remains valid, but do not involve adjustment of the instrument. Calibration verification failures require adjustment of the calibration, or recalibration, of the instrument or monitor.

Sampling instrument calibrations are documented in logbooks dedicated to the sampling instrument. The sampling instrument will be uniquely identified and the date of calibration, identification of standard(s) used for calibration (including certification date), calibration outcome (such as slope, intercept, or other metric indicating acceptable calibration), and any needed corrective actions will be documented in the appropriate logbook. Standards should not be used past their expiration date.

Laboratory analysis instrument calibrations are documented in laboratory logbooks indicating the date of calibration and a summary of the calibration. The calibration standards used must include a COA that is traceable to a NIST standard and that also uniquely identifies the standard material using a lot number with an expiration date. Calibration curve results such as line type, slope, intercept, correlation coefficient, and recovery of each standard level against the nominal concentration are summarized in calibration summary reports generated by the analysis instrument and in summary reports generated by the analyst.

B7.1 Instrument Calibration and Calibration Verification

Instrument calibration and calibration verification instructions are specified in the following SOPs:

- DAQ-03-001.1 Xonteck 911A UAT VOC Sampler, ECB Responsibilities
- DAQ-03-002.1 ATEC 2200 UAT Carbonyl Sampler, ECB Responsibilities
- DAQ-03-003.2 Markes-Agilent GC-MS VOC Canister Analysis, Operator Responsibilities
- DAQ-03-004.2 Thermo Ultimate 3000 UHPLC-UV-MS UAT and PAMS Carbonyl Analysis, Operator Responsibilities
- DAQ-07-003.1 MetOne AIO2 All-in-One Met Sensor, ECB Responsibilities

B7.1.1 Carbonyls Instrument Calibration and Calibration Verification

Carbonyls instruments requiring calibration include field sampling instruments and laboratory instruments used for sample analysis.

B7.1.1.1 Carbonyls Field Sampling Instrument Calibration and Calibration Verification

Carbonyl sampling unit MFC(s) will be calibrated initially when new samplers are received or when old samplers are received after being sent for repair to the instrument manufacturer and every 365 days thereafter or whenever persistent flow rate verifications fail acceptance criteria or when persistent failures of primary and collocated sample collection RPDs fail criteria. The flow calibration will be verified immediately after MFC calibration and routinely verified before and after each sampling event and during internal technical system audits. Flow calibration verifications will be within $\pm 10\%$ of the flow indicated on the sampler and the flow indicated on a NIST-traceable flow transfer standard.

B7.1.1.2 Carbonyls Laboratory Instrument Calibration and Calibration Verification

The carbonyls laboratory analytical instrument will be calibrated initially, following maintenance or repair that would reasonably impact the instrument response, and following consecutive failures of the SSCV/CCV. The UHPLC will be calibrated for the target compounds by analysis of at least five concentration levels covering the concentration range expected to bracket the concentrations of carbonyls in the sample extracts. More details on calibration and calibration verification can be found in SOP# DAQ-03-004.2.

B7.1.2 VOC Instrument Calibration and Calibration Verification

VOC instruments requiring calibration include field sampling instruments and laboratory instruments.

B7.1.2.1 VOC Field Sampling Instrument Calibration and Calibration Verification

The VOC sampler variable flow controller will be initially set prior to UAT field deployment with a certified, NIST traceable flow device. The variable flow controller will be verified by site operators with a different flow standard than the one used to establish the initial flow controller set point, minimally monthly thereafter. VOC sampler flow will be maintained between 7.2mL/min to 8.8mL/min. This flow range is optimal for obtaining super ambient pressurized canister samples, while preventing canister over pressurization (> 25 psig) during the sample collection period.

B7.1.2.2 VOC Laboratory Instrument Calibration and Calibration Verification

GC-MS instruments used for measuring VOCs in 6-L canisters will be calibrated initially, when maintenance to the instrument is reasonably expected to alter its calibration and following consecutive failures of Tier I Core compound results from the analysis of the SSCV or CCV/LCS. Markes-Agilent GC-MS calibration is described in more detail in SOP # DAQ-03-003.2 and is established by analysis of six concentration levels (0.2ppb, 0.5ppb, 1ppb, 2ppb, 5ppb, and 10ppb) which contains a mixture of 72 VOC compounds. A minimum of five out of six calibration levels must be included in the calibration curve to be considered a valid curve. The stock calibration gas (primary standard) will be NIST-traceably certified for all compounds present in the mixture. The calibration is then to be immediately verified by analysis of a NIST-

traceably certified SSCV containing the same mixture of 72 VOC compounds. All samples analyzed after the initial calibration and SSCV will be bracketed by the CCV standard to monitor GC-MS calibration drift. Additionally, the CCV will be analyzed after every 10th sample injection of an analysis sequence. The SSCV and/or CCV will be within $\pm 30\%$ of the nominal concentration or corrective action must be taken. If corrective actions do not improve results, the failing VOC compounds for the SSCV will be nulled with "AT" prior to AQS upload and failing VOC compounds for the CCV will be nulled with "AS" prior to AQS upload.

B7.1.3 Calibration and Calibration Verification for Meteorology Instruments

Meteorological instruments require manufacturer, wind tunnel calibration initially prior to placement into service, or whenever the calibration verification (CTS method) fails criteria. Instrument calibration will then be verified, at a minimum, annually thereafter by conducting the calibration verification QC checks listed in Section B5.1.3. Instruments which do not meet the listed calibration verification acceptance criteria will be recalibrated by adjusting the instrument response (e.g., thermocouple or hygrometer) and/or orientation (e.g., for wind direction) to match that of the reference standard or may be replaced with known calibrated instruments that meet the operational requirements given in Table A7-1. Data collected since the most recent acceptable calibration or calibration verification will be qualified or invalidated, as appropriate, when reported to AQS.

B7.2 Calibration Support Equipment

Calibration support equipment for UAT measurement instruments includes, but is not limited to, flow transfer standards, reference thermometers, reference barometers, volumetric labware, and MFCs. Calibration and calibration verifications will be performed by comparison to known standards which will be traceable to NIST standards. Such NIST traceability will be evidenced on a calibration certificate by the metrology lab, standards provider, or certification provider attesting to the accuracy or uncertainty associated with the standard. Such standard certification providers may be the manufacturer, in-house laboratory, third-party laboratory, or other suitable certifier. Such metrology certification providers typically operate under an International Organization for Standardization (ISO) quality standard or other similar performance standard which requires their certifications to be traceable to a NIST certification.

Support equipment requiring calibration and the associated calibration frequency and acceptance criteria are listed below in Table B7-1.

Table B7-1. Calibration Requirements for Critical Support Instruments

Critical Support Equipment	Specifications and Acceptable Uncertainty	Area of Use	Calibration ^a Frequency Requirement	Calibration Verification ^b Check Frequency
Flow transfer standard	≤ 2% of NIST-traceable standard across its range of flow rates	Calibration and verification of MFCs for carbonyls sampling units and variable flow controllers for VOC sampling units.	Annually and every 365 days thereafter	Calibration check is not required
Mechanical Pipette	Tolerance within specifications in Table 1 of SOP# DAQ-03-004.2	Delivery of known liquid volumes – preparation of carbonyls calibration standards	Initially and whenever two consecutive calibration verifications fail criteria	Performed quarterly according to SOP # DAQ-03-004.2
Class A Volumetric Labware	Meets Class A tolerances specific to the labware designated volume	Measuring final volume of standard solution preparation and sample extracts	Received with a certification of calibration	Calibration check is not required
Volumetric Syringe	Tolerance within manufacturer specifications	Delivery of known liquid or gas volumes	Received with a certification of calibration or initially calibrated gravimetrically at 10% and 100% of full volume	Calibration check is not required
Thermometer (not for reporting meteorological ambient temperature data)	0.1°C resolution ± 0.5°C accuracy of a NIST-traceably certified standard thermometer	Laboratory temperature monitoring, carbonyl sample receipt temperature and sample extract storage temperature – <u>note this is not a thermometer for reporting meteorological data</u>	Annually at temperature range of use	Annual calibration is sufficient

Table B7-1. Calibration Requirements for Critical Support Instruments

Critical Support Equipment	Specifications and Acceptable Uncertainty	Area of Use	Calibration ^a Frequency Requirement	Calibration Verification ^b Check Frequency
Balance	Tolerance within specifications listed in Appendix B of SOP# DAQ-03-004.2	Laboratory – Weighing standards, calibration verification of pipettes	Annually and every 365 days thereafter or when consecutive calibration checks demonstrate an out of tolerance condition	Quarterly
Certified Weights	Tolerances within those assigned to the class of weights	Laboratory – Calibration verification of balances	Annually and every 365 days thereafter	Annual calibration is sufficient
Rotronics HP-23A (temperature and humidity transfer standard)	Tolerances within specifications listed on the NIST traceable calibration certificate	Verify accuracy of sensors monitoring laboratory conditions and accuracy of sensors collecting meteorological conditions (relative humidity and ambient temperature)	Annually and every 365 days thereafter	Annual calibration is sufficient
Druck DPI barometric pressure standard	± 5mm Hg of a NIST-traceably certified standard	Verify accuracy of sensors monitoring laboratory barometric pressure and sensors measuring meteorological barometric pressure	Annually and every 365 days thereafter	Annual calibration is sufficient
Pressure Gauges	Within ± 0.5 psi or manufacturer-specified tolerance, whichever is smaller	Measuring canister pressure/vacuum and verification of sampler pressure gauge and verification of canister cleaning system pressure sensor and verification of dilution system pressure sensor	Annually and every 365 days thereafter	Annual calibration is sufficient

Table B7-1. Calibration Requirements for Critical Support Instruments

Critical Support Equipment	Specifications and Acceptable Uncertainty	Area of Use	Calibration ^a Frequency Requirement	Calibration Verification ^b Check Frequency
High Vacuum Gauges	Within manufacturer specified tolerance against a NIST traceable standard	Measuring canister vacuum, verifying accuracy of canister cleaning system high vacuum gauge.	Annually and every 365 days thereafter	Annual calibration is sufficient

^a Calibration refers to resetting (adjusting) the reading or setting or applying a correction factor to the instrument or standard to match a certified standard.

