



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION 4

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Mr. Patrick Butler, Ambient Monitoring Section Chief
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North Carolina Department of Environmental Quality
217 West Jones Street
Raleigh, North Carolina 27603

LSASD Project Number: 23-0105

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 Photochemical Assessment Monitoring Stations (PAMS) Required Site Network for Speciated Volatile Organic Compounds, Carbonyls, and Meteorological Parameters Including Mixing Layer Height, Revision 1, Feb 2023.

This QAPP was resubmitted for review on Feb 10th 2023. The quality assurance 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 photochemical assessment monitoring stations project adheres to all the applicable requirements and that the data generated is of sufficient quality to be used for the stated objectives. This QAPP should be reviewed internally by NC DAQ on an annual basis and revised when procedures change; at a minimum, the QAPP must be revised within five years.

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: 2023.02.24 10:08:24 -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.

Roy Cooper
Governor
Elizabeth Biser
Secretary
Michael A. Abraczinskas
Director



DAQ-01-007

**QUALITY ASSURANCE PROJECT PLAN
FOR THE NORTH CAROLINA DIVISION OF AIR QUALITY
Photochemical Assessment Monitoring Stations (PAMS) Required Site
Network for Speciated Volatile Organic Compounds, Carbonyls, and
Meteorological Parameters Including Mixing Layer Height
Revision 1**

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DISCLAIMER

This quality assurance project plan, or QAPP, covers the Photochemical Assessment Monitoring Stations (PAMS) required site network for speciated volatile organic compounds, carbonyls, and meteorological parameters including mixing layer height for the North Carolina Department of Environmental Quality, Division of Air Quality or DAQ. The Mecklenburg County Air Quality local program has established a PAMS monitoring site, but it is not included in this document. It is the responsibility of this local program to prepare and submit a separate PAMS QAPP.

Mention of commercial products or trade names will not be interpreted as endorsement. Some types of instruments currently in use may be described in text or in example figures or tables. Sometimes these products are given as a typical and perhaps well-known example of the general class of instruments. Other instruments in the class are available and may be fully acceptable.

Approval of PAMS Required Site SLT Monitoring Agency QAPP

DAQ has added or edited the National PAMS Required Site Quality Assurance Project Plan to specify details specific to the monitoring agency in the following Sections (indicated in yellow (R0) and in green for (R1) in the National QAPP):

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| A8 | Special Training Requirements/Certification | B7.2 | Calibration Support Equipment |
| A9 | Documentation and Records | B8 | Inspection/Acceptance Requirements for Supplies and Consumables |
| A9.1 | Recording of Data | B10 | Data Management |
| A9.2 | Chain of Custody Records | C.1.1.1 | Instrument Performance Audits |
| A9.4 | Records Archival and Retention | C1.2 | Corrective Actions |
| B1 | Sampling Process Design (Waivers) | C2 | Reports to Management |
| B1.1.2 | Speciated VOCs To Be Measured | D1.1 | Data Verification and Validation Responsibilities |
| B2 | Sampling and Measurement Methods | D2 | Data Verification and Validation Methods |

By signing below, the signatories indicate that DAQ has provided the appropriate details for the Sections listed above and has clearly identified all deviations from the National PAMS QAPP Revision 1.0 and provided documentation that the revisions provide equivalent or higher quality monitoring data.

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Date: 2/20/2023


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EPA Regional Office Acknowledgement and Approval

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PAMS Regional Coordinator **for Region IV**

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Quality Assurance Manager **for Region IV**

Foreword

This document is the Quality Assurance Project Plan (QAPP) for monitoring operations for the Photochemical Assessment Monitoring Stations (PAMS) Required Site Network for the parameters of speciated volatile organic compounds (VOCs), carbonyls, and meteorological measurements including mixing layer height (MLH). Any analysis performed by national contract laboratories will be covered in contract QAPPs approved by the Environmental Protection Agency (EPA) and will not need to be covered by the monitoring agency.

EPA developed this national QAPP to ease the burden on state and local air monitoring agencies (see note below) in developing a QAPP for their PAMS Required Site Program as well as to improve data quality and consistency in the PAMS data. This QAPP was developed in accordance with the EPA quality assurance (QA) requirements described in *EPA QA/R-5, EPA Requirements for Quality Assurance Project Plans* and the guidance in the accompanying document *EPA QA/G-5, Guidance for Quality Assurance Project Plans*.

This QAPP does not cover the measurement of ozone (O₃) or the suite of nitrogen oxides (NO, NO₂ [whether as true NO₂ or NO_x], and NO_y). Monitoring of the criteria pollutants O₃ and NO₂ for use in National Ambient Air Quality Standards (NAAQS) attainment decisions will already be occurring at the PAMS Required Site or at other sites operated by the responsible monitoring agency; as such, approved QAPPs governing required monitoring activities will already be available. NO and NO_y are measured by monitoring agencies operating National Core (NCore) sites and will also be covered by an existing QAPP. Mention or inclusion of these parameters in this QAPP is in a manner that will not be in conflict with current EPA requirements or the monitoring organization's approved QAPPs.

VOCs data collection for this QAPP focuses on the use of field automated instruments and the companion technical assistance document provides details on this instrumentation. Although the monitoring agency may submit a waiver for VOC canister sampling and laboratory analysis, this national QAPP will not cover those procedures and monitoring agencies will be required to submit a QAPP to cover VOC canister sampling and analysis.

This QAPP covers the meteorological measurements made at the PAMS site. Although a waiver is available for using meteorological data from nearby meteorology sites, this QAPP does not attempt to address QA activities for such alternate meteorology measurement data.

Monitoring agencies will add pertinent details to this national QAPP where indicated **in yellow highlights (R0)** and **in green highlights (R1)**. Monitoring agencies are expected to follow the QAPP as written unless the monitoring agency received approval for changes from the appropriate EPA Regional Office. Monitoring agencies may also develop their own QAPP in lieu of this document; such QAPPs will require EPA Regional approval.

NOTE: The Ambient Air Monitoring program uses the term "Monitoring Agency" and "Primary Quality Assurance Organization" (PQAO) in many of its regulations and guidance documents. In many cases the monitoring agency and the PQAO are the same entity; in a few cases, a PQAO may represent several monitoring agencies. This document uses the term "monitoring agency" throughout but is meant to cover both situations.

A. PROJECT MANAGEMENT

A1 Title and Approval

EPA QAPP Category II

By signing below, the Environmental Protection Agency (EPA) Office of Air Quality Planning and Standards (OAQPS) and EPA Regional technical and quality assurance (QA) leads for the Photochemical Assessment Monitoring Stations (PAMS) program have found this quality assurance project plan (QAPP) to be directly adoptable by any monitoring organization for the purpose of conducting monitoring for the PAMS Required Site Network Program once the monitoring organization specific details have been added. Signature by an EPA Regional representative, such as a Regional Administrator, QA manager, air monitoring program manager, or their delegated designee, signifies concurrence with all aspects of this QAPP.

Title: Quality Assurance Project Plan for the Photochemical Assessment Monitoring Stations (PAMS) Required Site Network for Speciated Volatile Organic Compounds, Carbonyls, and Meteorological Measurements Including Mixing Layer Height

The attached QAPP for the EPA PAMS Required Site Network is hereby approved and commits the participants of the program to follow the elements described within.

OAQPS Signature: _____ Date: _____
 Name: _____

Region 1 Signature: _____ Date: _____
 Name: _____

Region 2 Signature: _____ Date: _____
 Name: _____

Region 3 Signature: _____ Date: _____
 Name: _____

Region 4 Signature: _____ Date: _____
 Name: _____

Region 5 Signature: _____ Date: _____
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Region 6 Signature: _____ Date: _____
 Name: _____

Region 7 Signature: _____ Date: _____
 Name: _____

Region 8 Signature: _____ Date: _____
 Name: _____

Region 9 Signature: _____ Date: _____
 Name: _____

Region 10 Signature: _____ Date: _____
 Name: _____

A1.1 EPA Regional Approval of Monitoring Agency QAPP

The QA policies in EPA Order 5360.1 A2 require agencies that accept federal grant funding for their air monitoring programs to have a QA program with certain elements including quality management plans (QMPs), QAPPs, and the identification of a QA management function. To reduce the burden on state, local, or tribal (SLT) monitoring agencies, EPA has produced this National QAPP for PAMS Required Site Network monitoring agencies as a template and requires that SLT monitoring agencies review and either:

- (1) Revise this QAPP where indicated to reflect SLT policies and procedures; or
- (2) Develop their own QAPP to be consistent with the procedures outlined here.

The appropriate EPA Region must approve the resulting monitoring agency QAPP for conformance to the requirements of this national QAPP. SLT monitoring agencies will submit a list detailing the deviations and departures from this QAPP to the Region and supply supporting documentation to demonstrate that the quality aspects of this QAPP remain satisfied.

SLT monitoring agencies will complete the approval form on page 3 which indicates whether the SLT monitoring agency adopts this national QAPP (and has included the requested additional detail, as required) or develops its own QAPP. The monitoring agency must submit the completed form to its EPA Region with its PAMS QAPP.

A1.2 Corrections to the National QAPP or Supporting SOPs

The PAMS Required Site monitoring agency staff and their supervisors are responsible for implementing the applicable approved monitoring agency QAPPs and standard operating procedures (SOPs) and are responsible for the quality of the data. If changes or corrections are suggested for the approved national QAPP or supporting national SOPs, PAMS monitoring agency personnel will notify the Regional Representative who may notify the PAMS QA Lead at OAQPS. The PAMS QA Lead at OAQPS will review proposed changes with the EPA Regional PAMS Leads and determine if revisions to the national QAPP and/or national SOPs are appropriate. OAQPS will notify the PAMS monitoring agency site leads through a quality bulletin detailing amendment to the document(s). This quality bulletin (refer to example in Appendix A) will be distributed to the PAMS Required Site stakeholder e-mail list maintained by EPA OAQPS. When appropriate, new versions of the document(s) will be provided to the PAMS Required Site Network participants with instructions to discard the previous version.

Acknowledgments

This QAPP is the product of the combined efforts of EPA's OAQPS; EPA Regional offices; and SLT monitoring agencies. The following individuals are acknowledged for their contributions:

EPA Regions

Region:

- 1 Peter Kahn
- 2 Mazeeda Khan and Gavin Lau
- 3 Loretta Hyden and Howard Schmidt
- 4 Darren Palmer and Adam Zachary
- 5 Jacqueline Nwia and Bilal Qazzaz
- 6 Mark Sather
- 7 Matthew Brown and Leland Grooms
- 8 Ethan Brown
- 9 Michael Flagg
- 10 Chris Hall and Doug Jager

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T&B Systems, Inc. as a subcontractor to Battelle

David Bush
Ken Underwood

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ACRONYMS AND ABBREVIATIONS

| | |
|---------|--|
| ADQ | audit of data quality |
| AGL | above ground level |
| AMTIC | Ambient Monitoring Technology Information Center |
| AQS | Air Quality System |
| ASL | analytical support laboratory |
| auto-GC | automatic gas chromatograph |
| | |
| C | carbon |
| C2 | compounds containing two carbon atoms |
| C6 | compounds containing six carbon atoms |
| C12 | compounds containing twelve carbon atoms |
| CAA | Clean Air Act |
| CAP | corrective action plan |
| CAR | corrective action report |
| CBSA | core-based statistical area |
| cc/min | cubic centimeters per minute |
| CCV | continuing calibration verification standard |
| CDOC | continuing demonstration of capability |
| CDS | chromatography data system |
| CFR | Code of Federal Regulations |
| COC | chain of custody |
| CV | coefficient of variation |
| | |
| DART | Data Analysis and Reporting Tool |
| DAS | data acquisition system |
| DNPH | 2,4-dinitrophenylhydrazine |
| DQA | data quality assessment |
| DQI | data quality indicator |
| DQO | data quality objective |
| DST | daylight savings time |
| | |
| EMP | enhanced monitoring plan |
| EPA | United States Environmental Protection Agency |
| ESM B | extraction solvent method blank |
| | |
| FID | flame ionization detector |
| FEM | Federal Equivalent Method |
| FRM | Federal Reference Method |
| | |
| GC | gas chromatograph |
| | |
| HPLC | high performance (pressure) liquid chromatograph |

| | |
|-----------------|--|
| ID | inner diameter |
| IDOC | initial demonstration of capability |
| IP | implementation plan |
| IPA | instrument performance audit |
| ISO | International Organization for Standardization |
| LCS | laboratory control sample |
| LCSD | laboratory control sample duplicate |
| LIMS | laboratory information management system |
| m | meter(s) |
| MB | method blank |
| MDL | method detection limit |
| Min | minute(s) |
| MLH | mixing layer height |
| mm | millimeter(s) |
| m/s | meters per second |
| MQO | measurement quality objective |
| µg | microgram(s) |
| µg/cartridge | micrograms per cartridge |
| µm | micrometers |
| NAAQS | national ambient air quality standard |
| NATTS | National Air Toxics Trends Stations |
| NCore | National Core |
| ng | nanogram(s) |
| NIST | National Institute of Standards and Technology |
| nm | nanometer(s) |
| NO | nitrogen oxide |
| NO ₂ | nitrogen dioxide |
| NO _y | total reactive nitrogen |
| NWS | National Weather Service |
| O ₃ | ozone molecule |
| OAQPS | Office of Air Quality Planning and Standards |
| OD | outer diameter |
| OTR | Ozone Transport Region |
| PAMS | photochemical assessment monitoring station |
| PDMS | polydimethylsiloxane |
| PFA | perfluoroalkoxy |
| PLOT | porous layer open tubular |
| PM | particulate matter |
| ppb | part(s) per billion |
| ppbC | part(s) per billion carbon |
| ppbv | part(s) per billion by volume |

| | |
|---------------------|--|
| ppm | part(s) per million |
| PQAO | primary quality assurance organization |
| PT | proficiency test |
| PTFE | polytetrafluoroethylene |
| QA | quality assurance |
| QAU | quality assurance unit |
| QAIP | quality assurance implementation plan |
| QAPP | quality assurance project plan |
| QC | quality control |
| QMP | quality management plan |
| QS | quality system |
| RH | relative humidity |
| RPD | relative percent difference |
| RSD | relative standard deviation |
| RT | retention time |
| RTS | retention time standard |
| SB | solvent blank |
| SLAMS | state and local air monitoring stations |
| SLT | state, local, or tribal (monitoring organization) |
| SOP | standard operating procedure |
| SSCV | second source calibration verification |
| TAD | technical assistance document |
| TNMOC | total non-methane organic carbon |
| TSA | technical systems audit |
| TTP | through-the-probe |
| UAT | urban air toxics |
| UHPLC | ultra-high performance (pressure) liquid chromatograph |
| UV | ultraviolet |
| VOC | volatile organic compound |
| Watt/m ² | Watts per square meter |