^b Calibration verification checks are a comparison to a certified standard to ensure the instrument or standard remains within a prescribed tolerance. Instruments or standards which exceed the tolerance must be adjusted to be within prescribed tolerances or must be replaced.

B8 Inspection/Acceptance of Supplies and Consumables

Supplies and consumables include a wide variety of materials such as calibration standards, particulate filters for inlets and instruments, stainless steel tubing, high pressure cylinder regulators, GC-MS pre-concentrator traps, analysis instrument separation columns, carrier gasses, mobile phases, ozone scrubbers, etc. Where possible, supplies and consumables will be purchased from reputable vendors to ensure items purchased meet the required specifications. The list of consumables and supplies is too extensive to provide in its entirety in this QAPP; individual materials and the required specifications are listed in the applicable SOPs for the measurement methods. Materials will be inspected and confirmed to meet the specifications detailed in the respective SOP before being used and/or placed into service. Performance of the supply or consumable will be confirmed by verifying proper instrument function or operation evidenced by meeting applicable QC criteria. Inspection and acceptance of supplies and consumables are described in more detail in the ECB Responsibilities SOPs and Operator Responsibilities SOPs as it pertains to the specific piece of equipment used for UAT monitoring,

B8.1 Acceptance of Standard Materials

On an annual basis, the DAQ will inspect NIST-traceable transfer standard equipment that is subject to wear and tear during use (for example, temperature, pressure, and flow rate check devices). Such equipment will be returned annually to the vendor or an appropriate accredited metrology laboratory (as specified in Section B7.2) for cleaning, servicing, and recertification against NIST standards. Consult Table B7-1 for equipment requiring such annual certification.

Stock gaseous standards for calibration of the GC-MS instrument will be sourced from reputable certified gas vendors. Similarly, derivatized carbonyls calibration stock materials will be sourced from reputable chemical suppliers. Standard gases and carbonyls stock materials will preferably be NIST-certified or NIST-traceably certified and must be accompanied by a COA stating the

purity (for neat materials or pure gases) or certified concentration with associated uncertainty for each component as well as the expiration date.

The concentrations and expiration date listed on the vendor COAs will be referenced for standards preparation. Expired standards may not be utilized for instrument calibration or calibration verification unless the expiration has been extended following a process approved by the EPA.

COAs will be maintained by the DAQ and be available for inspection during TSAs. VOC standard expiration or recertification dates are typically one year or more and several vendors offer recertification services in which traceable concentrations are updated such that the useful life of the standard cylinder is extended. Recertification of standard gases may be more cost effective than purchasing new standards. Carbonyl standard expiration dates are typically two years or more. The carbonyl standards are not typically recertified, but instead a new stock standard is purchased when the current standard exceeds expiration dates.

Prior to acceptance or use of a standard material for calibration, particularly for custom-ordered materials, the COA will be inspected to ensure the correct compounds are included, that their concentrations are as requested and within requested tolerances (for all Tier I Core compounds), and that listed impurities are acceptably low.

B8.2 Acceptance of Sampling Media - Carbonyls

Prior to use in the field for sample collection, each lot of DNPH cartridges will be tested to ensure the background contamination is acceptably low. Minimally three cartridges per lot or 1% of the received lot, whichever is greater, will be extracted and analyzed to determine the average background concentration of each target carbonyl. Background concentrations vary within manufacturer lots, therefore the analyst is encouraged to select cartridges from different boxes within a given lot to characterize the lot's background variability. Each tested lot blank cartridge will meet the criteria in Table B8-1.

If the criteria in the table are not met, the lot will not be used for sampling and will be returned to the vendor.

Table B8-1. DNPH Cartridge Lot Blank Acceptance Criteria

Carbonyl Compound	Acceptance Limit (µg/cartridge)
Acetaldehyde	≤ 0.10
Formaldehyde	≤ 0.15
Acetone	≤ 0.30
All Other Carbonyl Compounds*	≤ 0.10

**Cartridge vendor does not test for "other carbonyl compounds" and will not accept the return shipment of contaminated cartridge lots if the "other carbonyl compounds" are outside acceptance criteria. If other compounds fail, the lot may be used but the failing compounds will be qualified prior to AQS upload,*

B8.3 Acceptance of Sampling Media – VOCs

All newly purchased canisters will be cleaned and certified using a canister cleaning system prior to field use. Newly purchased canisters will be cleaned and certified independently of older canisters currently in-use for VOC sampling.

The canister cleaning system can clean up to twelve canisters at a time. One canister per cleaning batch is selected to collect a representative sample of all canisters cleaned in the batch. The cleaning batch certification canister is analyzed for the presence of 72 VOC compounds. All VOC compounds must be < 0.2ppb. VOC compounds that fail cleanliness criteria are tracked with each batch of cleaned canisters and are flagged “CC” prior to AQS upload if the batch is used for sample collection. For newly purchased canisters that fail the first two or more consecutive cleaning batch cycles for Core I and target PT VOC compounds, the DAQ will consult with the canister manufacturer to either return the canisters or obtain additional guidance for achieving cleanliness criteria,

B9 Non-direct Measurements

Non-direct measurement data will be used to support UAT data validation activities. Additional details of the non-direct measurements are described in Section 10 of the PAMS TAD⁵ Revision 2 and in SOPs DAQ-03-003.5, and DAQ-03-004.5.

Non-direct measurement data may include historical UAT VOC and carbonyl data, data obtained from other sampling and analysis methods such as PAMS carbonyls and PAMS AutoGC and meteorological data obtained from nearby sites. All non-direct measurement data used to compare against recently acquired UAT data must go through at least Level 1 and Level 2 data review and verification activities.

B10 Data Management

DAQ will ensure that data are recorded, reviewed, verified, validated, reported, managed, and archived in a manner that permits reconstruction of activities throughout the data point lifecycle. The following DAQ SOPs contain information for managing UAT VOC sampling and analysis data, and UAT Carbonyl sampling and analysis data through the generation of the sampling media at the analysis lab, installation, and removal of sampling media in the field, and analysis of the field-collected samples by the analysis lab and reporting of the results to AQS.

- Section 5, 6, 7, and 8 of SOP# DAQ-03-001.1 Xontech 911A UAT VOC Sampler, ECB Responsibilities
- Sections 5, 6, 7, and 8 of SOP# DAQ-03-001.2 (Section 5 of old SOP# 2.51.2) Xontech 911A UAT VOC Sampler, Operator Responsibilities
- Sections 5, 6, 7, and 8 of SOP# DAQ-03-002.1 ATEC 2200 UAT Carbonyl Sampler, ECB Responsibilities

- Sections 5, 6, 7, and 8 of SOP# DAQ-03-002.2 ATEC 2200 UAT Carbonyl Sampler, Operator Responsibilities
- Sections 5, 6, 7, and 8 of SOP# DAQ-03-003.2 Markes-Agilent GC-MS UAT VOC Canister Analysis, Operator Responsibilities
- Sections 4, 5, 6, 7, and 8 of SOP# DAQ-03-003.5 Markes-Agilent GC-MS UAT VOC Canister Analysis, RCO Responsibilities
- Sections 5, 6, 7, and 8 of SOP# DAQ-03-004.2 Thermo Ultimate 3000 UHPLC-UV-MS UAT and PAMS Carbonyl Analysis, Operator Responsibilities
- Sections 4, 5, 6, 7, and 8 of SOP# DAQ-03-004.5 Thermo Ultimate 3000 UHPLC-UV-MS UAT and PAMS Carbonyl Analysis, RCO Responsibilities
- Sections 5, 6, 7, and 8 of SOP# DAQ-07-003.1 AIO2 All-in-one Met Sensor, ECB Responsibilities
- Sections 5, 6, 7, and 8 of SOP# DAQ-07-003.2/3 AIO2 All-in-one Met Sensor, Operator/Coordinator Responsibilities
- Section 5.5 of SOP# DAQ-15-006.5 Data Verification and Validation for Continuous Gaseous Pollutants

A general overview of the VOC and Carbonyl data point life cycle is provided below:

1. The analysis lab certifies the samplers and sample media as being clean for routine field use.
2. The analysis lab generates the sample information form and COC form and assigns the forms to the sample media.
3. The analysis lab ships the sample media and forms to the site operator, or the site operator picks up the sample media and forms in-person at the analysis lab.
4. The site operator receives the sample media and forms and inspects the sample media for damage and inspects the forms for accuracy.
5. The site operators take the sample media and forms to the field site for sampler installation and recording of field sampling data onto the forms.
6. The site operator performs pre-sample verifications and sample media installation and records this data on the forms.
7. The site operator performs post-sampling verifications and sample media removal and records this data on the forms.
8. The site operator makes sure all form entries are complete and legible.
9. The site operator ships the sampled media and filled out forms to the analysis lab.
10. The analysis lab receives the sample media and forms.
11. The analysis lab verifies the forms match the sample media and verifies the form entries are complete and legible.
12. The analysis lab performs calibration and verification of analysis instruments and support equipment.
13. The analysis lab performs sample media extraction and/or analysis.
14. The analysis lab generates sampling and analysis data packets, The data packets contain the COC forms, sample information forms, analysis instrument results, and QC summary reports summarizing the results of the sampling and analysis data that is tested against the measurement quality objectives and the acceptance criteria.

15. The analysis lab performs a two-level review (self-review and peer-review) on the sampling and analysis data packets.
16. The analysis lab sends the reviewed and verified data packets to the central office chemist for final data validation and reporting of the validated data to AQS.

A general overview of the meteorological data point life cycle is provided below:

1. Performed by ECB: meteorological sensor verification, field site installation, and connection of the sensor to the data acquisition system, periodic maintenance and auditing of the sensor, removal of the site sensor for return to manufacturer for calibration
2. Performed by meteorological sensor site operator (local program monitoring staff, and DAQ regional monitoring staff): review and verification of collected meteorological data
3. Performed by the central office/PPB and database manager: validation of the meteorological data, reporting of the data to AQS, and reconciliation of the reported data with the original data recorded and stored by the DAS.

C. ASSESSMENT AND OVERSIGHT

C1 Assessments and Response Actions

One of the major objectives of this QAPP is to specify the policies and establish procedures necessary to ensure UAT data are of sufficient quality and quantity to meet the NATTS DQOs. Site operators and laboratory staff have the responsibility to prevent non-conformances where possible and to minimize their impact to data quality and fitness for purpose once identified. Every effort will be made to anticipate and resolve potential non-conformances before the quality of UAT data is compromised. Non-conformances impacting data quality will be reported to the appropriate DAQ supervisor who will work with the site operators and/or laboratory staff to take corrective action. Adherence to the quality policies described in this QAPP will also be ascertained by way of various ongoing assessments, as given below.

C1.1 Types of Assessments

As part of the DAQ UAT Network QS, the following types of assessments will be conducted to ensure that the resulting data quality meets the UAT DQO and user needs:

- IPAs
- TSAs
- ADQs
- PTs

Details regarding assessments are described in Section 15 of the EPA QA Handbook, Volume II (EPA-454/B-17-001, January 2017), available by the following link on AMTIC:

<https://www3.epa.gov/ttn/amtic/files/ambient/pm25/qa/Final%20Handbook%20Document%2017.pdf>

Staff conducting assessments should be independent of staff performing routine UAT functions and have authority to inform management of non-conformances to approved, established procedures and policies. Staff conducting assessments will have authority to suggest to management to stop work activities if non-conformances have a severe impact on the quality of collected measurements or if staff safety is in jeopardy.

Refer to Table C1-1 for a summary of UAT assessments, description of the assessment, responsible party conducting the assessment, and frequency of performing the assessment.

Table C1-1. UAT Assessments

Assessment	Description	Responsible Party Conducting Assessment	Frequency
Instrument Performance Audit (IPA)	Measurement of carbonyls sampling unit flow and VOC sampler flow with a certified flow transfer standard independent of that used for instrument calibration or calibration verification	Level 3 Data Reviewer	Annually during active UAT monitoring
Technical Systems Audit (TSA)	Review of compliance with NATTS TAD Revision 3 requirements, this QAPP, associated SOPs, and best practices	EPA Regional Representative and National QA Support Contractor – note the triennial TSA may also include an IPA of the carbonyls sampler(s) and/or meteorological instruments	Once every three years, preferably during active UAT monitoring
Internal Technical Systems Audit	Review of compliance with NATTS TAD Revision 3 requirements, this QAPP, SOPs, and best practices	PPB Environmental Chemists not directly involved in the UAT sampling and analysis methods.	Annually during active UAT monitoring
Audit of Data Quality (ADQ)	Review of a representative amount of measurement data (~10%) from initial instrument calibration, sample analysis, and coding for reporting to AQS; includes evaluating that data in AQS were reported accurately	PPB Environmental Chemist and Level 3 Data Reviewer	Annually during active UAT monitoring and after submittal of a site's UAT data to AQS
Proficiency Test (PT)	Analysis of double-blind spiked sample	EPA through QA support contractor	Twice annually or as supplied through EPA QA support contractor

CI.1.1 Instrument Performance Audit

IPAs are an independent check of instrument performance by an individual not involved in routine operation and with reference standards independent from those used to calibrate the instrument or to perform routine calibration checks. IPAs involve comparing the output of an instrument to an independent reference standard and quantifying the difference between the measurement generated by the instrument undergoing assessment and the reference standard. The Level 3 Data Reviewer will conduct IPAs at UAT sites at least once per calendar year. The EPA Regional Representative or delegate may conduct IPAs of the pollutant and meteorology instruments, as equipment and capabilities permit, during the triennial TSA.

CI.1.1.1 Carbonyls Instrument Performance Audit

Flow rate bias in ambient air sampling for carbonyls has an inverse relationship with the resulting concentration bias. That is, flow rates that are biased low result in overestimation of air concentrations whereas flow rates that are biased high result in underestimation of air concentrations. Minimally once annually, the Level 3 Data reviewer, who is independent from routine site operations, will verify the flow rate of the carbonyls sampling unit against a certified, reference flow transfer-standard independent of the standard utilized to calibrate or perform monthly calibration verification of the sampling unit. This check will be performed at the flow rate at which UAT cartridges are collected and the flow measured by the flow transfer standard must be within $\pm 10\%$ of the flow indicated by the sampling unit. The assessor will notify the site operator in the event of a nonconformance. Corrective action will be required (i.e., MFC calibration, flow obstruction removed, etc.) before cartridge collection may resume. Previously collected sample data since the most recent acceptable flow check will be appropriately qualified (flagged) or invalidated when reported to AQS. Corrective action is also recommended for flow calibration assessments that indicate flows are approaching, but not exceeding the appropriate flow acceptance criterion.

CI.1.1.2 VOC Instrument Performance Audit

Flow rate bias in VOC sampling does not have the same impact as that of carbonyl sampling. Sample volume is not required for determining final VOC compound concentrations, but instead flow is used to validate sample collection. The DAQ VOC samplers target a flow rate range of 7.2 mL/min to 8.8 mL/min. The assessor will notify the site operator in the event of nonconformance; corrective action will be required (variable flow adjustment) before canister collection may resume and previously collected sample data since the most recent acceptable flow check will be appropriately qualified (flagged) or invalidated when reported to AQS.

CI.1.1.3 Meteorology Instrument Performance Audits

Meteorological instruments will operate year-round and be audited according to the procedures described in SOP# DAQ-07-003.1 MetOne AIO2 All-in-One Met Sensor ECB Responsibilities. Wind speed and wind direction will be audited using the CTS method. Relative humidity,

barometric pressure, and ambient temperature will be audited using transfer standards or through the CTS method. Auditing procedures are described in more detail in section 5 of SOP# DAQ-07-003.1. Currently, Garinger (covered by MCAQ QAPPs and SOPs), Millbrook and Candor are the only UAT sites with meteorology instruments. Meteorological IPAs for Millbrook and Candor will meet the acceptance criteria listed in Table 1 of SOP# DAQ-07-003.1.

CI.1.2 Technical Systems Audit

A TSA is an on-site review and inspection of a monitoring agency's ambient air monitoring program to assess its compliance with established requirements governing the collection, analysis, review, verification, validation, and reporting of ambient air quality data. TSA's are performed once every three years.

To increase the uniformity of TSAs, EPA has developed checklists for the NATTS Required Site program for both sampling and analysis operations, incorporating elements from the NATTS TAD Revision 3, compendium methods TO-15 and TO-11A. Monitoring agency TSAs will focus on siting criteria, adequacy of QSs, compliance with QS documents, and interviews of staff responsible for data generation, equipment and instrument calibration, day-to-day operations including sample collection (handling and custody), meteorology, and data management (such as records management and data verification, validation, and reporting).

The EPA Regional Representative will conduct the triennial TSA or may delegate that the audit be conducted by the National QA Support Contractor. The TSA will be conducted on field and laboratory activities. As much as possible, UAT TSAs will be scheduled in conjunction with NCore, PAMS, or other monitoring program audits at the site or laboratory to reduce the burden on DAQ and/or their laboratories, reduce contactor costs (for example, by conducting NATTS and PAMS TSAs within the same week), and to leverage EPA Regional staff time such that TSAs for multiple programs can be covered concurrently.

The EPA TSA will follow checklists and procedures for conducting and generating a final report according to EPA approved procedures and guidelines that are not covered by this document. DAQ management and staff will respond to EPA TSA reports and findings and improve procedures and/or flag data as directed by the final approved TSA report and subsequent corrective action plan.

CI.1.3 Internal Technical System Audit

DAQ will utilize a designated UAT internal TSA audit team that will perform a TSA on the VOC and carbonyls sampling and analysis methods and audit data reported to AQS. Internal TSAs will focus on the QS, compliance with QS documents, performance of analytical methods, sample handling and custody, and data review, verification, validation and reporting. The UAT internal TSA audit team will distribute the TSA report to the LAB and DAQ management. The LAB will respond to internal TSA audit findings deemed to impact data quality to DAQ management describing any corrective actions, root cause analysis, and demonstrate return to conformance. Such reports will identify the affected data. DAQ will document the outcomes of

the internal TSAs using DAQ's SOP for performing internal technical system audits DAQ-15-004, currently under development.

CI.1.4 Audits of Data Quality

ADQs evaluate the methods used to collect, interpret, and report data by examination of a representative amount of measurement data. The following activities and operations are evaluated against the required procedures as given in the DAQ QMP, QAPP, and SOPs:

- Recording and transfer of raw data
- Calculations and reductions or transformations of data
- Documentation of data handling procedures
- Reporting procedures for inputting data to AQS
- Comparison of data contained within AQS to data intended for input

The RCO chemist conducts ADQs each calendar quarter for VOCs, carbonyls, and meteorology parameters validated and uploaded to AQS. The RCO chemist submits these reports to the Level 3 reviewer/validator and management for review and the RCO chemist saves the final report in Laserfiche. Results of the ADQ will be documented by DAQ staff and be available for review during TSAs.

CI.1.5 Proficiency Testing

PT is a quantitative evaluation of the bias introduced in a part, parts, or in the best-case scenario, the entirety of a measurement process. It involves the analysis of a reference material of known value and composition that is blind to the monitoring agency and/or laboratory.

The PT program will evaluate the LAB for measurement bias, specifically for speciated VOCs and carbonyls. An EPA contractor will prepare VOCs and carbonyls samples for shipment to the LAB on a biannual basis. Samples are spiked with target analytes at concentrations blind to the laboratories and blind to DAQ staff. The LAB will analyze the PT sample(s) on the GC-MS (VOCs) or UHPLC (carbonyls) and will report the concentrations to the PT provider who will compile the reported concentrations for evaluation against the nominal value and against the overall NATTS lab average (with statistical outliers removed) and against the referee laboratory average (with statistical outliers removed).