A3 Distribution List

An electronic version of this QAPP will be available on EPA's Ambient Monitoring Technology Information Center (AMTIC) PAMS website available at the following link:

<https://www3.epa.gov/ttn/amtic/pamsguidance.html>

OAQPS will distribute this QAPP via e-mail to those individuals on its PAMS Required Site Network e-mail contact list. The EPA PAMS Regional Leads will be responsible for ensuring that this QAPP is distributed to the SLT monitoring agency Program Manager or Director of each PAMS Required Network field site. SLT monitoring agencies will be responsible for distributing this QAPP to analytical support laboratories (ASLs) conducting carbonyls and/or speciated volatile organic compound (VOC) analysis, as appropriate. For DAQ, the ASL for carbonyl analysis will be the Laboratory Analysis Branch (LAB) which is part of 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 PAMS QAPP for the LAB carbonyl analysis as all requirements for both collection and analysis of the data are covered in this PAMS QAPP. DAQ is using a national contract laboratory, ERG, for data validation of the PAMS Auto-GC speciated VOC data and its analyses are covered in contract QAPPs approved by the EPA. Table A3-1 provides the DAQ PAMS program distribution list. The EPA PAMS Regional Leads will also provide a copy of this QAPP to their Regional QA Staff.

Required Distribution

- EPA PAMS Regional Leads
- SLT monitoring agency Program Manager or Director
- PAMS Required Site Network monitoring leads
- EPA Regional QA staff
- PAMS Required Site Network analytical support laboratories

Table A3-1. DAQ PAMS Program Distribution List

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Table A3-1. DAQ PAMS Program Distribution List

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| Steven Walters, Chemist | DEQ, DAQ, AMS, PPB | 919-707-8453 | Steven.Walters@ncdenr.gov |
| Steven Rice, Database Manager | DEQ, DAQ, Technical Services, Mobile Sources Branch | 919-715-7220 | Steven.Rice@ncdenr.gov |
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| Tim Skelding, Ambient Monitoring Coordinator | DEQ, DAQ, RRO | 919-791-4270 | Timothy.Skelding@ncdenr.gov |
| Marshall Cannon, Environmental Specialist | DEQ, DAQ, RRO | 919-791-4200 | Marshall.Cannon@ncdenr.gov |
| Steve Helms, Environmental Specialist | DEQ, DAQ, RRO | 919-791-4200 | Steve.Helms@ncdenr.gov |
| Vacant, Environmental Technician | DEQ, DAQ, RRO | 919-791-4200 | |

A4 Project/Task Organization

The PAMS Required Site Network will measure ozone, its precursors, and meteorological variables, and will do so, unless otherwise authorized by EPA OAQPS, at the National Core (NCore) sites in metropolitan areas with core-based statistical area (CBSA) populations of 1

million or more as determined by 2010 census figures. SLT monitoring agencies are required to collect and report PAMS measurements listed in 40 Code of Federal Regulations (CFR) Part 58 Appendix D Section 5(b). These required measurements are detailed in Section A6.1.

Organizations essential to the execution of the PAMS Required Site monitoring program include EPA OAQPS, EPA Regional Offices, SLT monitoring agencies and their ASL, and the PAMS Support Contractor. The PAMS Required Site Network communication and responsibility structure is depicted in Figure A4-1.

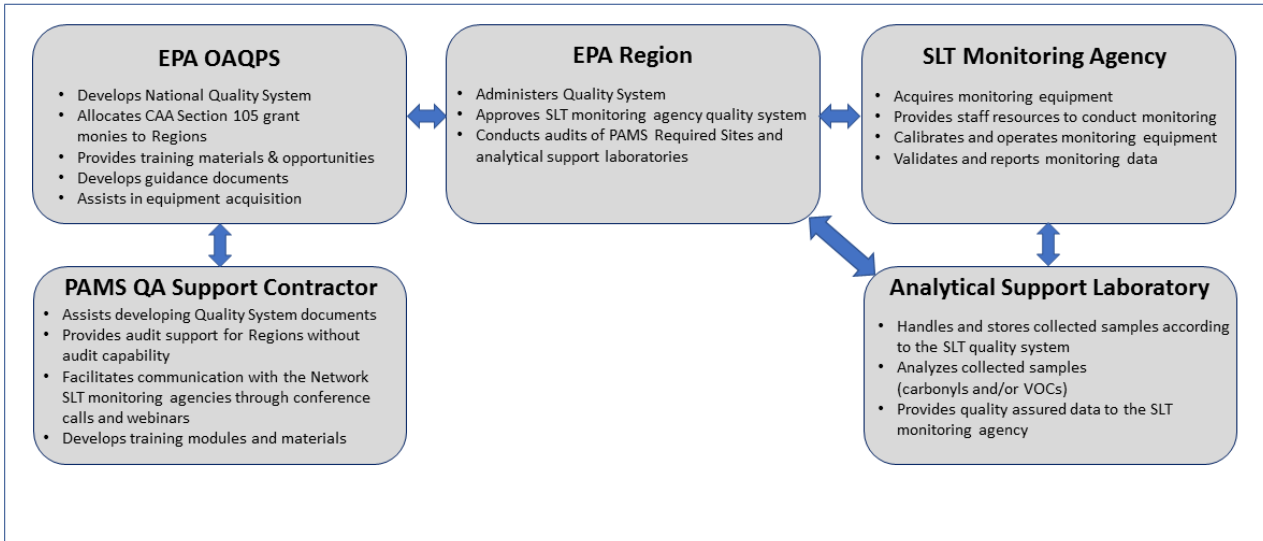


Figure A4-1. PAMS Required Site Network Communication and Responsibility Structure

A4.1 EPA OAQPS

OAQPS, with assistance from the EPA Regions, is responsible for defining and developing the national quality system (QS) for the PAMS Required Site Network. OAQPS also allocates the Clean Air Act (CAA) Section 105 grant monies to the EPA Regions which then distribute the funds to the SLT air monitoring agencies for execution of PAMS monitoring activities. OAQPS has the following responsibilities:

- Designating technical and QA leads for the PAMS Required Site Network
- Participating in the PAMS Required Site Workgroup
- Providing individual or group discussions with EPA Regions and monitoring agencies to help them determine and/or select appropriate instrumentation and ensure consistent execution of the monitoring activities across the network
- Developing and finalizing the PAMS Technical Assistance Document (TAD), this national QAPP, and national SOPs

-
- Organizing and conducting training course(s) for automatic gas chromatograph (auto-GC), ceilometer, and other pertinent instruments as well as technical and quality assurance activities, as needed
 - Developing and implementing the PAMS Technical Systems Audit (TSA) and Proficiency Testing (PT) programs
 - Setting TSA expectations and enforcing compliance
 - Conducting TSAs of the National Contract ASL
 - Approving QAPPs and SOPs from National Contract ASL

OAQPS will utilize a QA support contractor to assist in the development of the QS guidance documents, provide audit support, coordinate conference calls, and develop training materials.

A4.2 EPA Regional Offices

The EPA Regions administer the QS for the SLT monitoring agencies in their Regions, ensuring that the QS developed by each SLT monitoring agency complies with the national QS described in this document. The EPA Regional Offices are the major communication link with monitoring agencies and QAQPS; as such, they play an important role in the development and enforcement of effective policies and programs. The Regional Offices have the following specific responsibilities:

- Identifying a Regional PAMS QA Lead
- Participating in the PAMS Required Site Network Workgroup
- Reviewing and approving monitoring agency PAMS Required Site Implementation Plans (IPs) and waiver requests
- Reviewing and approving the national PAMS Required Site QAPP, monitoring agency specific QAPPs, and reporting approval of the monitoring agency QAPP to EPA's Air Quality System (AQS)
- Performing TSAs of PAMS Required Sites and applicable ASLs or delegating TSA conduct to the contractor
 - Identifying and communicating findings to OAQPS and SLTs
 - Ensuring that SLTs and ASLs write corrective action plans (CAPs) and that corrective actions are taken and are effective (i.e., that findings are addressed)
 - Recording TSA dates (i.e., occurrence and closeout) in AQS
- Providing QA oversight to PAMS Required Site monitoring agencies
- Providing technical assistance to PAMS Required Site monitoring agencies
- Serving as the communication liaison between OAQPS and PAMS Required Site monitoring agencies

A4.3 SLT PAMS Required Site Monitoring Agencies

DAQ is responsible for acquiring equipment, providing training to appropriate staff, operating instruments, and generating ozone precursor concentration and meteorological data, verifying the quality of the measurements, and reporting the PAMS measurements to AQS. DAQ has the following specific responsibilities:

- Participating in the PAMS Required Site Network Workgroup
- Developing and submitting the monitoring agency's PAMS Required Site IP
- Reviewing and providing input to the national PAMS QAPP, SOPs, and TAD
- Preparing and submitting waivers to PAMS requirements, as needed
- Selecting and purchasing instruments to measure PAMS parameters
- Ensuring that the DAQ PQAQ identifies the independent QA personnel that will oversee the QA Program for the DAQ PAMS Required Site monitoring, including:
 - Conducting annual internal audits of field and laboratory activities
 - Reviewing data quality and performing data validation activities
 - Ensuring technical personnel are competent to perform monitoring tasks
- Installing and testing equipment to meet the implementation date
- Entering validated data into AQS in accordance with the protocols described in this QAPP and the AQS Coding Manual
- Developing the DAQ PAMS QAPP and submitting for EPA Regional review and approval
- Reviewing the DAQ PAMS QAPP annually and revising this document as necessary and within 5 years of previous approval
- Developing the DAQ PAMS SOPs and maintaining and revising these documents as necessary and within 5 years of previous approval
- Reviewing SOPs for the LAB for compliance with this QAPP
- Implementing monitoring and analysis as described in the approved QAPPs and SOPs
- Ensuring the quality of the data generated by the LAB
- Attending field training courses as necessary to ensure personnel have the qualifications necessary to implement the PAMS Required Site program
- Developing and implementing CAPs based on nonconformances identified in internal and EPA TSAs
- Initiating PAMS monitoring by June 2021.

The roles and responsibilities of specific monitoring agency personnel are described in Section A6.2.

A4.4 Analytical Support Laboratory

The **LAB** is responsible for analyzing the carbonyls samples from the **Millbrook** Required PAMS site. Its responsibilities include, but are not limited to:

- Complying with the PAMS Required Site SLT monitoring agency QAPP
 - Performing QA/QC activities
- Following an approved SOP for receiving samples, extracting samples, and analyzing sample extracts
 - Notifying the **LAB supervisor and Level 2 and 3 data reviewers** of problems with samples
 - Extracting and analyzing carbonyls samples
 - Maintaining reagents and standards for analyzing carbonyls samples
 - Taking corrective action when procedural or acceptance criteria deviations occur
- Reporting sample and QC data to the **LAB supervisor and Level 2 and 3 data reviewers**
 - Verifying the laboratory data meet QA and QC acceptance criteria, are correct, are complete, and comply with **DAQ's** validation status readiness
 - Flagging data with appropriate laboratory qualifiers when procedural or acceptance criteria deviations are identified
- Developing and implementing CAPs based on nonconformances identified in internal and EPA TSAs

A4.5 PAMS Support Contractor

A support contractor will perform specific tasks associated with the PAMS Required Site program. The contractor responsibilities include, but are not limited to:

- Facilitating PAMS Required Site Workgroup conference calls
 - Developing agendas
 - Participating and leading technical and QA-related discussions
 - Summarizing conference call notes and identifying action items
- Assisting in the development of various documents
 - Developing the PAMS TAD, national QAPP, and national SOPs
 - Soliciting input to the documents from the PAMS Required Site Workgroup
 - Incorporating comments from the PAMS Required Site Workgroup into final national documents
- Developing training modules for field, lab, and audit activities
- Developing nationwide PAMS TSA and proficiency test (PT) programs
 - Submitting draft program design documents for the TSA and PT program to the OAQPS and to the PAMS Required Site Workgroup to seek stakeholder feedback
 - Incorporating PAMS Required Site Workgroup comments and finalizing the PT program description document and TSA checklist

-
- Executing and participating in TSAs with EPA Regions
 - Providing a yearly schedule of site evaluations for the EPA Regions
 - Assisting Regional staff with the execution of TSAs to ensure national consistency in the audit process
 - Working with Regional PAMS monitoring leads to review, evaluate, and closeout CAPs resulting from TSAs
 - Assisting monitoring agencies that require assistance implementing their CAPs
 - Facilitating and executing the PT program
 - Informing monitoring agencies of upcoming PTs
 - Generating and distributing PT samples
 - Collecting and reporting results to OAQPS, Regional staff, and monitoring agencies
 - Reporting PT results to AQS

A4.6 PAMS Required Site Workgroup

The PAMS Required Site Workgroup was formed to address the technical and QA aspects of the PAMS Required Site Program. Members of the group include personnel from the OAQPS, EPA Regions, the monitoring agencies, and EPA's support contractor. The PAMS Required Site Workgroup convened in May 2016 to start a dialogue on the aspects of the PAMS Required Site Network and the steps necessary to ensure a national QS are in place by the June 2021 implementation date for the PAMS Required Site network. The workgroup meets approximately monthly to discuss various technical and QA issues. The PAMS Required Site Workgroup will have the following responsibilities:

- Participating in the development and review of the PAMS TAD, national QAPP, and national SOPs
- Participating in the development and review of the PAMS TSA and PT programs
- Assisting in the development of training and initial and continuing demonstration of capability (IDOC and CDOC) programs
- Discussing PAMS Required Site network implementation
- Participating in the iterative data quality objective/data quality assessment (DQO/DQA) process for QS improvement

It is expected that the workgroup will continue to meet after the June 2021 implementation to discuss issues, best practices, and items pertinent to the PAMS Required Site Program to augment the overall quality system. The frequency of meetings will be determined by the workgroup based on the stakeholder needs.