Results for VOC and Carbonyl PT samples must be within $\pm 25\%$ of the assigned target value for each evaluated target compound. The assigned target value will be based on the network-wide performance. If the LAB results do not meet the bias acceptance criterion, the operator or analyst must take corrective action to address the cause of the nonconformance and demonstrate the corrective action is effective. Corrective action typically involves preparation of an internal spiked cartridge (internal PT sample) by the Level 3 reviewer or designee not directly involved with carbonyl analysis. The nominal concentration will be unknown to the carbonyl analyst and

the carbonyl analyst will submit results of the spiked cartridge to the Level 3 reviewer or designee. The Level 3 reviewer evaluates the submitted results against the nominal concentration and provides a pass/fail status.

If the failing condition is confirmed, at a minimum, qualify failing carbonyls for all samples reported to AQS since the last passing PT sample or passing internal PT sample and continue applying the data qualifier flag until a passing PT sample or passing internal PT sample result is achieved. Application of the data qualifier flag may require updates to data already reported to AQS.

CI.2 Corrective Actions

The DAQ corrective action process (CAP) is executed according to the steps described in SOP# DAQ-15-002 and summarized below.

For each nonconformance that cannot be corrected through routine maintenance and routine troubleshooting and corrective action described in the UAT network SOPs, a corrective action report (CAR) (document # DAQ-16-016) will be prepared which includes the following components:

- Unique CAR identifier
- Identification of the individual initiating the CAR (staff person's name)
- Date of discovery of nonconformance
- Date of CAR initiation
- Area or procedure affected (e.g., carbonyls sample collection)
- Description of the nonconformance (what happened and how it does not conform)
- Investigation of the nonconformance (how discovered, what is affected by the nonconforming work)
- Root cause analysis (what caused the nonconformance)
- Investigation for similar areas of nonconformance
- Immediate and long-term (if needed) remedial corrective actions (and documentation of when completed)
- Due date for remedial action completion (immediate and long-term, as needed)
- Impact assessment of nonconformance (data flagging, invalidation, etc.)
- Assessment of corrective action effectiveness
- Demonstration of return to conformance
- Follow up audit to ensure corrective actions were effective (with date completed)
- Approval of closure of the CAR by the DAQ director and QAM

Situations that require a CAR include, but are not limited to:

- Repeated and consecutive calibration failures
- Incorrect sample storage conditions
- Persistent and consecutive blank contamination
- Incorrect procedures followed

- Repeated and consecutive QC parameter failures
- Unacceptable PT results confirmed through analysis of an internal PT sample

A root-cause analysis will be performed as soon as possible so remedial actions may be taken to correct the problem before it affects other procedural areas or additional samples and to minimize recurrence of the problem. For problems where the root cause is not immediately obvious, a stepwise approach will be taken to isolate the specific cause(s) of the nonconformance(s). Incorrect conclusions may result if too many variables are altered at one time, rendering the corrective action process ineffective. DAQ will seek assistance from instrument manufacturers and other SLTs performing NATTS sampling and analysis methods in instances in which a root cause is not evident. In such events, all correspondence will be documented in the CAR.

The development and implementation of a CAP, the details of which may be captured in one or several CARs, is an integral part of the assessment process and must be completed as a follow-up to each internal and external TSA. The EPA support contractor and/or EPA Region may assist in development of the CAP for TSAs conducted by EPA Region IV and/or the support contractor; however, the responsibility of implementing corrective actions lies with the monitoring agency. A CAP generally addresses the following points:

- identification of the root cause for each nonconformance
- immediate corrective action(s) needed to correct each nonconformance
- determination of the existence of similar non-conformances elsewhere in the QS
- corrective actions to preclude recurrence of the specific and similar non-conformances
- assignment of responsibility for implementing each corrective action
- completion dates for each corrective action
- demonstration of return to conformance

Documenting the follow-up activities will ensure that a subsequent assessment team will be able to track corrective activities, verify their efficacy, and confirm return to conformance.

If DAQ sampling sites do not meet IPA acceptance criteria or the LAB does not meet PT acceptance criteria, EPA Region IV and DAQ may decide to perform additional PTs as part of their root cause analysis and demonstration of return to conformance. Information on root causes and corrective actions will be documented in DAQ corrective action reports/plans and reported to Region IV and to OAQPS, as requested, so that lessons learned may be shared.

C2 Reports to Management

DAQ management will be apprised of the results of all independent assessments conducted on DAQ sites and the LAB operating in support of the UAT program. DAQ QA staff will report assessment outcomes to management in a timely manner. DAQ reports passing assessments to management as part of routine data reporting. Assessments that do not pass are reported to

management and may require initiation of the CAP by generating a CAR as described in SOP DAQ-15-002.

C2.1 Assessment Reports

DAQ staff performing assessments or scheduling outside assessments are responsible for creating the assessment report summarizing the assessment results or making sure external assessment reports are forwarded to the appropriate DAQ staff. For example, the Level 3 reviewer performs an instrument performance audit (IPA) on a VOC canister sampler. The Level 3 reviewer creates a report that summarizes the IPA results including a pass/fail status for the assessment, the date the assessment took place and the standards used to perform the assessment. The Level 3 reviewer sends this report to the direct supervisor for review and approval; once approved the reports is shared with upper management and other UAT staff.

An example of an external assessment report is a PT sample report provided by an EPA approved QA support contractor. This support contractor spikes the sample media and summarizes the results of the reported results to all participating laboratories. The PT provider provides a summary report of the results, and the Level 3 reviewer ensures the PT report is forwarded to upper management and UAT staff.

Failing assessments may require additional corrective action where applicable. These assessment reports are forwarded to management upon completion of the report (for an internal audit) or when received from an external assessor (e.g., EPA Regional Representative or PT provider). Assessment reports received by an external assessor are typically already formatted and do not require additional report creation by DAQ staff. Reports resulting from internal QA activities (e.g., TSA, IPA, ADQ, PTs, etc.) will identify operational and data quality non-conformances, resource needs (e.g., staff training, equipment), and results from relevant external assessments.

C2.2 Network Summary Reports

The DAQ Central Office environmental chemist runs the following reports from AQS:

- AMP251,
- AMP350,
- AMP350MX,
- AMP430 and
- AMP450NC.

After reviewing the reports, the DAQ Central Office environmental chemist archives the reports in the Laserfiche Ambient Monitoring folder and generates an ADQ report summarizing findings and conclusions and sends an email to the level 3 reviewer/validator and management attaching the ADQ. The ADQ summarizes site(s) performance (attainment of the MQOs) for the DQI completeness.

In addition to the DAQ Central Office environmental chemist ADQ report, the Level 3 reviewer of carbonyl and VOC sampling and analysis data (DAQ Central Office Chemist) monitors

overall method precision by calculating a coefficient of variation of the RPDs between primary and collocated sample collections. At the conclusion of each calendar quarter, the Level 3 reviewer prepares a precision summary report for the VOC method and a precision summary report for the carbonyl method. The precision summary report typically includes the current calendar quarter of data and includes RPD data obtained since the beginning of the calendar year.

Bias is monitored through twice per year performance testing using an EPA approved contractor and the results of the PT samples are provided by the EPA approved contractor summarizing the PT results and providing a synopsis of any data quality issues experienced that may impact the final PT results. Historical PT sample results are available for review. The PT sample results reports are shared with DAQ management and staff directly involved with the UAT sampling and analysis methods.

The DAQ Central Office Chemist monitors sensitivity through MDL calculations and reports carbonyl MDL results to AQS through raw data transaction files.

D. DATA VALIDATION AND USABILITY

D1 Data Verification and Validation Requirements

The process used for data verification and validation determines the degree to which measurements have met applicable data quality specifications provided in Section A7. Data generated for the parameters listed in Table B1-1 will undergo data verification and validation prior to reporting to AQS. Data verification is the process of evaluating the completeness, correctness, and conformance or compliance of data against established method, procedural, or contractual specifications; verification is meant to ensure that data accurately reflect the conditions at the site when the observations occurred. Data validation extends the evaluation of data beyond data verification to determine the quality of a specific data set. The goal of data validation is to evaluate whether the data meets the stated data quality objective(s) and that overall quality goals established during the planning phase have been achieved; for example, to determine if precision and bias met their respective MQOs. A critical component of data validation is also the comparison of the data being validated to other co-collected or historical data to identify potential anomalies in the data that may be concealed behind acceptable precision, bias, and completeness metrics (such as in cases where transient sources bias concentrations temporarily high). Only after a given dataset has been reviewed, verified, and validated can an ADQ be performed to determine if it is fit for its intended purpose. Data verification and validation requirements are described briefly in the next several sections.

The process DAQ will use for review and verification of carbonyl sampling and analysis data are detailed in Section 6 of SOP# DAQ-03-004.2 Thermo Ultimate 3000 UHPLC-UV-MS UAT and PAMS Carbonyl Analysis Operator Responsibilities.

The process DAQ will use for review and verification of VOC sampling and analysis data are detailed in Section 6 of SOP# DAQ-03-003.2 Markes-Agilent GC-MS UAT VOC Canister Analysis Operator Responsibilities.

The process DAQ will use for the review and verification of meteorological sensor data are detailed in Section 8 of SOP# DAQ-07-004.2/3 AIO2 All in One Met Sensor Operator/Coordinator Responsibilities.

The processes DAQ will use for validation of carbonyl sampling and analysis data are detailed in Section 5 of the SOP# DAQ-03-004.5 Thermo Ultimate 3000 UHPLC-UV-MS UAT and PAMS Carbonyl Analysis RCO Responsibilities.

The process DAQ will use for validation of VOC canister sampling and analysis data are detailed in Section 5 of the SOP# DAQ-03-003.5 Markes-Agilent GC-MS UAT VOC Canister Analysis RCO Responsibilities.

The process DAQ will use for validation of meteorological sensor (AIO2) data are detailed in Section 5.5 of SOP# DAQ-15-005.5.

Personnel performing data review, verification and validation activities will:

- Be familiar with typical diurnal variations in meteorological data. For example, ambient temperature typically goes up in the morning, reaches a maximum in the late afternoon and comes back down while relative humidity follows an opposite trend of going down as temperature increases and up as temperature decreases.
- Be familiar with the types of instrument malfunctions that occur to field and laboratory instrumentation that cause characteristic irregularities in reported data.
- Be familiar with different types of chromatographic separation methods and recognize the analytical instrument issues that may cause irregularities in the reported data.
- Recognize that cyclical or repetitive variations (at the same time each day or at periodic intervals during the day) in continuous meteorological measurements may be caused by excessive line voltage, temperature variations, or external interference on the sensors.
- Recognize that emissions from nearby sources (such as carpool lines at schools, etc.) can cause erroneous or non-representative measurements.