A5 Problem Definition/Background

Ozone is formed by the reaction of certain VOCs with oxides of nitrogen in the presence of solar radiation. Reducing tropospheric ozone pollution requires reducing or eliminating emission sources of VOCs and oxides of nitrogen. Modelers predict production of ground-level ozone by running complex models which are continually refined to better estimate the ozone concentration

forecast under various meteorological conditions. Modelers assess model skill and refine model functionality by comparison of model outputs to actual chemical and meteorological measurements taken at PAMS sites. Modelers prefer the error in the collected measurement data to be less than the error in the associated models.

The primary objective of the PAMS air monitoring program is to provide data to evaluate and support the development of air quality models and measurement quality objectives (MQOs) were developed with this objective in mind. The data will be used for other important purposes including tracking trends in ozone precursor concentrations to aid ongoing efforts to attain the ozone National Ambient Air Quality Standard (NAAQS). The PAMS program began in 1993 and was revised in 2006 by the EPA to permit PAMS to be more customized and aligned with the needs of the responsible air quality agencies. On October 1, 2015, EPA further revised the implementation of the PAMS program. The final rule in its entirety may be found elsewhere.¹ The following are the highlights of the changes that occurred to the PAMS program because of the promulgation of the new regulations:

- **Network Design** - The first part of the network design change involved EPA requiring PAMS measurements during the PAMS (summer) sampling season, defined as June 1 through August 31, at all NCore sites in CBSAs with a population of 1 million people or more. The final network design will result in approximately 40 PAMS Required Sites, 14 of which are existing PAMS sites as shown in Table A5-1. The final requirements have waiver provisions which allow monitoring agencies to make PAMS measurements at alternative locations such as existing PAMS sites or at existing NATTS sites and to avoid being required to make PAMS measurements in areas with historically low O₃ concentrations. Therefore, the final site locations and network size may differ from what is shown in Table A5-1.

The second part of the network design requires states with moderate or above ozone non-attainment areas and states in the Ozone Transport Region (OTR - includes Connecticut, Delaware, the District of Columbia, Maine, Maryland, Massachusetts, New Hampshire, New Jersey, New York, Pennsylvania, Rhode Island, Vermont, and Virginia) to develop and implement Enhanced Monitoring Plans (EMPs) for additional monitoring of ozone precursors and meteorological conditions. These EMPs are intended to provide monitoring agencies with the flexibility to implement enhanced monitoring to suit the needs of their area. EMPs will not be further described within this document. If agencies are conducting EMP activities, those details may be added to the agency specific PAMS QAPP for EMPs. Additional information may be found in the following documents:

- Summary of Final Photochemical Assessment Monitoring Stations (PAMS) Network Designs. September 25, 2015.²
- Federal Register. Environmental Protection Agency. October 26, 2015. 40 CFR Parts 50, 51, 52, 53, and 58; [EPA-HQ-OAR-2008-0699; FRL-9933-18-OAR]; RIN 2060-AP38 National Ambient Air Quality Standards for Ozone¹

Table A5-1. Required Sites in CBSAs with a Population Greater than 1,000,000²

| Region | State | AQS ID | CBSA | Population | Existing PAMS? |
|--------|-------|-------------|---|------------|----------------|
| 1 | MA | 25-009-2006 | Boston-Cambridge-Newton, MA-NH | 4,732,161 | Yes |
| 1 | NH | 33-015-0018 | Boston-Cambridge-Newton, MA-NH | 4,732,161 | Yes |
| 1 | RI | 44-007-1010 | Providence-Warwick, RI-MA | 1,609,367 | Yes |
| 2 | NJ | 34-013-0003 | New York-Newark-Jersey City, NY-NJ-PA | 20,092,883 | No |
| 2 | NY | 36-081-0124 | New York-Newark-Jersey City, NY-NJ-PA | 20,092,883 | Yes |
| 2 | NY | 36-055-1007 | Rochester, NY | 1,083,393 | No |
| 3 | DE | 10-003-2004 | Philadelphia-Camden-Wilmington, PA-NJ-DE | 6,051,170 | No |
| 3 | DC | 11-001-0043 | Washington-Arlington-Alexandria, DC-VA-MD | 6,033,737 | Yes |
| 3 | MD | 24-033-0030 | Washington-Arlington-Alexandria, DC-VA-MD | 6,033,737 | Yes |
| 3 | PA | 42-101-0048 | Philadelphia-Camden-Wilmington, PA-NJ-DE | 6,051,170 | No |
| 3 | PA | 42-003-0008 | Pittsburgh, PA | 2,355,968 | No |
| 3 | VA | 51-087-0014 | Richmond, VA | 1,260,029 | Yes |
| 4 | AL | 01-073-0023 | Birmingham-Hoover, AL | 1,143,772 | No |
| 4 | FL | 12-011-0034 | Miami-Fort Lauderdale-West Palm Beach, FL | 5,929,819 | No |
| 4 | FL | 12-057-3002 | Tampa-St. Petersburg-Clearwater, FL | 2,915,582 | No |
| 4 | GA | 13-089-0002 | Atlanta-Sandy Springs-Roswell, GA | 5,614,323 | Yes |
| 4 | KY | 21-111-0067 | Louisville/Jefferson County, KY-IN | 1,269,702 | No |
| 4 | NC | 37-119-0041 | Charlotte-Concord-Gastonia, NC-SC | 2,380,314 | No |
| 4 | NC | 37-183-0014 | Raleigh, NC | 1,242,974 | No |
| 4 | TN | 47-157-0075 | Memphis, TN-MS-AR | 1,343,230 | No |
| 5 | IL | 17-031-4201 | Chicago-Naperville-Elgin, IL-IN-WI | 9,554,598 | Yes |
| 5 | IN | 18-097-0078 | Indianapolis-Carmel-Anderson, IN | 1,971,274 | No |
| 5 | MI | 26-163-0001 | Detroit-Warren-Dearborn, MI | 4,296,611 | No |
| 5 | MI | 26-081-0020 | Grand Rapids-Wyoming, MI | 1,027,703 | No |
| 5 | MN | 27-003-1002 | Minneapolis-St. Paul-Bloomington, MN-WI | 3,495,176 | No |
| 5 | OH | 39-061-0040 | Cincinnati, OH-KY-IN | 2,149,449 | No |
| 5 | OH | 39-035-0060 | Cleveland-Elyria, OH | 2,063,598 | No |
| 6 | TX | 48-113-0069 | Dallas-Fort Worth-Arlington, TX | 6,954,330 | Yes |
| 6 | TX | 48-201-1039 | Houston-The Woodlands-Sugar Land, TX | 6,490,180 | Yes |
| 7 | KS | 20-209-0021 | Kansas City, MO-KS | 2,071,133 | No |
| 7 | MO | 29-510-0085 | St. Louis, MO-IL | 2,806,207 | No |
| 8 | CO | 08-031-0025 | Denver-Aurora-Lakewood, CO | 2,754,258 | No |
| 8 | UT | 49-035-3006 | Salt Lake City, UT | 1,153,340 | No |
| 9 | AZ | 04-013-9997 | Phoenix-Mesa-Scottsdale, AZ | 4,489,109 | Yes |
| 9 | AZ | 04-019-1028 | Tucson, AZ | 1,004,516 | No |
| 9 | CA | 06-037-1103 | Los Angeles-Long Beach-Anaheim, CA | 13,262,220 | Yes |

Table A5-1. Required Sites in CBSAs with a Population Greater than 1,000,000²

| Region | State | AQS ID | CBSA | Population | Existing PAMS? |
|--------|-------|-------------|---------------------------------------|------------|----------------|
| 9 | CA | 06-065-8001 | Riverside-San Bernardino-Ontario, CA | 4,441,890 | Yes |
| 9 | CA | 06-073-0003 | San Diego-Carlsbad, CA | 3,263,431 | Yes |
| 9 | CA | 06-067-0006 | Sacramento-Roseville-Arden-Arcade, CA | 2,244,397 | Yes |
| 9 | CA | 06-085-0005 | San Jose-Sunnyvale-Santa Clara, CA | 1,952,872 | No |
| 9 | NV | 32-003-0540 | Las Vegas-Henderson-Paradise, NV | 2,069,681 | No |
| 10 | OR | 41-051-0080 | Portland-Vancouver-Hillsboro, OR-WA | 2,348,247 | No |
| 10 | WA | 53-033-0080 | Seattle-Tacoma-Bellevue, WA | 3,671,478 | No |

EPA modelers are the primary data users; however, it is expected that the chemical and meteorological measurements will aid SLTs in identifying potential sources of ozone precursors and will help inform emissions reduction strategies. The updated PAMS Required Site network is spatially diverse, covering a variety of urban areas with varied and unique geographic, topographic, and meteorological conditions. The resulting dataset will result in a better understanding of ozone formation and emissions reductions that will be most impactful for a specific area to increase the likelihood that ozone concentrations will come into attainment with the ozone NAAQS.

A5.1 Monitoring Agency PAMS Required Site(s)

The DAQ PAMS required site is in Raleigh, NC. Site information is shown in Table A5-2 below.

Table A5-2. PAMS Required Sites Covered by this QAPP

| Site AQS ID | Site Name | Site Location (Address) | County |
|-------------|-----------|--|--------|
| 37-183-0014 | Millbrook | 3801 Spring Forest Road, Raleigh, NC 27616 | Wake |

A6 Project Task/Description

This section provides a summary of the work to be performed and the schedule for implementation, including: ambient air measurements, collecting samples, acquiring samples; performing chemical analysis; carrying out QA/QC procedures to achieve data quality goals; and meeting the schedules for continued network implementation, operation, and data reporting.

A6.1 Required Measurements

SLT monitoring agencies will operate and maintain the instruments and equipment needed to make meteorological and chemical measurements for the PAMS Required Site program. Instruments and methods are listed in Table A6-1. The monitoring agency will specify the instrument models in its PAMS IP within its annual network monitoring plan. An example IP

suitable for documenting instruments to be deployed is included in Appendix E. The required measurements are listed in 40 CFR Part 58 Appendix D Section 5 and are reproduced below:

- Hourly averaged concentrations of speciated VOCs;
- Three sequential 8-hour average concentrations of carbonyls determined on a 1-in-3-day schedule (refer to Table B1-2);
- Hourly averaged concentrations of O₃ (not covered in this QAPP - see the DAQ NCore QAPP DAQ-01-001);
- Hourly averaged concentrations of nitrogen oxide (NO), “true” nitrogen dioxide (NO₂), and total reactive nitrogen (NO_y) (none of which are covered in this QAPP - see the DAQ NCore QAPP DAQ-01-001);
- Hourly averaged ambient temperature;
- Hourly vector-averaged wind direction;
- Hourly vector-averaged wind speed;
- Hourly average atmospheric pressure;
- Hourly averaged relative humidity (RH);
- Hourly precipitation amount;
- Hourly averaged mixing layer height (MLH);
- Hourly averaged intensity of solar radiation; and
- Hourly averaged intensity of ultraviolet (UV) radiation.

This QAPP covers the use of continuous GCs and meteorological measurements at the PAMS site location only. Refer to 40 CFR Part 58 Appendix D Section 5(d) and 5(e) and Appendix E of this QAPP, which describe options, with waivers, for collecting speciated VOCs using canisters and using meteorological data from nearby locations (such as airports). The monitoring agency will be required to submit alternative QAPP documentation to cover the options described in the waiver.

Table A6-1. Measurements and Associated Instruments for PAMS Required Sites

| Measurement Parameter | Instrument and/or Method |
|-----------------------|---|
| Speciated VOCs | Markes-Agilent auto-GC with thermal desorption and dual FID |
| Carbonyls | Carbonyls-specific sampler capable of three sequential 8-hour samples – Collection and analysis per EPA Compendium Method TO-11A The LAB will use a Thermo Ultimate 3000 ultra-high performance liquid chromatograph (UHPLC) as described in Method TO-11A and in PAMS TAD Section 5.0 |
| Ozone | Federal Reference Method/Federal Equivalent Method (FRM/FEM) ozone analyzer ^a |

| Measurement Parameter | Instrument and/or Method |
|-----------------------|---|
| True NO ₂ | FRM/FEM True NO ₂ analyzer – photolytic conversion with chemiluminescent detection or by cavity attenuated phase shift spectroscopy ^a |
| NO/NO _y | NO _y analyzer ^a |
| Ambient Temperature | thermometer or thermistor |
| Wind Direction | cup and vane, propeller and vane, or sonic anemometer |
| Wind Speed | |
| Atmospheric Pressure | aneroid barometer, pressure transducer |
| Relative Humidity | hygrometer |
| Precipitation | tipping bucket |
| Mixing Layer Height | ceilometer |
| Solar Radiation | pyranometer |
| Ultraviolet Radiation | pyranometer |

^a Ozone, true NO₂, and NO/NO_y are described in the DAQ NCore QAPP DAQ-01-001.