D1.1 Data Verification

In the data verification process, UAT measurement data will be evaluated for completeness, correctness, and conformance/compliance according to the program requirements. The goal of data verification is to ensure and document that the reported results reflect the activities performed and measurements acquired and meet the prescribed method performance criteria. Any deficiencies in the data will be documented and, where possible, resolved by corrective action. UAT data verification applies to activities in the field as well as in the LAB performing VOC canister cleaning, canister analysis, and carbonyl cartridge extraction and analysis. Data verification includes routine (self) review of collected data by the instrument operator and subsequent technical (peer) review performed by trained personnel who did not conduct the initial measurement.

D1.1.1 Routine (Self) Review

The instrument operator(s) will perform the initial steps of the routine (self) review portion of data verification, which includes reviewing recorded data to ensure the records are complete and comply with the acceptance criteria in the DAQ SOPs. It is typically most efficient for this individual to make corrections to collected data and document these corrections such that the impact of any subsequent problem is minimized immediately. Such reviews typically cover 100% of the collected data such that transcription errors (if applicable) are minimized and that QC criteria are within acceptable limits.

Recorded data (measurements, observations, etc.) will be reviewed at a frequency (see frequencies in Table D1-1) that minimizes the loss of data when errors or conditions are found that risk additional data loss if the problem is not corrected. This routine (self) review is typically limited in scope to a particular phase of the data collection activities and is a first step in the overall data verification process, which covers the generation of data from the “cradle to the grave.” The frequency for the various activities is specified in Table D1-1.

Table D1-1. Routine Review Activities and Associated Frequency

Verification Activity	Frequency
Measurement data that exceed the instrument calibration range	Monthly for Met; every analytical sequence for VOC and carbonyl analysis; each sampling event for sampling equipment
Carbonyl and VOC concentration data are complete (sample collection and COC forms are not missing information, expected electronic files are recorded, and logbook entries are complete)	Every analytical sequence for VOC and carbonyl analysis
Samples/data were collected in accordance with the sample design and approved SOP	Monthly or every analytical sequence
Sample collection and handling procedures were followed correctly	Monthly or every analytical sequence
Data files are properly identified	Monthly or every analytical sequence
Computer file entries match hand entered data sheets	Monthly or every analytical sequence
Analytical procedures used to generate data were implemented as specified	Monthly or every analytical sequence
Instruments were calibrated properly (i.e., before sampling began, at the specified frequency, included the proper number of points at levels that bracketed the range of reported results)	Monthly or every analytical sequence
QC check criteria were met and routine corrective actions are taken when criteria are not met	Monthly or every analytical sequence
Chromatography is acceptable (stable baseline, adequate peak separation, etc.) and that analyte identification is appropriate based on the established RT windows	Every analytical sequence
Carbonyls and VOC canister sample holding times were met and the analysis laboratory reviewed and verified carbonyl and VOC analysis data	When carbonyls and VOC data are reviewed
Deviations from stated procedures or acceptance criteria are documented and impacted data are flagged or invalidated per DAQ policy	Monthly or every analytical sequence
Measurements that are known to be invalid because of instrument malfunctions are invalidated as per DAQ policy	Monthly or every analytical sequence
Data are substituted from a backup in the event of failure of the primary data acquisition system	Monthly
Corrections and changes to the data records are documented	Monthly or every analytical sequence

DI.1.2 Technical (Peer) Review

Once the data have undergone routine review by the instrument operator, the data is to be comprehensively technically reviewed by an individual (a peer) not involved with the data generation. The technical review serves to verify that the routine review was completed properly and expands the routine review activities. The technical reviewer performs many of the same activities performed by the instrument operator during routine review but does not verify instrument operation or status in real time. The technical reviewer verifies correctness of the data generation process by ensuring that documentation is clear and traceable from the sample measurement back through to the certified standards and verifies that the data comply with governing SOPs and this QAPP. The technical reviewers will perform their activities at an appropriate frequency to ensure technical reviews are completed within a month of the data collection. More frequent reviews are recommended to maintain a manageable workload. The technical reviewer will verify (where applicable):

- Measurements below the MDL are reported (not censored) and flagged appropriately [*note - EPA intends to add automatic flagging functions to AQS for data based on the proximity to the MDL*]
- Concentration measurements exceeding the instrument calibration range were calculated correctly and flagged appropriately
- Measurement data are complete (sample collection and COC forms are not missing information, expected electronic files are recorded, and logbook entries are complete)
- Samples/data were collected in accordance with the sample design and approved SOP
- Sample collection and handling procedures were followed correctly
- Data files are properly identified
- Computer file entries match hand entered data sheets
- Analytical procedures used to generate data were implemented as specified
- Instruments were calibrated properly (i.e., before sampling began, at the specified frequency, included the proper number of points at levels that bracketed the range of reported results)
- Calibration standards were within expiration
- Calibration standards and check standards preparation calculations are correct and that the nominal (known or theoretical) value is input into the instrument, as appropriate
- Supporting equipment to make critical measurements (MFCs, adjustable pipettes, pressure transducers, etc.) are within calibration and have passed the most recent applicable calibration checks
- Routine QC checks met acceptance criteria
- Chromatography is acceptable (stable baseline, adequate peak separation, etc.) and that analyte identification is appropriate based on the established retention time (RT) windows

- Chromatographic integration is performed correctly and consistently
- Carbonyls and VOC canister sample holding times were met and the primary analyst reviewed and verified carbonyl and VOC analysis data
- Deviations from stated procedures or acceptance criteria are documented and impacted data are flagged or invalidated per DAQ policy
- Measurements that are known to be invalid because of instrument malfunctions are invalidated as per DAQ policy
- Data have been substituted from a data backup (such as the instrument) in the event of failure of the primary DAS
- Changes to the data records have been documented and are attributable to the person making the change

D1.2 Data Validation

Data validation is a process that investigates the individual data points within the context of other co-collected data or data collected at a similar location in proximity to the site to determine the quality of the data relative to their expected end use. For example, after a given dataset has been verified and validated (one calendar quarters' worth of data) an overall precision assessment be performed to determine whether the DAQ can achieve the stated, UAT-specific DQO. The overall precision report is performed by the Level 3 reviewer (DAQ central office chemist) and involves the evaluation of the coefficient of variation of the RPDs determined from primary and collocated sample collections.

Additionally, data validation activities build on the data verification processes described in section D1.2 and will not be conducted on data which have not been verified. Additional data review may be required during data validation, including repeating some steps of the data verification process such as reviewing QC data, calculations, or raw data. Data validation examines the dataset for internal, historical, and spatial consistency:

- Level 0 Data Validation – Includes data verification activities discussed in Section D1.2. Some of these activities can be automated using pre-programmed criteria by the analysis or sampling instrument software as an initial review of data. Programs may include the application of qualifiers when a parameter rate of change or upper range limit is exceeded. These are various evaluations that DAQ prescribes at a specified frequency (i.e., every day, once a week) and are the initial first step in the evaluation of data validity.
- Level 1 Data Validation – Evaluates internal consistency of the dataset to identify values that appear atypical when compared to the values of the entire dataset. Tests for internal consistency are conducted to identify measurements that do not conform to expectations - outliers and extreme differences within the dataset that warrant further investigation. After tracing the path of the measurement, if nothing unusual is found, the value can be assumed to be a valid result with an environmental cause. Unusual values are identified

during the data interpretation process as extreme values or outliers. Outliers and extreme differences can be identified and confirmed using statistical tests or may be identified by graphical and visual presentation of the data. Visualization tools (plots, graphs, charts, etc.) are powerful as they allow the user to quickly identify values that are atypically higher or lower or that do not conform to a typical or expected pattern, unlike reviewing data in tabular format. Visualization tools include scatter plots, time-series plots, or fingerprint plots, among others, such as those listed in Section 10.4 of Revision 2 of the PAMS TAD.

- Level 2 Data Validation – Data that have undergone Level 1 validation for internal consistency are then compared with historical data to evaluate temporal consistency of the dataset with previous datasets. The historical data may be recent (e.g., one week or one month prior) or may cover a longer period (e.g., the previous year or years). Simple statistical analysis and visualization tools are useful here, as they enable identification of values that do not conform to expectations.
- Level 3 Data Validation – Data that have undergone Level 2 validation for temporal consistency may then be evaluated for spatial consistency against data collected at nearby sites, i.e., those in the same airshed, regional network, or DAQ, to identify systematic bias.

Levels 2 and 3 data validation will be performed using historical data from the same site or nearby comparable sites if historical data from the site are not available. The ability to conduct these validation levels is dependent on the monitoring history (e.g., for PAMS, air toxics programs, criteria pollutant monitoring, etc.) at the site or nearby sites within the airshed.

Data validation activities will be documented in sufficient detail such that an inspector or auditor may recreate the validation activity as part of an internal or external TSA or by the DAQ central office environmental chemist during ADQs. Sampling and analysis data will be reviewed and verified with every analysis sequence. Sampling and analysis data will be validated and reported to AQS at the conclusion of each calendar quarter, so that the dataset is manageable. For example, VOC and carbonyl analysis results will be reviewed, verified, and validated with each analytical sequence and reported to AQS within 90 days of a completed calendar quarter. Larger timeframes of collected data (3-12 months) may have to be used to assess overall precision (CV) for the collection methods and/or comparisons to other UAT monitoring site data. Data validation activities should be completed in sufficient time to allow for potential corrections to data, uploading data to AQS, and confirming data uploads to AQS were successful and accurate. Data validators are encouraged to begin validation on datasets as soon as data review and verification has been completed on the appropriate size dataset as detailed in Table D1-2.

Table D1-2. Dataset Durations (Sizes) for Validation

Parameter	Appropriate Duration (Size) of Dataset
VOCs	Preferably one analytical sequence, not to exceed one calendar quarter's worth of sampling and analysis data.
Carbonyls	Preferably one analytical sequence, not to exceed one calendar quarter's worth of sampling and analysis data.
Meteorology	Preferably one month of data.