A6.2 Personnel to Accomplish Tasks

DAQ staff performing PAMS monitoring activities are listed below. Please see the organizational chart in Figure A6-1 and the subsequent position descriptions. Monitoring agencies are expected to be organized with positions and roles (however named) to accomplish PAMS monitoring tasks. Monitoring agencies will identify those individuals participating in the PAMS Program within the monitoring agency PAMS Required Site QAPP.

NOTE: Monitoring agencies will identify personnel responsible for implementing the QA Program in the monitoring network on the approval form on page 3. Such individuals include the program lead, the QA lead, and monitoring staff receiving the approved QAPP.

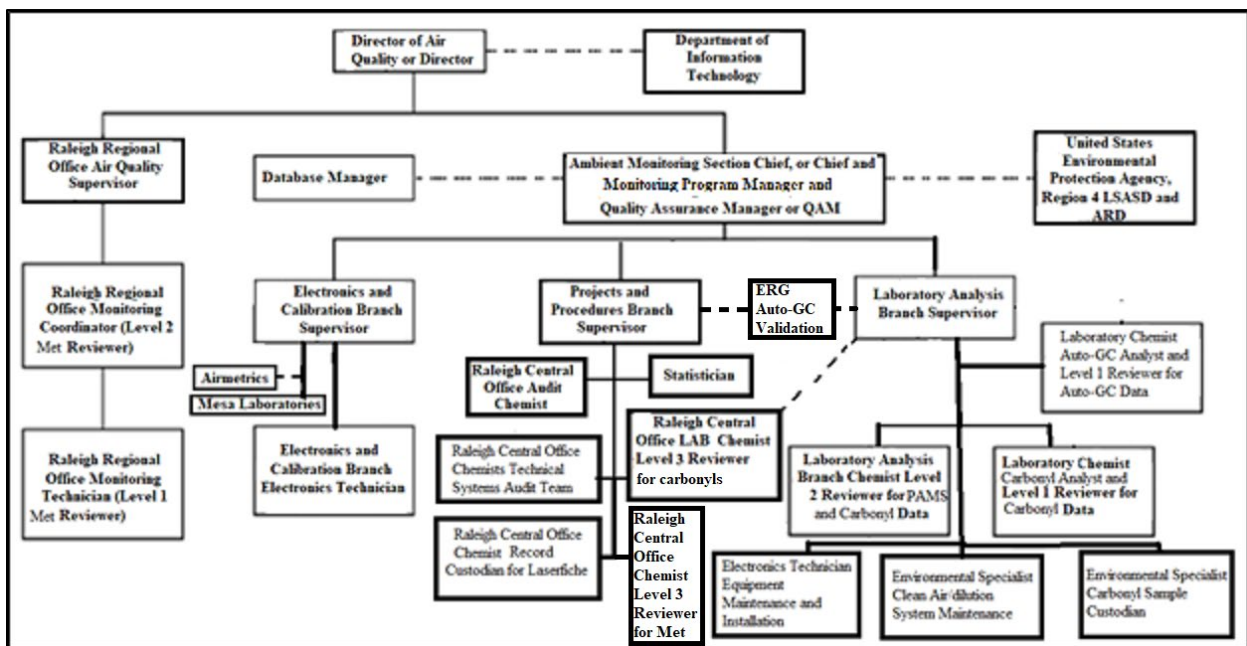


Figure A6-1. DAQ PAMS Monitoring Organizational Chart

Ambient Monitoring Section Chief, or Chief, Monitoring Program Manager and Quality Assurance Manager: The Chief/QAM reports to the Director of Air Quality. The Chief/QAM has the overall responsibility for managing the office according to monitoring agency policy. This individual maintains overall responsibility for the management and administrative aspects of the technical and QA programs; as such, he or she is responsible for establishing QA policy and for resolving QA issues identified through the QA program. The Chief/QAM has “stop work authority” and will make final decisions regarding monitoring issues. Major responsibilities include, but are not limited to:

- Managing and reviewing budgets, contracts, grants, and proposals
- Reviewing, overseeing, and evaluating overall air monitoring activities
- Assuring that the office develops and maintains a current QS
- Acquiring resources sufficient to enable the collection of required environmental data
- Maintaining an active line of communication with monitoring staff supervisor(s)
- Ensuring there are sufficient staffing resources to conduct the PAMS measurements and supporting data processing activities
- Serving as the arbiter on final data quality/validity determinations and corrective action effectiveness

Environmental Program Branch Supervisors and Regional Office Supervisor: The Environmental Program Branch Supervisors report to the Chief/QAM and Regional Office Supervisors report to the DAQ Director. Both positions serve as monitoring liaisons to the EPA Region. The Environmental Program Supervisors and Regional Office Supervisor consult with the Chief/QAM on monitoring and make recommendations, when appropriate. The Environmental Program Supervisors and Regional Office Supervisor duties include, but are not limited to:

- Supervising the activities of monitoring staff
- Communicating with EPA Regional personnel on issues related to routine monitoring and QA activities
- Maintaining overall responsibility for the monitoring network design, review, and assessment
- Maintaining oversight of QA/QC activities, which includes ensuring staff correctly implement and complete regulatory and QS requirements as described in the approved QAPP and SOPs, along with verifying that DQOs and MQOs prescribed in the approved QAPP are met
- Documenting deviations from established procedures and methods
- Directing staff to implement corrective actions based on audit outcomes
- Developing and maintaining this QAPP

-
- Training staff in the requirements of the QAPP and supporting SOPs
 - Facilitating technical training on instrument operations, maintenance activities, and data management to ensure staff remain proficient and are cognizant of updates to program requirements
 - Ensuring timely and appropriate updates to the QAPP and SOPs
 - Assisting in acquiring equipment and maintaining equipment inventories
 - Overseeing preventive maintenance and equipment certification activities are completed in accordance with the schedules specified in the QAPP and SOPs
 - Coordinating and reviewing collected data, which includes performing data quality assessments and flagging suspect data
 - Providing support for monitoring agency databases and data reporting to EPA AQS
 - Reviewing AQS data QA/QC files to ensure overall data accuracy and completeness
 - Generating AQS reports to verify successful and accurate upload of monitoring data
 - Reviewing budgets, contracts, and proposals related to monitoring

Monitoring Staff such as Laboratory Chemists, Electronics Technicians, Environmental Specialists, Regional Monitoring Coordinators, and Regional Monitoring Technicians:

Staff calibrating and operating instruments and equipment generating data for the PAMS Required Site Network must have the necessary training commensurate with their job duties. Due to the complexity of the instruments needed for the required measurements, site operators must be well-organized and capable of critical thinking to successfully operate, maintain, and troubleshoot the instruments needed for PAMS measurements. Monitoring agency monitoring staff consist of site operators, instrument technicians, and support staff who conduct routine monitoring operations. Monitoring staff report directly to their respective **Environmental Program Supervisors** which include the Laboratory Analysis Branch (LAB); the Environmental Program Supervisor overseeing the Electronics and Calibration Branch (ECB); and the **Regional Office Supervisor** and are responsible for implementing the PAMS Required Site QS as described in this QAPP and the supporting SOPs. Responsibilities include, but are not limited to:

- Maintaining proficiency with procedures applicable to their assigned duties
- Seeking training opportunities and attending training where needed
- Installing, calibrating, maintaining, and operating monitoring instruments
- Authoring, reviewing, and revising monitoring agency SOPs
- Reading, reviewing and contributing to the development of the monitoring agency QAPP
- Reading SOPs required to implement job responsibilities
- Documenting deviations from established SOPs, the QAPP, and monitoring agency policies

-
- Recording monitoring activities promptly and traceably including instrument calibration, maintenance, sample handling, and chain of custody
 - Documenting unusual events that may impact measurement data
 - Handling sampling media and instruments to maintain their integrity and avoid contamination
 - Verifying instrument calibrations by conducting ongoing QC checks
 - Taking and documenting corrective action when acceptance criteria are exceeded and when nonconformances are identified whether in routine operations or during a TSA, instrument performance audit (IPA), or audit of data quality (ADQ)
 - Communicating site problems with their respective Environmental Program Supervisors and Regional Office Supervisor
 - Working with internal QA staff and external auditors to conduct TSAs, IPAs, and ADQs
 - Ensuring a sufficient supply of resources such as spare parts, reference standards, sampling media, and consumables are available to facilitate instrument repairs and to minimize down time
 - Performing first level review of measurement data and flagging suspect data
 - Retrieving collected samples (carbonyls)
 - Ensuring data from automated instruments are recorded and backed up to assure redundancy

Quality Assurance Unit Staff such as the Raleigh Central Office Chemists and Technical Systems Audit Team: Monitoring agencies/PQAOs will have QA personnel consisting of staff independent of routine monitoring tasks. QA staff may include an overall lead (QA manager, coordinator, or officer). These DAQ staff members report to the Environmental Program Supervisor for the Projects and Procedures Branch (PPB) but also have direct access to the Ambient Monitoring Section Chief, who is two levels of management above the staff responsible for routine monitoring activities. QA staff will typically be responsible for overseeing the QA functions for numerous monitoring networks operated by the monitoring agency. QA staff members will have the authority to independently report technical and QA issues to management, identify audit findings, and oversee corrective actions on findings affecting data quality. QA staff member duties include, but are not limited to:

- Ensuring that all QS documentation meets programmatic needs and is reviewed and approved prior to the start of data collection
- Scheduling and performing internal TSAs on PAMS Required Site monitoring activities. TSAs involve interviewing site operators and data validators, observing processes to assess compliance with the approved QAPP and SOPs, and ensuring siting requirements of the monitoring equipment are met

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- Scheduling and performing internal IPAs on monitoring agency sampling equipment with reference standards independent of those employed to routinely calibrate and verify calibration of the sampling instruments
 - Scheduling and performing internal ADQs to assess the accuracy of data collection, data transformation, data reduction, and data reporting operations to AQS, which involves verification of the validity of a representative amount of collected measurement data
 - Documenting the outcomes of internal IPAs, TSAs, and ADQs and reporting the outcomes to management
 - Managing the document control system
 - Evaluating the quality of measurement data for compliance with the established DQO (if any/as applicable) and MQOs for the various data quality indicators (DQIs)
 - Ensuring corrective actions are taken **because** of QS nonconformances
 - Assessing effectiveness of corrective actions and conducting follow-up audits to demonstrate return to conformance
 - Maintaining QA-related documents, files, and records

Raleigh Central Office Chemists and Statisticians Responsible for PAMS Data Validation (Level 3 data reviewers): Monitoring agency data validation staff will have sufficient training to be familiar with the PAMS measurement system data outputs, quality control of the measurement systems, typical variations in measurement values, interactions and relationships between PAMS measurements (e.g., expected ratios of concentrations of various VOCs), chemical constituents of greatest concern, and tools used to evaluate and investigate the technical validity of PAMS measurement data. Data validators may consist of monitoring agency technicians, QA staff, or other qualified individuals depending on what level of data validation is occurring. Final validation must take place by personnel independent of technical monitoring staff. Data validators report to the **Environmental Program Supervisor overseeing the Projects and Procedures Branch (PPB).**

Analytical Support Laboratory (ASL): ASL staff, **also known as Laboratory Analysis Branch staff, report directly to the Environmental Program Supervisor for the LAB.** The LAB staff will comply with the portions of this QAPP which apply to the laboratory analysis of carbonyls and speciated VOCs. The specific employee reporting hierarchy requirements of the ASL is outside of the scope of this QAPP; however, each ASL will minimally have a structure similar to the monitoring agency whereby there is a Director or Manager, an analyst and/or technician to perform laboratory activities, and a QA staff member with authority to independently review and assess laboratory operations for the PAMS Required Site program work. ASL technicians calibrating and operating data generating laboratory instruments and equipment for the PAMS Required Site Network will have the necessary training commensurate with their job duties. Due to the complexity of the instruments needed for the required measurements, technical staff must be well-organized and capable of critical thinking to successfully operate, maintain, and troubleshoot the laboratory instruments needed for PAMS measurements. ASL QA staff will similarly have experience and training necessary to properly perform independent assessment of

the instrument calibration and operation, data reduction, data verification, and data reporting processes.

DAQ is using a national contract laboratory, ERG, for data validation of the PAMS Auto-GC speciated VOC data and its analyses are covered in contract QAPPs approved by the EPA. For all other analyses DAQ is serving as its own ASL. Thus, this QAPP serves as the ASL QAPP for carbonyl analysis and the ASL SOPs are included in this QAPP. The ASL for carbonyl analysis also follows the DEQ QMP.

A6.3 Schedule for PAMS Required Site Activities

DAQ will conduct the PAMS Required Site activities listed in Table A6-2. DAQ plans to collect PAMS carbonyl samples from June 1 to August 31 during each ozone season. DAQ plans to operate the auto-GC during the entire North Carolina ozone season (from March 1 to October 31) starting in 2023. DAQ was not able to meet the original PAMS program milestone of beginning operation of the AutoGC in the 2021 ozone season due to excessive instrument issues. DAQ intends to start monitoring for hourly, speciated VOCs using the AutoGC starting March 1, 2023 (start of the 2023 ozone season) and run the AutoGC until October 31 each year (end of ozone season). DAQ plans to take the auto-GC down for routine maintenance during the non-ozone season and intends to have the AutoGC operational before the March 1 start of ozone season each year.