D1.3 Reporting of Validated Data to AQS

After the data validation, measurement data will be uploaded to AQS. Data will be uploaded to AQS within 90 days of the end of the calendar quarter in which the samples/data were collected.

Prior to upload, the data validator will verify flagged data have been qualified appropriately, which may involve performing automated parity checks on the data translated into AQS format and performing spot checks on the transformed data. Carbonyls will include the associated MDL in the AQS coded data. VOC data is qualified based on whether the detected concentration range is above or below the analysis instrument calibration range. The data validator is encouraged to have an independent reviewer verify data have been appropriately coded for AQS submission. Such verification checks will be documented.

Once reported to AQS, DAQ will query AQS to verify the data were uploaded properly and perform parity checks to verify there are no discrepancies. Such verifications will be documented.

D1.3.1 Reporting Values Below Method Detection Limits (Chemical Parameters)

Instrument sensitivity for chemical parameters for the UAT network is characterized by determining the MDL as described in Section 4.1 of the NATTS TAD Revision 3. The determined MDL for each parameter represents the lowest concentration that can be detected above background with 99% certainty. Concentrations measured at less than the MDL, so long as the qualitative identification criteria have been met (analyte is positively identified), are valid and the measured concentration will be reported to AQS. **There will be no substitution of the values (such as ½ MDL) or censoring (reporting as 0) concentrations measured below the MDL.**

For VOCs and carbonyls measurements for which the target analyte is not qualitatively identified, the concentration will be reported as zero (0) and the QA Qualifier "ND" added when coded for input to AQS. This combination of concentration and qualifier indicates to the data user that the measurement was made but the analyte was not identified and could not be quantitated.

D2 Data Verification and Validation Methods

The DAQ will employ a combination of software tools such as sampling and analysis instrument control software, DART, Envista ARM, Envistas Ultimate, excel spreadsheet and excel macros to perform data review, verification, and validation procedures. Specific data review, verification and validation procedures including the identity of software tools DAQ will use are described in more detail in the following SOPs:

- Section 6 of SOP# DAQ-03-004.2 (review and verification of carbonyl sampling and analysis data).
- Section 6 of SOP# DAQ-03-003.2 (review and verification of VOC sampling and analysis data).
- Section 8 of SOP# DAQ-07-004.2/3 (review and verification of meteorological data).
- Section 5 of SOP# DAQ-03-004.5 (validation of carbonyl sampling and analysis data).
- Section 5 of SOP# DAQ-03-003.5 (validation of VOC sampling and analysis data).
- Section 5.5 of SOP# DAQ-15-005.5 (validation of meteorological data).

D2.1 Data Verification Methods

Field sampling and lab analysis instrument operators and Level 2 data reviewers will ensure data are complete and correct and comply with this QAPP and supporting SOPs. The result of the data verification is that all data have been reviewed to ensure that data are traceable – that they were generated with instruments that had been calibrated with certified standards according to an approved standard process, that the instrument calibration and other QC checks were performed at the proper frequency and met criteria, and that all calculations and transformations are correct. Data verification activities are tailored to verify that data are error-free and are flagged (qualified) or invalidated when data integrity is compromised.

The self-reviews and peer-reviews of UAT sampling and analysis data include following a data review checklist and answering the data review questions and providing comments summarizing observations of the verification process. Additional verification includes examining data manually, for example, direct examination of chromatograms generated by laboratory analysis instrumentation, direct examination of 1-minute data for continuous monitoring methods (meteorology), direct examination of hand-transcribed data such as site logbooks or instrument logbooks.

Automated methods include using an excel macro to generate an internal standard QC summary report specific to the GC-MS analysis instrument. Based on the results of the internal standard summary report, data qualifier flags can be assigned to VOCs detected in samples that fail internal standard QC criteria. Recall, data verification activities are tailored to the specific parameter being verified. The UHPLC-UV-MS analysis instrument does not use internal standards and therefore an internal standard summary report is not generated for the carbonyl sampling and analysis method.

D2.2 Data Validation Methods

This section describes UAT sampling and analysis data validation methods. The data validation methods used by DAQ are useful in identifying anomalous data and increasing confidence in datasets. Data validators use a combination of automatic and manually methods to validate data and to confirm the application of a null flag or qualifier flag to the suspect data point or points.

D2.2.1 Data Visualization Methods

Graphical techniques permit comparison of concentrations of each UAT parameter to the expected concentrations and relative concentrations of other datasets to inspect for values which stand out. These graphical techniques can combine and contrast different parameters temporally and spatially to help accentuate data which may stand out from the dataset and warrant further investigation. Some of the simplest of these graphical tools are available in Microsoft Excel, DART and in DAS software systems and include the following:

- Time series plots
- Scatter plots
- Fingerprint plots
- Stacked bar charts
- Pollution roses
- Box plots
- Diurnal profiles

The processes DAQ will use for data visualization, comparison and validation are detailed in the SOPs listed in section D2 above.

D2.2.2 Statistical Methods

A critical part in validating data within a dataset and against external datasets is to generate simple statistics. For example, calculating a ratio of formaldehyde to acetaldehyde concentrations detected in ambient samples is a quick and efficient method for determining whether an ambient carbonyl sample may be impacted by a nearby source or contaminated during sample handling. Other compound ratios include n-pentane to cyclopentane, benzene to toluene, and m, p-xylene to o-xylene. Additional statistical checks include calculating relative percent difference between primary and collocated sample pairs and highlighting RPDs that exceed acceptance criteria. Furthermore, additional statistical checks include calculating urban and rural concentration sums of BTEX (benzene, toluene, ethylbenzene, and xylenes) to determine a total BTEX concentration. The urban and rural BTEX concentrations are visually compared to verify the ongoing trend of urban BTEX concentration (ppb) \geq rural BTEX concentration (ppb). Other urban and rural comparisons can be made using formaldehyde concentrations.

D2.2.3 Examination of Supporting Data

Data validation requires the data validator to examine materials and records that support the reported parameter measurements but are not directly reported data. These supporting data sources are integral in identifying data that may be compromised and require qualification or invalidation. Data validators will review the following supporting data sources and verify compromised data are appropriately flagged or invalidated:

Technical Systems Audit Reports: TSAs may uncover non-conformances that can affect the validity of data. For example, if it is found that a site maintenance worker has stored a gasoline container near the inlet probe, the associated VOC data impacted during that time period would likely be invalidated, or at a minimum, qualified. TSA reports and related CAPs will be reviewed during data validation to ensure findings that impact measurement data quality have been addressed through corrective action and data validators will assess the impact of any findings on acquired data undergoing validation.

Audits of Data Quality Reports: Findings from ADQs may directly impact reported data and indicate errors or problems in data transformations, transcriptions, calculations, or reporting. The findings may result in the need to recalculate data, reprocess data, or update reported data in AQS if the error cannot be corrected. For example, an ADQ may identify a VOC does not meet completeness for a specific calendar quarter. Review of the AQS transaction file indicates the VOC compound was null coded due to a GC-MS calibration failure as indicated by application of null code "AT". In this case, the GC-MS could be recalibrated to try and eliminate the AT null code and the affected samples could be re-analyzed. If the new calibration curve passes for the VOC and samples are reanalyzed, the new results are used to update AQS. If the instrument is not recalibrated or recalibration does not remove the AT null code, the original results reported with the null code are not updated in AQS.

Instrument Performance Audit and Proficiency Test Results: Deviations from acceptance or advisory limits during IPAs or PTs indicate bias is present in the measurement system. The validator will review IPA and PT reports for unacceptable results, will verify that corrective actions have been taken to address the out-of-tolerance condition when routine troubleshooting and maintenance do not correct the non-conformity, and may qualify or invalidate affected data based on the severity and scope of the nonconformance. For example, for PT results that show a failing status and a nominal spiked value that is below the reportable limit of the VOC analysis instrument, no additional flagging will be applied to the failing parameter. When an IPA identifies a carbonyl sampler flow rate is out of control (i. e., $\pm 10\%$ of the sampler design flow) and it is proven the devices used to perform the IPA are valid and have been calibrated to the acceptable accuracy and frequency as prescribed in this QAPP, DAQ will apply a QA qualifier to all carbonyl concentrations obtained from the biased sampler back to the most recent passing flow check.

Laboratory Analysis Result Reports: The LAB results reports may include sample narratives or include QC sample results that provide context for the sample measurements. Data provided by the LAB will be verified with respect to the laboratory processes and method QC acceptance criteria; the LAB will flag data when operational or QC criteria nonconformances occur and notify the LAB Supervisor and data reviewers performing the verification and validation reviews. This will typically involve data flags or comments on electronic data deliverables. It is the responsibility of the verification and validation data reviewers to ensure that subsequent sample measurement data transformations and calculations are appropriate, accurate, and flagged properly.

Precision Sample Results: When available, validators will evaluate the precision of duplicate and/or collocated sample results to ensure they meet acceptance criteria. Poor agreement

between duplicate or collocated and primary sample pairs is indicative of a problem with the measurement system or data transformation/reduction process and will be investigated. Results for sample precision pairs will be minimally qualified when precision acceptance criteria are exceeded, unless a technically justifiable rationale is determined and documented. If consecutive precision failures (typically 3 or more) are observed, corrective action should be taken immediately to improve the non-conformance.

Operator Notes and Site-Specific Information: Data validators will review operator notes recorded in the site logbook, maintenance logs, and on sample collection or COC forms to assess unusual events or instrument problems that may impact measurement result validity or representativeness. Examples include unusual events such as forest fires, temporary violations of siting criteria such as nearby construction, or operational difficulties with the monitoring instrumentation. DAQ will use its best judgment about the impact of site conditions on the acceptability of the data and may consult with the EPA NATTS Regional Representative.

Corrective Action Reports: Data validators will review CARs, whether in-process or completed, to investigate corrective actions impacting collected measurements undergoing validation. Conditions deemed to impact sample results may result in corrections to data, qualification, or invalidation, as appropriate.

D2.2.4 Treatment of Deviations from Requirements

Deviations from procedural or QC criteria call for DAQ to correct the data where possible (e.g., adjustment of sampler clock to match NIST time not adjusted for DST), take corrective action to limit the impact or recurrence of such deviations, appropriately flag or invalidate affected data when reported to AQS, and notify EPA Regional representatives when a significant amount of data (e.g., 10% of the quarterly values or the potential inability to meet the completeness MQO) are affected.

D2.2.4.1 Identifying Compromised Data in AQS

If data affected by deviations cannot be appropriately corrected, DAQ will identify compromised data within AQS by addition of a qualifier or combination of qualifiers. Qualifiers associated with UAT data are indicated in Table D2-3 below. Note that at the time this QAPP was published, qualifiers for specific deviations had not been defined and were not available in AQS; however, EPA periodically updates the AQS qualifier list which is published at the following link:

<https://aqs.epa.gov/aqsweb/documents/codetables/qualifiers.html>

Data compromised by QC criteria failures will either be flagged or invalidated in AQS as described below and in Tables B5-1 and B5-3 for carbonyls and B5-2 and B5-4 for VOCs.

Flagging Data in AQS: Compromised monitoring data will be flagged in AQS only if the data are considered valid for most purposes and uses. AQS permits users to label each data point with up to ten QA qualifiers and/or informational (INFORM) qualifiers.

Invalidating Data in AQS: Data of uncertain origin, data with unacceptable levels of uncertainty, or data which are known to not be an ambient measurement will not have an associated measurement value included in AQS. Such data may be the result of instrument failure, known instrument contamination, irrecoverable data, data corruption, or other issues. Invalid data are reported to AQS with a Null (NULL) Code Qualifier which eliminates the associated measurement parameter concentration and indicates the reason for the invalidation. AQS accepts a single NULL qualifier and does not permit addition of other qualifiers (QA or INFORM) to the data point.

As discussed further below, data will be qualified and estimated with descriptive QA and INFORM flags where the data are compromised but remain valid. In general, such qualification is preferable to invalidation as there remains a measurement value for the data user to access. The data user can then determine whether to use the data value based on the information indicated by the associated qualifier(s). Invalidation removes the measurement entirely from the data point and is therefore of minimal use to an end data user.

Table D2-1. AQS Qualifiers and Null Codes for UAT

Qualifier Code	Qualifier Description	Qualifier Type
2	Operational Deviation	QA
3	Field Issue	QA
4	Lab Issue	QA
5	Outlier	QA
7	Below Lowest Calibration Level	QA
CC	Clean Canister Residue	QA
CF	Canister bias: NATTS/UATMP Data for compounds that have failed certification for the canister	QA
DI	Sample was diluted for analysis	QA
DN	DNPH Peak less than NATTS TAD requirement, reported value should be considered an estimate	QA
EH	Estimated; Exceeds Upper Range	QA
FB	Field Blank Value Above Acceptable Limit	QA
HT	Sample pick-up hold time exceeded	QA
LB	Lab blank value above acceptable limit	QA
LJ	Identification Of Analyte Is Acceptable; Reported Value Is An Estimate	QA
LK	Analyte Identified; Reported Value May Be Biased High	QA
LL	Analyte Identified; Reported Value May Be Biased Low	QA
MD	Value less than MDL	QA
ND	No Value Detected	QA
NS	Influenced by nearby source	QA
QX	Does not meet QC criteria	QA
SB	Sampler Bias: NATTS/UATMP Data for compounds that have failed certification for the sampler	QA

Table D2-1. AQS Qualifiers and Null Codes for UAT

Qualifier Code	Qualifier Description	Qualifier Type
SP	NATTS/UATMP data with spike recovery outside acceptable limits	QA
SQ	Values Between SQL and MDL	QA
SX	Does Not Meet Siting Criteria	QA
TB	Trip Blank Value Above Acceptable Limit	QA
TT	Transport Temperature is Out of Specs.	QA
V	Validated Value	QA
VB	Value below normal; no reason to invalidate	QA
AB	Technician Unavailable	NULL
AC	Construction/Repairs in Area	NULL
AD	Shelter Storm Damage	NULL
AF	Scheduled but not Collected	NULL
AG	Sample Time out of Limits	NULL
AH	Sample Flow Rate out of Limits	NULL
AI	Insufficient Data (cannot calculate)	NULL
AL	Voided by Operator	NULL
AM	Miscellaneous Void	NULL
AN	Machine Malfunction	NULL
AP	Vandalism	NULL
AQ	Collection Error	NULL
AR	Lab Error	NULL
AS	Poor Quality Assurance Results	NULL
AT	Calibration	NULL
AU	Monitoring Waived	NULL
AV	Power Failure	NULL
AW	Wildlife Damage	NULL
AX	Precision Check	NULL
AY	QC Control Points (zero/span)	NULL
AZ	QC Audit	NULL
BA	Maintenance/Routine Repairs	NULL
BB	Unable to Reach Site	NULL
BE	Building/Site Repair	NULL
BH	Interference/co-elution/misidentification	NULL
BI	Lost or damaged in transit	NULL
BJ	Operator Error	NULL
BK	Site computer/data logger down	NULL
DA	Aberrant Data (Corrupt Files, Aberrant Chromatography, Spikes, Shifts)	NULL
DL	Detection Limit Analyses	NULL
MC	Module End Cap Missing	NULL

Table D2-1. AQS Qualifiers and Null Codes for UAT

Qualifier Code	Qualifier Description	Qualifier Type
SA	Storm Approaching	NULL
SC	Sampler Contamination	NULL
TC	Component Check & Retention Time Standard	NULL
TS	Holding Time Or Transport Temperature Is Out Of Specs.	NULL
XX	Experimental Data	NULL
IC	Chem, Spills & Industrial Accidents	INFORM
ID	Cleanup After a Major Disaster	INFORM
IE	Demolition	INFORM
IH	Fireworks	INFORM
II	High Pollen Count	INFORM
IJ	High Winds	INFORM
IK	Infrequent Large Gatherings	INFORM
IM	Prescribed Fire	INFORM
IP	Structural Fire	INFORM
IQ	Terrorist Act	INFORM
IR	Unique Traffic Disruption	INFORM
IS	Volcanic Eruptions	INFORM
IT	Wildfire-U, S.	INFORM
J	Construction	INFORM

D2.2.4.2 Corrective Action Process

DAQ's corrective action process will be followed in cases of systematic problems or problems affecting a significant amount of data. This process is described in Section C1.2.

D3 Reconciliation of Results with DQOs

The DQO and intended uses for the UAT Network data are discussed in Section A7.1. The DQO for the UAT Network is to detect a 15% difference or trend over three annual average concentrations within acceptable limits of decision error. To achieve this DQO, the DAQ will monitor and control the DQIs of bias, sensitivity, representativeness, completeness, and precision to ensure DAQ achieves the DQO.

DAQ intends to monitor the precision DQI and completeness DQI using a calendar quarter's worth of data. DAQ intends to monitor representativeness once per calendar year and this is completed during the annual network review. DAQ intends to monitor the bias DQI through twice per calendar year PT samples or on whatever frequency PT samples are available from the EPA approved contractor (not to exceed two PTs per calendar year). DAQ currently participates in the NATTS PT sample program for carbonyls and VOCs. DAQ has participated in the

NATTS PT program for several years which means that DAQ can provide results spanning over several years. DAQ intends to monitor sensitivity through once per year MDLs calculated for each analysis system used for routine sample analysis. This means that an MDL is calculated for the carbonyls and two MDLs are calculated for the VOCs. Recall, two systems are used for VOC analysis.

The overall precision summary report is generated by the Level 3 reviewer and monitors precision by calculating a CV using the RPDs from primary and collocated sample pairs. A separate CV is calculated using RPDs from replicate analysis pairs. Lastly, another CV is calculated using RPDs from LCS and LCSD pairs.

Each precision test (i.e., primary/collocated sample pairs, replicate sample pairs, and LCS/LCSD sample pairs) is calculated individually, allowing the end user to focus on specific areas of the sampling and analysis methods if precision fails to meet acceptance criteria. The overall precision summary report can be tailored to include smaller or larger sets of data.

In all precision tests, the CV must be $\leq 15\%$ for each VOC and carbonyl reported to AQS.

The DAQ will evaluate the quality and suitability of the data and may request revisions to the MQOs controlling the DQIs which may involve adjusting limits to sensitivity, bias, or precision, for example. These adjustments will be communicated to the EPA through updates to this QAPP and supporting SOP documentation. Additionally, adjustments to the MQOs will be communicated to the EPA and EPA approved contractors that are involved with updates to the NATTS TAD and compendium method documents.

REFERENCES

1. US EPA, April 1999. Air Toxics Monitoring Concept Paper (draft). J, David Mobley, Emissions, Monitoring and Analysis Division, and Shally Shaver, Emissions Standards Division, OAQPS, February 2000. Air Toxics Monitoring Concept Paper (revised draft). Air Toxics Monitoring Strategy Subcommittee, OAQPS.
<https://www3.epa.gov/ttnamti1/files/ambient/airtox/cncp-sab.pdf>
2. US EPA. Technical Assistance Document for the National Air Toxics Trends Station Network, Revision 3. Available on AMTIC here:
https://www3.epa.gov/ttn/amtic/files/ambient/airtox/NATTS%20TAD%20Revision%203_FINAL%20October%202016.pdf
3. US EPA. Compendium Method TO-15. Determination of Volatile Organic Compounds in Air Collected in Specially Prepared Canisters and Analyzed by Gas Chromatography / Mass Spectrometry (GC/MS), available on AMTIC here:
<https://www3.epa.gov/ttnamti1/files/ambient/airtox/to-15r.pdf>
4. US EPA. Compendium Method TO-11A. Determination of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed by High Performance Liquid Chromatography, available on AMTIC here:
<https://www.epa.gov/sites/production/files/2019-11/documents/to-11ar.pdf>
5. US EPA. Technical Assistance Document for Sampling and Analysis of Ozone Precursors for the Photochemical Assessment Monitoring Stations Program, Revision 2. Available on AMTIC here:
https://www.epa.gov/sites/production/files/2019-11/documents/pams_technical_assistance_document_revision_2_april_2019.pdf
6. See “MODEL AIO 2 ALL IN ONE WEATHER SENSOR OPERATION MANUAL Document No, AIO2-9800 Rev, F”
7. U. S, EPA, (2008) Quality Assurance Handbook for Air Pollution Measurement Systems, Volume IV: Meteorological Measurements (Version 2. 0), Prepared by Office of Air Quality Planning and Standards

**APPENDIX A DAQ-16-017 Memorandum Documenting
Changes to the Quality System**

DIVISION OF AIR QUALITY
Ambient Monitoring Section
217 West Jones Street / 1641 Mail Service Center
Raleigh, NC 27699-1641

Click or tap to enter a date.