Table A6-2. PAMS Required Site Activities

| Activity | Start Date | Completion Due Date | Details |
|--|--|---|---|
| Instrument and Support Equipment Maintenance | November 1, annually (end of ozone season) | March 1 annually (start of ozone season) | Complete annually prior to beginning annual monitoring - Preventive maintenance for measurement instruments, sample collection instruments and support equipment |
| Reference Standards Acquisition, Certification, or Recertification | November 1, annually (end of ozone season) | March 1 annually (start of ozone season) | Complete annually prior to beginning annual monitoring - Reference standard materials (calibration stock gases or carbonyls standards) and reference standard instruments will be acquired, certified, or recertified, as appropriate |
| Instrument warm up, conditioning, and calibration | November 1, annually (end of ozone season) | March 1 annually for auto-GC (start of ozone season) and June 1 annually for carbonyls (start of PAMS season) | Shakedown period for each instrument to ensure stable and accurate instrument performance prior to June 1 for carbonyls and prior to ozone season on March 1 for the auto-GC |
| Quality Systems Review and Revision | November 1, annually (end of ozone season) | March 1 annually (start of ozone season) | Review of the PAMS Required Site QAPP and supporting SOPs to ensure policies and procedures are accurate and current – completed once validated data from the previous year are reported to AQS and prior to beginning monitoring for the calendar year |

Table A6-2. PAMS Required Site Activities

| Activity | Start Date | Completion Due Date | Details |
|---|--|---|---|
| Demonstration of Capability | November 1 annually (end of ozone season) | March 1 annually for auto-GC (start of ozone season) and June 1 annually for carbonyls (start of PAMS season) | Staff will complete training and trainer will approve by signature (Refer to DAQ training form in Appendix D). Capability of instrument operators and data validators will be evaluated each year by the shakedown auditors and documented on the DAQ training forms. Monitoring agency management (i.e., immediate supervisor) of the instrument operators, data validators, and auditors will also evaluate performance twice a year during the interim and final Valuing Individual Performance reviews. |
| Shakedown Audit, may occur over several consecutive days between the start date and completion due date | November 1 | June 1 | Readiness assessment to determine areas requiring resources or correction to ensure systems are online and calibrated prior to or during PAMS monitoring |
| Proficiency Test (PT) for Speciated VOCs and Carbonyls | As provided by EPA approved QA support contractor, typically 1 st and 3 rd quarters during the calendar year | As prescribed by the EPA approved QA support contractor | Sample with concentrations of target speciated VOCs and carbonyls blind to the site operator and/or support laboratory – conducted prior to and toward the end of each PAMS season. |
| PAMS Monitoring | March 1 annually for Auto-GC June 1 annually for carbonyls | October 31 annually for Auto-GC August 31 annually for carbonyls | Beginning and ending of Monitoring as Required in 40 CFR Part 58 Appendix D Section 5 and described in Section A.7.3.1.1 of this QAPP – monitoring agencies may monitor outside of these dates if their ozone problem begins earlier and/or lasts beyond this period |
| Internal Technical Systems Audit (TSA) | June 1 annually | August 31 annually | Review of monitoring agency compliance with PAMS Required Site program requirements, QAPP, SOPs, and best practices – conducted by monitoring agency QA – conduct of the TSA will occur during active monitoring for agencies conducting monitoring beyond June 1 to August 31 |

Table A6-2. PAMS Required Site Activities

| Activity | Start Date | Completion Due Date | Details |
|------------------------------------|---|---|--|
| Instrument Performance Audit (IPA) | June 1 annually | August 31 annually | Conduct of the IPA will occur during active monitoring for agencies conducting monitoring beyond June 1 to August 31 measurement of the carbonyls sampling unit flow with a certified reference flow transfer standard – conducted by monitoring agency QA assessment of meteorological measurements by comparison to a certified reference standard – conducted by monitoring agency QA |
| Audit of Data Quality (ADQ) | Not before data are reported to AQS | Prior to review and revision of PAMS QA documents for the following year's monitoring | Review of a representative amount of PAMS measurement data for accuracy from instrument calibration, sample measurement, and final reporting to AQS |
| Data Verification and Validation | March 8 annually for Auto-GC data and June 8 annually for Carbonyl data | Prior to data reporting to AQS | Data verification and validation begins approximately one week after start of data collection to ensure data meet acceptance criteria and ensure the workload is manageable. |
| Data Reporting to AQS | Not before data validation is completed | Within 180 days of the end of the calendar quarter in which the measurement data were collected | Input of validated measurement data to AQS. Upload of all PAMS parameter data to AQS and verification that data were uploaded correctly |

A6.4 Summary of Assessment Techniques

PAMS project staff will assess the performance of the PAMS Required Site activities by conducting independent assessments. PAMS project staff will perform the assessments as detailed in Section C.1.1.

A7 Quality Objectives and Criteria

The primary objective of the PAMS Required Site network is to provide data of known quality for use by EPA modelers and scientists.

A7.1 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) meet the project outcomes within known certain levels 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.

Although a formal DQO process was not undertaken on the PAMS Required Site Network to determine a PAMS Required Site DQO, EPA solicited input on data needs from PAMS monitoring agencies and EPA modelers, i.e., from the primary users of the PAMS information. Measurement quality objectives (the MQOs) for the various data quality indicators (DQIs) were established based on the expertise of EPA modelers and data analysts and their data quality needs for ozone and ozone precursor model evaluation and model inputs. Modelers compare their model outputs to observed concentrations. For such comparisons the measured concentrations are considered to be the true value thus minimizing bias and imprecision was determined to be most important for the improvement of model skill. Monitoring agencies measuring PAMS parameters and other experts in PAMS measurements reviewed the proposed MQOs to ensure they were reasonable and attainable. Additionally, if more sensitive or accurate measurement methods become available and are deemed to be necessary to meet modelers’ needs, the MQOs may be modified and refined to accommodate the updated methods.

A7.2 Data Quality Indicators

The 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. Since O₃ and NO₂ are criteria pollutants and are used for designating compliance with the NAAQS, the MQOs in Table A7-1 duplicate those listed in the validation templates of the EPA QA Handbook Volume II. The DAQ is proposing the bias and precision criteria listed in Table A7-1 for the meteorological parameters of ambient temperature, relative humidity, barometric pressure, wind speed, and wind direction. The DAQ is aware the MQO criteria for wind speed and wind direction does not match the proposed CTS limits in Table 2-2 in EPA’s QA Handbook Volume IV for average difference and standard deviation of the differences. The DAQ has performed extensive CTS testing using sonic anemometers and cannot routinely achieve the proposed CTS limits in Table 2-2 in the Volume IV handbook. Please see Appendix G and Appendix H for examples of 2021 and 2022 CTS audit results, respectively. The CTS audits were conducted at the Millbrook PAMS required site. DAQ plans to update these criteria as more collocated meteorological data are collected. Additional detail on the various checks used to measure and assess the DQIs may be found in the Quality Control Measurements Section B1.2.

EPA technical staff, their QA support contactors, monitoring equipment vendors, and the monitoring agencies also provided feedback on the MQOs for various DQIs that would be considered achievable under field conditions. These MQOs were then discussed with monitoring agencies and other PAMS measurement subject matter experts to ensure that the MQOs were attainable and reasonable, and if not, the MQOs were further refined as listed in Table A7-1. EPA modelers found these to be acceptable.

Table A7-1. PAMS DQIs and Associated MQOs

| Method or Parameter | DQI | | | | |
|---|---|---|--|--|--|
| Chemical Measurements | Representativeness (Sampling Frequency) ^a | Bias | Precision | Sensitivity (Detection Limit) | Completeness |
| Auto-GC speciated VOCs | Continuous, hourly average | ≤ 25% ^b | ≤ 25% ^c | ≤ 0.5 ppbC | ≥ 75% |
| True NO ₂ and NO/NO _y | | < ±15.1% or ± 1.5 ppb ^d whichever is greater | < 15.1% or 1.5 ppb ^e whichever is greater | ≤ 0.001 ppm | ≥ 75% |
| Ozone | | < ± 7.1% or ± 1.5 ppb ^d whichever is greater | < 7.1% or 1.5 ppb ^e whichever is greater | ≤ 0.002 ppm | > 90%(average) daily max available in O ₃ season with minimum of 75% in any 1 year ⁱ |
| TO-11A (carbonyls) | Three sequential 8-hour samples every 3 rd day ^{e, f} | ≤ 25% ^g | ≤ 15% ^h | ≤ 0.25 µg/m ³ | ≥ 85% |
| Meteorology | Representativeness (Sampling Frequency) ^a | Bias ^k | Precision ^k | Sensitivity (Resolution) | Completeness |
| Ambient Temperature | Continuous, hourly average | ≤ ± 0.5 °C | ≤ ± 0.25 °C | ≤ 0.1 °C | ≥ 75% |
| Relative Humidity | | ≤ ± 5% RH | ≤ ± 2.5% RH | ≤ 0.5% RH | |
| Barometric Pressure | | ≤ ± 2 hectopascal (hPa) | ≤ ± 1 hPa | ≤ 0.1 hPa | |
| Wind Speed | | ≤ ± 1.0 meter/second (m/s) | ≤ ± 0.5 m/s | ≤ 0.1 m/s | |
| Wind Direction | | ≤ ± 10 degrees (°) | ≤ ± 10° | ≤ 1 degree | |
| Solar Radiation | | ≤ ± 5% | | ≤ 1 Watt per square meter (Watt/m ²) | ≥ 75% |
| UV Radiation | | ≤ ± 5% | | ≤ 0.01 Watt/m ² | |
| Precipitation | | ≤ ± 10% | | ≤ 0.25 mm/hr | |
| Mixing Layer Height | | ≤ ± 5 m or ± 1%, whichever is greater | | ≤ 10 m | |

^a Spatial representativeness is addressed in monitor siting as specified in Section A7.3.1.2.

^b Assessed with twice-annual PT samples and across the entire PAMS season as the upper bound of the mean absolute value of the percent differences across all single-point QC checks. For functional form of the calculation, see 40 CFR 58 Appendix A Section 4.1.3, Equations 3, 4 and 5.

^c Measured as the upper bound of the coefficient of variation (CV) across all single-point QC checks in the PAMS season. For functional form of the calculation, see 40 CFR 58 Appendix A Section 4.1.2, Equation 2. Acceptance criteria listed here for criteria pollutants duplicate those in the EPA QA Handbook validation templates. Changes to the QA Handbook requirements will supersede those criteria listed here.

^d Measured as the upper bound of the mean absolute value of the percent differences across all single-point QC checks in the PAMS season. For functional form of the calculation, see 40 CFR 58 Appendix A Section 4.1.3, Equations 3, 4, and 5. Acceptance criteria listed here for criteria pollutants duplicate those in the EPA QA Handbook validation templates. Changes to the QA Handbook requirements will supersede those listed here.

^e Carbonyls sampling by TO-11A may be substituted with continuous formaldehyde monitoring and reporting of the hourly average. MQOs for continuous formaldehyde monitors have not been established at the time this document was written.

^f Carbonyls sampling will follow the 1-in-3 day sampling schedule as prescribed in Table B1-2 and the national sampling calendar available at the following link on AMTIC: <https://www.epa.gov/amtic/sampling-schedule-calendar>

^g Assessed with twice-annual PT samples.

^h Measured as the coefficient of variation of the RPDs across, as applicable, all (i) duplicate/collocated field-collected cartridges; duplicate LCSs, and (iii) replicate laboratory analyses in the entire PAMS season. See Sections 2.5.1 and 2.5.2 of the NATTS 2011-2012 Quality Assurance Annual Report available here:

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

ⁱ Refer to 40 CFR Part 50 Appendix U, Section 4

^j the DAQ will not conduct the hard target test because the Millbrook PAMS Required Site lacks sufficient space for the hard target test to be completed safely. DAQ will follow alternate guidance from Vaisala or EPA and publish said guidance in future revisions of this QAPP and ceilometer SOPs. Currently, DAQ uses an optical termination hood to zero the instrument to look for “zero” bias.

^k bias and precision for these meteorological parameters is determined using the collocated transfer station (CTS) method by comparing the site sensor against a separately calibrated audit sensor. For a CTS audit pair of data (site sensor, audit sensor) to be considered valid, a minimum of 48, 1-hour averages that cover at least two diurnal cycles must be included in the CTS bias and precision calculation. Additionally, for the CTS audit point pair to be considered valid, the hourly averaged wind speed for the same hour must be > 1.0 m/s. If an hourly averaged wind speed does not meet this criterion for either the site sensor or the audit sensor, the CTS audit point pair is discarded and not included in the CTS bias and precision calculations.

EPA reserves the right to revise the prescribed MQOs after the first year of the program to determine the suitability and how “achievable” the MQOs have been.

A7.3.1 Representativeness

A7.3.1.1 Temporal Representativeness

To adequately characterize the concentrations of ozone and ozone precursors during PAMS season (defined by default as June 1 to August 31 – when resources allow, DAQ plans to operate from March 1 to October 31 for speciated VOCs only), the sampling frequency for the required parameters is prescribed as follows. The sampling frequency for ozone, true NO₂, NO_y, speciated VOCs, and meteorological parameters is for sampling to occur continuously daily and the collected data averaged for each hour. Ozone, true NO₂, and NO/NO_y measurements at the Millbrook PAMS Required Site will be described in and comply with the DAQ QAPP DAQ-01-001 governing the NCore measurements of criteria pollutants at the site. This document covers meteorological parameters, speciated VOC parameters, and carbonyl parameters. Due to the labor-intensive aspects of manual sample collection of carbonyls onto cartridge media and the difficulty in achieving adequate sensitivity, carbonyls sampling is not required hourly, but instead is required on a 1-in-3-day schedule consisting of three sequential 8-hour samples (refer to the sampling schedule in B1.1.1 for start and stop times). Carbonyl samples will be collected per the national sampling calendar available at the following link on AMTIC:

<https://www.epa.gov/amtic/sampling-schedule-calendar>

Carbonyls collection onto 2,4-dinitrophenylhydrazine (DNPH) cartridges may be substituted with continuous formaldehyde measurements for which the concentration data are reported as the hourly average. DAQ will collect carbonyl sample cartridges on a 1-in-3-day schedule consisting of three sequential 8-hour samples following the start and stop time listed in table B1.1.1 of this document. The PAMS carbonyls will be collected, annually from June 1 through August 31.

The average hourly measurement of ozone precursors collected continuously (with the exception of the required compromise presently required for carbonyls) provide a sufficient number of data points at a sufficient time resolution to ensure that the measurements characterize the concentration patterns over the course of the PAMS season at a given PAMS Required Site. Incorporating the meteorological measurements reported as an hourly average provides a robust dataset representative of the conditions at the site. DAQ will operate the auto-GC from March 1 through October 31 starting in 2023. In 2021 and 2022, DAQ was not able to operate the auto-GC during these two ozone seasons due to excessive instrument issues. DAQ will perform routine maintenance on the auto-GC during the ozone off season (November 1 to February 28). Meteorological, true NO₂, NO_y, NO and ozone monitoring will occur year-round.

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, the monitoring agency must consult with the EPA Regional office to request a waiver. See Volume 1 of the DAQ network plan at the following link for the most up to date site descriptions and potential siting issues affecting the Millbrook PAMS Required Site:

<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 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 during PAMS season and must have unrestricted airflow in an arc of at least 180°. As most of the PAMS Required Sites will be located at existing NCore sites, EPA does not expect that probes will be mounted on the side of a building. The probes at the Millbrook PAMS Required Site extend at least a meter above the roof of the building.

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

| | |
|----------------|------------------------------------|
| PAMS VOCs | 2 to 15 m above ground level (AGL) |
| PAMS 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 meters above the inlet probe, the inlet probe must be 4 meters or more from the wall.

Spacing from Trees: Trees can provide surfaces for O₃ or NO₂ adsorption or reactions and may prevent the accurate measurement of other PAMS parameters when of a sufficient height and leaf canopy density to interfere with airflow. To avoid such interferences, inlet probes must be minimally 10 meters from the dripline of the nearest tree.

Spacing from Roadways: Mobile sources represent a significant source of ozone precursors; 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 PAMS sites are urban 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 ^a (meters) | Minimum distance ^a (meters) |
|---|--|--|
| ≤ 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

Siting of meteorology equipment for the required measurements is specific to each instrument type. General siting criteria for the meteorology instruments follows.

Wind Speed and Wind Direction: The standard height for surface layer wind measurements is 10 m AGL.^{4,6,7} 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.^{4,7} 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, must be documented in the site characterization documentation. See Volume 1 of the DAQ network plan describing potential siting issues that may affect wind speed and wind direction measurements at the Millbrook PAMS Required site.

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 ambient temperature and RH measurements is 2 meters AGL.⁶ 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 unwatered 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, roof tops, 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.⁸ The DAQ replaced its current meteorological equipment with a MetOne AIO2 meteorological sensor which measures five meteorological parameters (relative humidity, ambient temperature, barometric pressure, wind speed, and wind direction) in a single, all-in-one sensor that is mounted at 10 meters AGL on an open lattice tower. The DAQ also stated in the 2021-2022 network plan that the 30 m horizontal placement of the sensor from any paved area is not possible to achieve at the Millbrook site due to the surrounding urban environment.

Solar Radiation and Ultraviolet Radiation: Solar and UV radiation measurements will be taken in a location with an unrestricted view of the sky in all directions. Locations where there are obstructions that could cast a shadow or reflect light on the sensor, such as light-colored walls or artificial sources of radiation, must be avoided. The elevation to the horizon as viewed from the pyranometer must not exceed 5°. Sensor height is not critical for pyranometers; consequently, tall platforms or roof tops are typical locations.

Barometric Pressure: Barometric pressure instruments will be located in a ventilated shelter about 2 m above ground level. 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 has

replaced its current meteorological equipment with a MetOne AIO2 meteorological sensor which mounts the barometric pressure sensor at 10 meters AGL on an open lattice tower.

Precipitation: Precipitation gauges will be located on level ground in an open area. Obstructions will not be closer than two times their height from the instrument. The area around the precipitation gauge should be covered with natural vegetation and should not be located on a paved or hard surface (e.g., the roof of a monitoring shelter) to minimize splashing. The mouth of the gauge will be level and will not be lower than 30 cm above ground level (to avoid being covered with snow). To ensure accessibility for technicians, the instrument should be mounted not higher than 2 m above ground level. A wind shield/wind screen (such as an Alter-type wind shield consisting of a ring with approximately 32 free-swinging separate metal leaves) will be employed to minimize the effects of high wind speeds.

Mixing Layer Height (MLH): The ceilometer for determining MLH measurements is intended for more macro-scale application than are the surface meteorological measurements. Consequently, the location of the ceilometer need not be associated with any particular PAMS surface site. Factors that will be considered in selecting a site for the MLH monitor include whether the upper-air measurements for the proposed location are likely to provide the necessary data to characterize the meteorological conditions associated with high ozone concentrations, and the extent to which data for the proposed location of the ceilometer may augment an existing upper-air network. The ceilometer must be securely installed on a stable level surface such as a concrete pad or wooden platform suitably located to provide an unobstructed view of the sky. A wide-open location is recommended where there are no tall trees, overhead lines, or antennas nearby. Proximity to powerful radars should also be avoided. Any object in the cone projecting upward created by an angle of 25° from vertical will impede the ability of the ceilometer to properly measure atmospheric backscatter. Common interfering objects would include powerlines, tree branches, tower support guidewires, flagpoles, or similar features which may be permanently or transiently present above the ceilometer. The DAQ will not conduct the hard target test because the Millbrook PAMS Required Site lacks sufficient space for the hard target test to be completed safely. Instead of the hard target test, DAQ will follow alternate guidance that DAQ expects the EPA to provide soon and the DAQ plans to publish said guidance in future revisions of this QAPP and ceilometer SOPs. An optical termination hood is used to zero the instrument to measure “zero” bias.

A7.3.2 Completeness

Generation of a dataset sufficient to characterize the daily concentrations of ozone, ozone precursors, and parameters of interest to PAMS requires that a minimum number of the intended measurements are 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 as detailed in Table A7-1.

For continuous measurement methods reported as the hourly average, uncollected or invalidated measurement results are lost, and cannot be made up. For hourly measurements, 45 minutes will be considered a valid hour and 18 hours a valid day. Note that due to limitations with the instrument cycling for sample collection and measurement, a valid sampling hour for speciated

VOCs is 40 minutes of sampling for the hour, for which 30 minutes of this 40-minute period must occur during the sampling hour. The overall completeness listed in Table A7-1 will be based on acquiring data for the entire PAMS season determined as the total valid samples out of the samples possible. For continuous measurements, this will be based on approximately 2208 hours. For carbonyls samples, the total possible sampling days is 30 or 31 days, depending on the sampling calendar for the year. For carbonyls sample collection, if a sample day is missed, a null code "AF" (scheduled but not collected) will be reported to AQS for the sample run date; if the sample is invalidated for a particular reason, an appropriate null code will also be reported to AQS for the sample run date. A make-up sample must be collected as soon as practical according to the make-up sampling policy below.

Carbonyls Make-up Sample Policy: For invalidated or missed carbonyls sampling events, a make-up sampling event will be conducted. A replacement carbonyls sample set (three 8-hour samples) will be collected as close to the original sampling date as possible, should not exceed two weeks from the originally scheduled collection date, and will be collected within PAMS season. Make-up samples will be collected according to the following:

1. Before the next scheduled sampling date, if possible, or at the discretion of the DAQ staff with regards to individual work assignments and staff availability.
2. Within two weeks of the missed collection date, with preference given that the rescheduled date occurs on a weekday or weekend day to match that of the original schedule and must not be rescheduled after the end of the PAMS carbonyl sampling season (August 31).

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.

Precision for Continuous Measurements: Precision assessments for NO₂, NO_y and ozone are addressed in the DAQ NCore QAPP DAQ-01-001 for NCore monitoring.

Precision for Speciated VOCs: Precision is assessed by analysis of replicate calibration verification standards. A sequential (back-to-back) analysis of the continuing calibration verification (CCV) is performed for the speciated VOCs precision check. As an overall MQO, the precision is evaluated as the upper bound of the coefficient of variation (CV) across all single-point CCVs in the PAMS season. For functional form of the calculation, see 40 CFR 58 Appendix A Section 4.1.2, Equation 2.

Within run precision is evaluated by comparing replicate measurements in a pair-wise fashion to determine the relative percent difference (RPD) between the two measurements which must be ≤ 25% for each assessed target compound. RPD is calculated by dividing the absolute value of the difference between the two measurements by the average of the two measurements. Precision will be further evaluated on an ongoing basis for groups of CCVs by calculating the relative

standard deviation (RSD) which is found dividing the standard deviation of the measurements by the average of the measurements. RSD for $n > 2$ replicate measurements must be $\leq 25\%$. When determining RSD for speciated VOCs, all measurements in the desired time window (e.g. including the precision CCVs for one month, two months, or all of PAMS season) will be included unless there is a valid reason for exclusion (such as instrument problem or other documented technical issue). Ambient sample data for target analytes failing precision criteria will be appropriately qualified or invalidated, as appropriate, when reported to AQS. Monitoring agencies must take corrective actions for precision acceptance criteria failures of priority compounds and should take corrective actions for optional compounds failing precision criteria, though they are not required. Monitoring agencies should evaluate precision on an ongoing basis to determine whether precision criteria are in jeopardy and take corrective actions to ensure precision across the monitoring season does not exceed criteria.

Precision for Meteorology Measurements: Precision is determined using the collocated transfer station method as described in section 5.2 in SOP# DAQ-07-003.1.

Precision for Carbonyls: Field sampling precision must be assessed for carbonyls at minimally 10% of the PAMS Required Network Sites. The Millbrook site will not be one of the field sampling precision sites. Such precision assessments entail collection of duplicate samples (a pair of samples collected through a common inlet probe) or collocated samples (a pair of samples each collected through independent inlet probes) concurrently with the primary sampling events. The monitoring agency can choose to assess precision by either the duplicate or collocated method. Duplicate or collocated cartridges will be collected at a rate of minimally 10%, equivalent to three per month. Precision of duplicate and collocated samples is assessed as the RPD of the concentrations measured for the collocated or duplicate pair and must be $\leq 20\%$ for samples for which both cartridges measure ≥ 0.5 microgram per cartridge ($\mu\text{g}/\text{cartridge}$). Duplicate or collocated samples for which one or both cartridges measure < 0.5 $\mu\text{g}/\text{cartridge}$ are not required to meet this acceptance criterion. Duplicate or collocated results that do not meet the precision acceptance criterion will be qualified when entered in AQS and will prompt the LAB and field operations to perform corrective actions to investigate the precision sample result discrepancy for priority compounds. Corrective actions should be taken for precision failures for optional carbonyl compounds, but they are not required.

Precision of laboratory extraction and analysis procedures is to be assessed by preparation and analysis of duplicate laboratory control samples (LCS) consisting of a pair of blank DNPH cartridges spiked with target compounds at the laboratory and extracted and analyzed with collected field samples. Precision of the LCS and LCS duplicate (LCSD) is assessed as RPD which must be $\leq 20\%$. An LCS/LCSD pair is to be prepared, extracted, and analyzed minimally twice quarterly. Ambient sample results associated with LCS/LCSD results that do not meet the precision acceptance criterion will be qualified when entered in AQS and will prompt the LAB to perform corrective actions to correct the discrepancy for priority compounds. Corrective actions should be taken for LCS/LCSD precision failures for optional carbonyl compounds, but they are not required.

Precision of laboratory analysis is assessed by replicate analysis of an extract from a field-collected cartridge (not a trip or field blank). Precision of the replicate analysis is assessed as

RPD which must be $\leq 10\%$ for samples that measure $\geq 0.5 \mu\text{g}/\text{cartridge}$. A replicate analysis is to be performed with each analysis batch (defined as a sequence of samples extracted as a single group over a finite time interval, typically 20 field-collected cartridges). Failures of priority compound replicate sample results will prompt the **LAB** to take corrective action which should include reanalysis of the sample extract to confirm the failure. If the analytical precision failure cannot be corrected, associated ambient sample results will be qualified when entered in AQS for affected compounds. Corrective actions should also be taken for replicate analysis failures for optional carbonyl compounds, but they are not required.

The network MQO for carbonyls is based on an evaluation of the entire PAMS season's data. In all cases a CV of $\leq 15\%$ must be met. For more information on how the CV is calculated, see the 2011-2012 NATTS Quality Assurance Annual Report, available at the following link on AMTIC:

<https://www3.epa.gov/ttnamti1/files/ambient/airtox/to-11ar.pdf>

Note that this precision MQO is different than the precision acceptance criteria for the individual pairs of duplicate or collocated samples, the imprecision of which are permitted to exceed 15%. Such method-specific precision requirements apply to comparing two measurements and do not apply to larger ($N > 2$) sample sets.