QA BULLETIN NUMBER Click or tap here to enter text.

TO: Click or tap here to enter text.

THROUGH: Click or tap here to enter text.

FROM: Click or tap here to enter text.

SUBJECT: Click or tap here to enter text.

Click or tap here to enter text.

Replace and Discard Original	<input type="checkbox"/>
Add Material to Document	<input type="checkbox"/>
Retain this bulleting until further notice	<input type="checkbox"/>
Discard this bulleting after noting contents	<input type="checkbox"/>
This bulleting will be invalid after:	Click or tap to enter a date.
This bulletin will be incorporated into Click or tap here to enter text. by	Click or tap to enter a date.

**APPENDIX B UAT and PAMS Carbonyl Sample Information
Form**

North Carolina Division of Air Quality Laboratory Analysis Branch DAQ-16-009 Carbonyl Cartridge Sample Information Form (SIF)					
NC DAQ Laboratory Analysis Branch: 4403 Reedy Creek Road, Raleigh, NC 27607 Phone: (919)-733-9777					
Document #: DAQ-16-009, Revision 0.0, Effective: 7/1/2021					
Laboratory Setup Information					
Sample Program (Circle one): PAMS UAT					
Sample Type (Circle one): SAMPLE FIELD BLANK TRIP BLANK DUPLICATE/COLLOCATED SAMPLER CERTIFICATION					
QC Sample Type (Circle One): CARTRIDGE BLANK CARTRIDGE SPIKE CARTRIDGE SPIKE DUPLICATE MDL SPIKE PT SPIKE CARTRIDGE LOT BLANK					
Sampling Site:				Sample #:	
DNPH Cartridge Lot#:				Sample Channel #:	
Lab setup by (initial & date):				Scheduled Sampling Date:	
Field Setup Information					
Sampler SN or FAS#:				Site Operator (initials, date & time of setup):	
Sampler Expiration Date:				NIST Device Date, Time and S/N:	
As Found Sampler Display Date & Time:				AS Left Sampler Display Date, Time: (if adjustment made)	
Time Difference (mins):	Time Difference less than 5 minutes? Yes No				
NIST Flow Standard (S/N and Exp. Date):				Measured Pre Sample Flow Rate (L/min):	Acceptable Range (0.9 L/min - 1.1 L/min)
DNPH Cartridge Scheduled Sampling Date/Time:				Leak Check Pass? (Circle One):	Yes No Leak Rate (L/min):
Acceptable Range (< 0.03 L/min)					
Field Recovery Information					
Site Operator (initials, date, time of pickup)				Sample Start Date & Time:	
				Sample Stop Date & Time:	
SAMPLE VOLUME (L):				Sample Duration (hrs):	
NIST Flow Standard (S/N and Exp. Date):				Measured Post Sample Flow Rate (L/min):	
Field Comments:					
Laboratory Receipt/Login Information					
Sample Received by:				Sample Receipt Temperature (°C):	
Date and Time Sample Received:				S/N of NIST Traceable IR-Gun:	
Laboratory Comments:					
Extraction Date:		Extracted by (initials):		Extraction Manifold Port Number:	

APPENDIX C VOC Canister COC Form

NC DAQ Laboratory Analysis Branch
Air Sampling Canister Chain of Custody

NC Division of Air Quality Laboratory 4403 Reedy Creek Rd Raleigh, NC 27607 (919) 733-9777	Sampling Site
	Sample #

Pre-Sample (Lab)						
Canister #	Cleaning Batch #	Canister Vacuum Inches Hg (Lab)	Canister COC #	Canister COC Sealed by Initials, Date, & Time (Lab)		
Sample Setup and Collection (Field)						
Sampler ID#: _____		Flow meter ID#: _____		<input type="checkbox"/> Sampler COC seal intact		<input type="checkbox"/> Canister COC seal intact
<input type="checkbox"/> Exp. Date Checked		<input type="checkbox"/> Exp. Date Checked		<input type="checkbox"/> Same # as sealed		<input type="checkbox"/> Same # as sealed
Sampler COC Broken by Initials, Date, & Time	Canister COC Broken by Initials, Date, & Time	Canister Vacuum Inches Hg (Field)	Leak Check (psig) (≤ 0.1 psi over 10 min)			
			Start	End	Diff.	Pass/Fail
<input type="checkbox"/> Timer Clock checked against NIST <input type="checkbox"/> Timer Adjusted (Details noted in comments below)						
Pre-Sampling Avg Flow Check: _____ mL/min			#1:	#2:	#3:	#4:
Acceptable Range: 8 mL/min to 12 mL/min (max)						
Sampling Date & Day	Timer Start Time	Timer End Time	Canister Pressure (psig)	Sampler COC #	Canister and Sampler COCs Sealed by Initials, Date, & Time	
				Canister COC #		
Post-Sampling Avg Flow Check: _____ mL/min			#1:	#2:	#3:	#4:
Acceptable: 8 mL/min to 12 mL/min (max)						
Adjusted Sampling Avg Flow Check: _____ mL/min			#1:	#2:	#3:	#4:
Acceptable: 8 mL/min to 12 mL/min (max) (NA = No Adjustment)						
Comments:						
Post Sampling (Lab)						
Sample Received by Initials, Date, & Time	<input type="checkbox"/> Canister COC seal intact		COC Broken by Initials, Date, & Time	Canister Pressure psig (Lab)		
	<input type="checkbox"/> Same # as sealed					
Comments:						
Intra-Laboratory Canister Transfers						
VOC Lab Relinquished by: _____				Date/Time: _____		
PAMS Lab Received by: _____				Date/Time: _____		

**APPENDIX D UAT and PAMS Carbonyls Chain of Custody
Form**



DAQ-16-008 Carbonyl Cartridge Sample Chain of Custody Form

Sample ID	Pre-sample Storage Location	Sample Type	Scheduled Sample Date	Shipment Method*	Shipment Tracking Number	Post-sample Storage Location
Relinquished by	Date/Time		Received by	Date/Time		

DAQ-16-008
 Revision 0.1
 Effective: 07-01-2021

*Shipment Abbreviations: **UPS** = United Parcel Service
FEDEX = FedEx Corporation
SV = State Vehicle

APPENDIX E List of Standard Operating Procedures

Document #	SOP Title	Brief Summary
DAQ-03-001.1	Xonteck 911A UAT VOC Sampler, ECB Responsibilities	Sampler certification and site installation
DAQ-03-001.2 and 2.51.2	Xonteck 911A UAT VOC Sampler, Operator Responsibilities	Sampler operation and sample collection
DAQ-03-002.1	ATEC 2200 UAT Carbonyl Sampler, ECB Responsibilities	Sampler certification and site installation
DAQ-03-002.2	ATEC 2200 UAT Carbonyl Sampler, Operator Responsibilities	Sampler Installation, Calibration, and Certification
DAQ-03-003.2	Markes-Agilent GC-MS VOC Canister Analysis, Operator Responsibilities	Instrument operation, calibration, sample analysis, Level 1, and Level 2 data review
DAQ-03-003.5	Markes-Agilent GC-MS VOC Canister Analysis, RCO Responsibilities	VOC Canister Analysis Data Validation
DAQ-03-004.2	Thermo Ultimate 3000 UHPLC-UV-MS UAT and PAMS Carbonyl Analysis, Operator Responsibilities	Instrument operation, calibration, sample analysis, Level 1, and Level 2 data review
DAQ-03-004.5	Thermo Ultimate 3000 UHPLC-UV-MS UAT and PAMS Carbonyl Analysis, RCO Responsibilities	Carbonyl Analysis Data Validation
DAQ-03-005.1	Entech 3100A Canister Cleaner, ECB Responsibilities	Verifications and adjustments to the Entech 3100A system components and system configuration
DAQ-03-005.2	Entech 3100A Canister Cleaner, Operator Responsibilities	Operation and data review of silica-lined canisters and/or silco canisters cleaned using the Entech 3100A
DAQ-03-006.1	Entech 4700A Precision Static Dilution System, ECB Responsibilities	Verification and adjustments to the Entech 4700 dilution system
DAQ-03-006.2	Entech 4700A Precision Static Dilution System, Operator Responsibilities	Operation and review of VOC standard mixes prepared in 6-Liter canisters used to calibrate and verify analysis instruments
DAQ-07-003.1	MetOne AIO2 All-in-One Met Sensor, ECB Responsibilities	Instrument certification, installation, auditing, and manufacturer calibration
DAQ-07-003.2	MetOne AIO2 All-in-One Met Sensor, Operator Responsibilities	Instrument operation, communication, Level 1, and Level 2 data review
DAQ-14-001.5	SOP on Preparing SOPs	Procedures on how to develop DAQ SOPs

Document #	SOP Title	Brief Summary
DAQ-14-002.5	SOP and QAPP Tracking Database	Instructions on how to number documents and track and document annual reviews and updates
DAQ-14-003	Records Retention and Archival Policies	DAQ procedures on how to archive documents and the length of time to retain them
DAQ-15-002	Corrective Action Process	DAQ process for correcting identified issues that affect data quality or validity
DAQ-15-003	Standard Operating Procedures for Training Ambient Monitoring Staff and Documenting and Tracking Training (currently undergoing development)	DAQ process for conducting and documenting training
DAQ-15-004.5	Shakedown Audits and TSAs (currently under development)	DAQ process for conducting PAMS annual shakedown audits and internal technical systems audits
DAQ-15-005.5	Data Validation for Continuous Gaseous Monitors and Meteorological Data	Level 3 Data Validation of meteorological data