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 PAMS season and thereafter their calibration must be periodically demonstrated to remain valid by comparison with a known traceable certified reference standard or instrument. For chemical 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. The required frequency for periodic ongoing checks for PAMS instruments is described below. The overall bias MQOs for the continuous parameters for the entire PAMS season are shown in Table A7-1. The nightly continuing calibration checks and zero background checks for the auto-GC are described in Section B5.1.2.

For carbonyls, bias resulting from field activities is assessed and minimized by a combination of pre-deployment bias checks and flow calibration and calibration verification for sample collection instruments and by periodic collection of field and trip blanks. Laboratory bias is minimized by calibration and verification of detector response for the UHPLC analysis instrument. Following annual maintenance and prior to field deployment at the beginning of each PAMS season, a positive bias verification and flow calibration are performed on the carbonyls sampling unit. The positive bias verification is briefly described in Section B5.1.1 and is detailed in Revision 2 of the PAMS TAD (<https://www3.epa.gov/ttnamti1/pamsguidance.html>) and in the SOP# DAQ-09-002.1 ATEC 8000 PAMS Sequential Carbonyl Sampler ECB Responsibilities.

The positive bias verification procedure must demonstrate that the sampling unit contribution for target carbonyls is $< 0.2 \mu\text{g}/\text{cartridge}$ greater than the sequentially collected reference sample.

The sampling unit must meet this specification before field deployment. *Note: Monitoring agencies are encouraged, but not required, to take corrective action to eliminate apparent contamination from samplers even if the $0.2 \mu\text{g}/\text{cartridge}$ threshold is not exceeded.*

Sampling unit flow rates must be verified before field deployment and monthly thereafter against a National Institute of Standards and Technology (NIST)-traceably certified reference flow transfer standard. Indicated flow rates must be within $\pm 10\%$ of the flow transfer standard. If the flow is not within $\pm 10\%$, ambient sample data since the most recent passing flow check will be qualified or invalidated.

Laboratory bias is controlled by establishing a multi-point calibration curve with subsequent analysis of a CCV standard every 12 hours of analysis. This CCV must demonstrate the instrument calibration remains within $\pm 15\%$ of the original response. If this criterion is exceeded, corrective action will be performed to demonstrate appropriate calibration response and the extracts since the last passing CCV will be reanalyzed. If reanalysis cannot be performed, ambient sample data for affected target analytes will be qualified when reported to AQS. The CCV is followed by a solvent method blank when additional samples are to be analyzed to demonstrate that the instrument has returned to a stable baseline and that there is no carryover or significant interferences in the instrument system. Poor or infrequent instrument or instrument inlet maintenance will also cause bias in reported concentrations for speciated VOCs and carbonyls. Instrument maintenance is described in Section B6.4 of this QAPP and in the supporting instrument SOPs.

Bias of speciated VOCs and carbonyls will be assessed twice annually just prior to PAMS season and toward the end of PAMS season through analysis of PT samples. Bias of speciated VOCs and carbonyl measurements will be additionally assessed by evaluation of the ongoing single-point QC checks. For the functional form of this calculation, refer to 40 CFR Part 58 Appendix A, Section 4.1.3, Equations 3, 4, and 5.

Bias of meteorological measurements is controlled by ensuring instruments are appropriately calibrated prior to field deployment and by performing periodic comparison checks to a known calibrated instrument exposed to the same conditions (whether controlled or ambient) or to known reference conditions. Once calibrated, meteorological instrument calibration bias will be verified annually according to the CTS method. Note that this calibration verification is separate than the annual instrument performance audit described in Section C1.1.1.2. Bias assessment for meteorological instruments is described below:

- Wind anemometers – The bias of sonic anemometers is determined by the collocated transfer station method by comparing the site sensor to a separately calibrated sonic anemometer of the same design as the site sensor over at least 48 collocated pairs of hourly averaged wind speed values covering at least two diurnal cycles. Additionally, to be considered a valid collocated pair of wind speed values, the average wind speed for the same hour must be $> 1.0 \text{ m/s}$ for the site sensor and the audit sensor. Measurement

bias, or the average difference between the site sensor and audit sensor, will be maintained to within ± 1.0 m/s.

- Wind vanes – The bias of sonic wind vanes is determined by the collocated transfer station method by comparing the site sensor to a separately calibrated sonic wind vane of the same design as the audit sensor over at least 48 collocated pairs of hourly averaged wind direction values covering at least two diurnal cycles. Additionally, to be considered a valid collocated pair of wind direction values, the average wind speed for the same hour must be > 1.0 m/s for the site sensor and the audit sensor. Measurement bias, or the average difference between the site sensor and audit sensor will be maintained to within $\pm 10^\circ$. Additionally, using sonic wind vanes with an internal compass allows the user to enter a declination angle into the sensor memory. This declination angle corrects all wind direction measurements to be relative of true north. The declination angle is unique to the current geographical location of the site sensor. To determine the current declination angle based on geographical location, the National Oceanic and Atmospheric Administration offers a magnetic declination calculator at the following website:

<https://www.ngdc.noaa.gov/geomag/calculators/magcalc.shtml>

- Ambient temperature probes – Bias of temperature probes used for meteorological parameters such as ambient temperature, is assessed by the collocated transfer station method by comparing the site sensor to a separately calibrated audit sensor over at least 48 collocated pairs of hourly averaged ambient temperatures covering at least two diurnal cycles. Bias, or the average difference between the site sensor and audit sensor, for ambient temperature probes must be maintained to be within $\pm 0.5^\circ\text{C}$.
- Other temperature probes - Bias of temperature probes used to monitor laboratory room temperatures, refrigerator temperatures, shelter temperatures, and probes used to measure temperatures of carbonyl cartridges received at the ASL may be performed by comparison to a NIST-traceably certified thermometer or thermistor. The calibration check is performed at a single point. The temperature probe is to be within $\pm 0.5^\circ\text{C}$ from the certified reference standard.
- Precipitation gauges – bias is assessed by adding a known volume of water with a volumetrically certified device (such as a graduated cylinder) and verifying the instrument is reporting to within $\pm 10\%$ of the known added volume.
- Hygrometers – Bias of hygrometers is assessed by the collocated transfer station method by comparing the site sensor to a separately calibrated audit sensor over at least 48 collocated pairs of hourly average relative humidity values covering at least two diurnal cycles. Bias, or the average difference between the site sensor and audit sensor, for relative humidity must be maintained to within $\pm 5.0\%$. Bias may also be assessed by comparison of the hygrometer to a reference standard at minimally two (typically four) different humidity levels covering a typical range of 35 to 90% RH. The dew point provided by the hygrometer must be within $\pm 1.5^\circ\text{C}$ of the reference standard for $\text{RH} \geq$

40% and within $\pm 5\%$ for RH < 40%.

- Pyranometers – bias is assessed by comparison of the pyranometer to a NIST-traceably certified pyranometer for one diurnal cycle and must be within $\pm 5\%$ of the reference standard for both solar radiation and UV radiation.
- Barometers – Bias of barometers used for meteorological measurements is assessed by the collocated transfer station method by comparing the site sensor to a separately calibrated audit sensor over at least 48 collocated pairs of hourly averaged barometric pressure values covering at least two diurnal cycles. Bias, or the average difference between the site sensor and audit sensor, for barometric pressure must be maintained to within ± 2.0 hPa. Bias for barometric pressure sensors used to monitor laboratory room conditions is assessed by a single point comparison of the laboratory barometer to a NIST-traceably certified barometer and must be within ± 3 hPa of the reference standard.
- Ceilometers – bias will be assessed by aiming the instrument at a target placed at a fixed known distance from the ceilometer. This may be accomplished by tilting the ceilometer and aiming it at an object at a known distance. The ceilometer reported measurement must be within ± 5 m or $\pm 1\%$ of the known distance, whichever is greater. The DAQ will not conduct the hard target test because the Millbrook PAMS Required Site lacks sufficient space for the hard target test to be completed safely. Instead of the hard target test, DAQ will follow alternate guidance that DAQ expects the EPA to provide soon and publish the EPA guidance in future revisions of this QAPP and ceilometer SOPs. DAQ currently uses an optical termination hood to zero the instrument and measure “zero” bias.

Acceptably low bias in the measurements from each of the individual meteorological instruments will be verified as described in Section B5.1.3.

Note that instrument bias will be additionally verified independently through assessments (instrument performance audits - IPAs) such as those described in Section C1.1.1. These assessments do not replace the routine bias checks described in this section.

A7.3.5 Sensitivity

Sensitivity must be established for each of the chemical measurements (speciated VOCs and carbonyls) by experimentally determining the method detection limit (MDL). The MDL for speciated VOCs and carbonyls is to be established annually by analysis of replicate standard samples prepared at a concentration approximately two- to five-fold the expected MDL. MDLs are determined for each measurement method as described in Revision 2 of the PAMS TAD in Sections 4.3 and 5.6 for speciated VOCs and carbonyls respectively; the procedure is described briefly below.

MDLs are determined according to the Method Update Rule revision of the MDL procedure described in 40 CFR Part 136 Appendix B by analyzing a series of low concentration standard

sample replicates and a series of blanks. The spiked samples and blanks are prepared and analyzed over the course of three or more different dates and an average and standard deviation are calculated from the resulting spike data and blank data. The calculated spike standard deviation is multiplied by an appropriate Student's T statistic according to the number of spiked samples to calculate an MDL for the spikes, MDL_{sp} . The blank standard deviation is multiplied by an appropriate Student's T statistic according to the number of blanks and added to the average blank value to calculate an MDL for the blanks, MDL_b . The higher of the MDL_{sp} and MDL_b is reported for the site MDL for the target analyte. MDLs will be determined annually prior to PAMS season and may not exceed those listed in Table A7-1. Note that for sites that operate year-round or extended monitoring seasons, the MDL will be determined each year and applied to the subsequent measurements.

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°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 (site operators, laboratory 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 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 quality assurance and management personnel) must minimally have read and documented attestation of compliance with the appropriate quality system 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.

Monitoring agency staff must comply with all applicable quality system requirements and will attest in their training records that they have read and will comply with pertinent quality systems documents, such as the monitoring agency PAMS QAPP and SOPs describing the duties for which they are responsible (refer to Section A9).

As PAMS monitoring is not typically conducted year-round, site operations staff should dedicate time during the non-sampling season prior to PAMS season to re-familiarize themselves with the pertinent procedures and operation of instruments and equipment. Staff will review and, as necessary, revise quality systems 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 Site Operator Training

Site operators require special training to calibrate, operate, maintain, and troubleshoot instruments and support equipment needed to make PAMS measurements. Each site operator will possess the appropriate skills and education to perform their assigned tasks. At the discretion of the monitoring agencies, instrument vendors may train site operators on how to set up, calibrate, and operate auto-GCs, carbonyls samplers, and ceilometers during installation. 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 IDOC process. The IDOC must be completed before data collection activities may begin. A member of the QA unit or management will observe the site operator performing the procedures as described in the applicable SOP as part of the approval process. Annually thereafter, and before the beginning of PAMS season, a member of the QA team or management will observe site operators performing the procedures to complete a CDOC. This can be done concurrently with the annual shakedown audit. The DAQ training forms are included in Appendix D.

Calibration, operation, and maintenance for the various instruments require expertise gained through training and practice. The operation of the auto-GC and associated equipment is complex and requires an operator familiar with the fundamentals of gas chromatography and a thorough understanding of the instrument systems to operate, maintain, and troubleshoot the auto-GC. Staff will more quickly adapt to the intricacies of the auto-GC if they have prior experience operating GC systems, generating and evaluating chromatographic data, and working with VOCs. Auto-GC operators are encouraged to spend time prior to PAMS season with the instrument and chromatography data system (CDS) to become familiar with the general operation, calibration procedures, data outputs, and data handling.

The level of training required for conducting carbonyls sampling and operating ceilometers is less rigorous than for auto-GC operation. Site operators will need to be familiar with the instrument operation including troubleshooting, software menu navigation, data retrieval, maintenance, and calibration routines. Operation of other meteorological instruments require site technicians 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 PAMS Required Site 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. EPA will conduct monthly calls and/or webinars with PAMS Required Site network monitoring agencies 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, shakedown, and troubleshooting. These training calls and/or webinars may be continued in out years following implementation based on training needs indicated by the PAMS Required Site workgroup.

A8.2 Auditor Training

Monitoring agency quality assurance staff performing assessments (described in Section C) will not need to be proficient in operating PAMS instruments; however, 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 quality system documents, minimally consisting of the monitoring agency PAMS QAPP and SOPs governing the processes to be assessed and will complete written attestation signifying compliance with the quality system (an example form is provided in Appendix D).

EPA intends to provide training materials, audit checklists, and training sessions for auditors prior to the 2021 implementation. Auditors will attend minimally one training session for PAMS auditing, subject to training session availability. 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).

EPA expects to develop checklists for conducting TSAs of the PAMS sites and ASLs. These checklists in concert with TSA training sessions (that EPA is expected to conduct) will be a resource for auditors to build confidence in conducting PAMS TSAs, IPAs, and ADQs.

A8.3 Laboratory Analysis Branch Analyst Training

Once the LAB staff member 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 PAMS program 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 four LCSs 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 LCS meets spike recovery acceptance criteria (Formaldehyde recovery within 80 to 120%, all other target analytes recovery within 70 to 130%; precision with LCS as $RSD \leq 20\%$). 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 in one of three ways:

1. Achieving spike recovery within the method specification (Formaldehyde recovery within 80 to 120%, all other target analytes recovery within 70 to 130%) for analysis of an LCS (spiked cartridge) whose concentration of target analytes is blind to the analyst;
2. Acceptable performance on all target analytes for a PT sample;
3. Achieving spike recovery within the method specification (Formaldehyde recovery within 80 to 120%, all other target analytes recovery within 70 to 130% and the coefficient of variation (CV) of an entire calendar quarter's worth of LCS/LCSD pairs is $\leq 15\%$ for all target analytes.

Either the level 2 or level 3 reviewer of carbonyl sampling and analysis data or a member of the QAU will approve the analyst CDOC by approval signature. Laboratory management will approve the analyst's competency through the interim and final Valuing Individual Performance review process that occurs each year in January and July.

Similarly, the CDOC process for the Markes-Agilent AutoGC can be completed in one of two ways as detailed below:

1. Analysis of a blind sample prepared in a Silco canister or equivalent via DAQ SOP-03-006.2 by another LAB staff member and achieving results within the $\pm 30\%$ recovery window for all target compounds.
2. Acceptable performance for all target compounds on a PT sample.

Either the level 2 or level 3 reviewer of carbonyl sampling and analysis data or a member of the QAU will approve the analyst CDOC by approval signature. Laboratory management will approve the analyst's competency through the interim and final Valuing Individual Performance review process that occurs each year in January and July.

A9 Documentation and Records

The monitoring agency will establish and maintain document control procedures for the timely preparation, review, revision, approval, issuance, use, retirement, and archival of documents and records. The categories and types of records and documents that are applicable to the PAMS Required Site Program are presented in Table A9-1.

DAQ document management practices and procedures are described in more detail in SOPs DAQ-14-001 SOP for Preparing SOPs and DAQ-14-002.5 SOP and QAPP Tracking Database and DAQ-14-003 Records Retention and Archival Policies.

Documentation and records generated and maintained include:

1. Monitoring agency PAMS QAPP
2. PAMS SOPs
3. Sample collection records in electronic and written format
4. Logbooks and data sheets in electronic and written format
5. Training records
6. Instrument and equipment calibration information
7. Quality assurance documentation (for example, outcomes of TSAs, IPAs, and ADQs; and corrective action plans and reports) in electronic and written format
8. Documentation that supports data review, validation, and certification activities.

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. The monitoring agency will have an SOP, combination of SOPs, or similar controlled document that describe how to execute routine procedures, including, but not limited to, instrument operation, maintenance, sample collection, and analysis for each of the PAMS 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 nonconformances. Where activities involve a potential physical hazard, safety precautions will be addressed.

Table A9-1. Pertinent Documents and Records for PAMS Required Site(s)

| 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 re-evaluation |

Table A9-1. Pertinent Documents and Records for PAMS Required Site(s)

| Categories | Record/Document Types |
|---|--|
| Environmental Data Operations (Field and Lab) | QA Project Plan(s) (QAPPs) Standard operating procedures (SOPs) 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 Corrective action reports and supporting documentation Network reviews |

The monitoring agency 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 quality system 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 PAMS Required Site Network matures, the national QS documents will require revision to accommodate lessons learned and best practices. Revisions to the national QS documents will be handled in a manner that ensures only current approved procedures are available. To ensure that PAMS Required Site monitoring agency and EPA Regional 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 PAMS Required Site stakeholders as described in Section A1.2 to announce the changes and indicate when the changes are effective. When revisions to the national PAMS Required Site guidance and QS documents are announced, monitoring agencies will revise their QS documents accordingly, where applicable.

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 PAMS program SOPs. Please see Appendix F in this document for a complete list of DAQ PAMS program SOPs. The control of these documents is described in more detail in the document management SOPs referenced in Section A9 above. The SOP DAQ-14-002.5 SOP and QAPP Tracking Database describes the DAQ QAPP and SOP document control program.

A9.1.1 Paper Records

Documentation requirements for the PAMS Required Site 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 an auto-GC sample collection and analysis), 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.⁹ 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 (carbonyls samples) will be accompanied by a chain-of-custody (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 monitoring agency or laboratory document control system. Completed COC forms (or a copy thereof) will be retained by the laboratory as part of the official analytical record. DAQ COC procedures are covered in SOPs DAQ-09-002.2 ATEC 8000 PAMS Sequential Carbonyl Sampler Operator Responsibilities and DAQ-03-004.2 Thermo Ultimate 3000 UHPLC/UV/MS UAT and PAMS Carbonyl Analysis Operator Responsibilities.

COC procedures and requirements are detailed in Section B3.1.1. The DAQ COC form (specific to carbonyls samples) is included in Appendix B.

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 hard copy forms, in electronic spreadsheets, electronic pdfs, in data management software systems, or by another appropriate means as defined in the monitoring agency-controlled document (e.g., QMP, QAPP, or SOP) governing the activity. Documentation methods include 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 200.333 and further clarified in Section 5.0 of the EPA QA Handbook.¹⁰ 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 records for a minimum of four complete calendar years from the date of collection. However, if any litigation, claim, negotiation, audit, or other action involving the records has been started before the expiration of

the four-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 four calendar-year period, whichever is later.

PAMS Required Site 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, 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 PAMS site, or Envidas, the RCO, or Envista ARM, and on network servers in the LAB, ECB, RRO and RCO. The DIT backs up data stored in Envista ARM as well as records on the network server in the LAB, ECB, RRO 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 PAMS measurement methods are continuous and do not involve the collection of samples on to discrete media except for carbonyls. Therefore, sample retention applies only to carbonyls samples. Once carbonyls 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 such as "QX" or other qualifier flag when reported to AQS. Extracts will not be archived and will be disposed properly according to hazardous waste procedures established by the laboratory.

B. DATA GENERATION AND ACQUISITION

B1 Sampling Process Design (Experimental Design)

The objective of the PAMS experimental design is to provide an air quality database for use in ozone prediction model evaluation and refinement. A secondary objective is to characterize ozone precursor concentrations and temporal patterns and associated meteorological conditions to assist state and local air pollution control agencies in evaluating, tracking the progress of, and if necessary, refining control strategies for attaining the ozone NAAQS. The rationale and description for the sampling design of the approximately 40 Required PAMS sites can be found in Section 1 of the PAMS Required Site Quality Assurance Implementation Plan (QAIP) available at the following link on AMTIC:

<https://www3.epa.gov/ttnamti1/pamsguidance.html>

The QAIP describes procedures approved by EPA OAQPS and Regions for applying for waivers. Waivers, if applicable to the monitoring agency, will be described in the monitoring agency QAPP and approved by the Region. An example monitoring agency IP including an example waiver is included in Appendix E. See Volume 1 of the DAQ network plan at the following link for the DAQ IP and for potential siting issues at the Millbrook PAMS Required site:

<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 PAMS Required Sites. This QAPP describes the QS for those parameters in bold:

- **carbonyls**
- **meteorological parameters:**
 - **ambient temperature**
 - **vector-averaged wind direction**
 - **vector-averaged wind speed**
 - **atmospheric pressure**
 - **relative humidity**
 - **precipitation**
 - **mixing layer height**
 - **solar radiation**
 - **UV radiation**
- **speciated VOCs**
- true NO₂ and NO/NO_y
- ozone

True NO₂, NO/NO_y, and ozone are described simply for convenience; however, the QS for these criteria pollutant gases is covered under **the DAQ NCore QAPP DAQ-01-001**, which details gaseous criteria pollutant monitoring for the NCore network. The submittal and approval dates of the appropriate QAPP can be found in AQS. The approved QAPPs are to be maintained by the monitoring agency and a copy is to be kept on file at the EPA Regional office.

B1.1 Sample Collection Schedule

Sampling at PAMS Required Sites will be conducted June 1 through August 31 of each year, at a minimum **although DAQ plans to operate from March 1 through October 31 for speciated VOCs (AutoGC)**. Monitoring agencies may elect to extend monitoring for PAMS parameters to begin before June 1 and end later than August 31 and will detail the monitoring period in Section A7.3.1.1 Parameters will be measured according to the schedule shown below in Table B1-1.

Continuous instrument measurements (meteorology, speciated VOCs, O₃, true NO₂, and NO/NO_y) 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. However, for the continuous chemical measurement methods, automated nightly and weekly QC checks will be performed during the overnight hours and should rotate between specific times to ensure that there will be a representative ambient measurement for each of the daily 24 one-hour periods across all days of the week. For example, the nightly auto-GC CCV and blank require two hours to perform. If always performed from 01:00 to 03:00, there will not be representative ambient data for that two-hour period. An example rotation schedule would start the QC checks on Monday at 23:00, Tuesday at 00:00, Wednesday at 01:00 and so on. An example schedule is described in Section 4.6 of Revision 2 of the PAMS TAD and in the national auto-GC SOPs.

Table B1-1. PAMS Required Site Sampling Schedule by Parameter

| Parameter | Sampling Duration and Frequency | Value Reported |
|--|---|----------------|
| Ozone ^a | Continuously, daily | Hourly average |
| True NO ₂ ^a | Continuously, daily | Hourly average |
| NO/NO _y ^a | Continuously, daily | Hourly average |
| Speciated VOCs by auto-GC | Hourly 40-minute sample, daily | Hourly average |
| Carbonyls (TO-11A) | 3 sequential 8-hour samples on a 1-in-3 days schedule | 8-hour average |
| Formaldehyde (Continuous) ^b | Continuously, daily | Hourly average |
| Meteorological Parameters | Continuously, daily | Hourly average |

^a Monitoring for ozone, true NO₂, and NO/NO_y are not covered in this QAPP. Please refer to **the DAQ NCore QAPP# DAQ-01-001** for associated requirements.

^b Continuous formaldehyde monitoring with hourly average concentration reporting can be substituted for the carbonyl sequential collection of three 8-hour samples every 3rd day. Note that several manufacturers were developing continuous formaldehyde monitoring instruments at the time of publication of this QAPP.

The time reported for the sample collection is to be the local standard time 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 beginning of the following

hour. For example, the hourly average represented for 9:00 AM covers 09:00:00 through 09:59:59.

B1.1.1 Carbonyls by TO-11A¹

Carbonyls samples will be collected as three sequential 8-hour samples every third day per the national sampling calendar available at the following link on AMTIC:

<https://www.epa.gov/amtic/sampling-schedule-calendar>

These primary sequential carbonyls samples will be collected according to the schedule shown below in Table B1-2:

Table B1-2. Carbonyls Sampling Schedule

| Sequential Sample | Collection Start Time (local standard time) | Collection End Time (local standard time) |
|-------------------|--|--|
| A | 04:00 | 12:00 (noon) |
| B | 12:00 (noon) | 20:00 |
| C | 20:00 | 04:00 (the following day) |

This schedule aims to characterize the morning commute in sample A, the evening commute in sample B, and most of the overnight period in sample C, and will allow for the shifting of the commuting periods due to DST at sites where DST is observed. Each 8-hour sample will be collected for 8 hours ± 20 minutes and must begin and end within fifteen minutes of the designated sampling start or stop time.

In cases where samples and/or sample results are invalidated, a replacement primary carbonyls sample set (three 8-hour samples) will be collected as described per the make-up policy in Section A7.3.2. Carbonyl samples are to be invalidated when a sample volume cannot be calculated or when the sample duration cannot be determined or when lab errors do not allow the extracted sample to be analyzed. All other circumstances will be qualified with the appropriate descriptor.

Target carbonyls analytes are those identified in bold and noted as “carbonyls” in Table B2-2. All sites will measure and report formaldehyde and acetaldehyde (the two priority carbonyl compounds) and are encouraged to analyze for benzaldehyde and acetone (optional compounds).

¹ For the purposes of this QAPP, it is assumed that PAMS Required Sites will perform time-integrated sampling for the measurement of carbonyls and will not perform near-real time continuous monitoring. Instruments capable of the continuous measurement are not yet commercially available for routine monitoring. Further, QA criteria have not been established for these instruments for use at PAMS Required Sites. EPA will develop QA/QC for continuous formaldehyde monitors once such are available and have demonstrated appropriate comparability with Compendium Method TO-11A for formaldehyde measurements.

Note that the only exception to this is for sites operating continuous formaldehyde monitors reporting hourly averages; in such instances only formaldehyde must be measured.

B1.1.2 Speciated VOCs by Auto-GC

To ensure that 75% of each sample is collected during the scheduled hour, at least 30 minutes of the 40-minute sampling period will occur during the hour. Sample collection should commence at the beginning of the hour but must commence no earlier than 10 minutes before the beginning of the hour and no later than 30 minutes after the beginning of the hour. For example, for sample collection of the 10:00 hour, sample collection must commence between 09:50 and 10:30 for the sample to be valid for the 10:00 hour. Sample collection beginning between 30 minutes and 50 minutes after the hour, between 10:30 and 10:50 in this example, must be invalidated.

Target speciated VOCs analytes are listed in Table B2-2 and are classified as olefin, aromatic, paraffin, halogenated, monoterpene olefin, alkyne, or alcohol. The site will measure and report all compounds listed as a priority compounds as well as total non-methane organic carbon (TNMOC). Sites are encouraged to analyze and report the compounds listed as optional. **DAQ intends to report all required and optional compounds that meet the data quality objectives described in this QAPP unless otherwise designated in Table B2-2.**

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 the chemical measurement parameters (carbonyls and speciated VOCs) 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 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 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 activities 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, speciated VOCs, meteorology, and carbonyls laboratory analysis, respectively.

DAQ and the LAB will track QC sample performance with QC charting. Inspection of QC charts permits the identification of trends or drifts in performance which can be addressed before an

out-of-control condition occurs (before blanks are unacceptably high, before positive control recoveries are unacceptably low, etc.).

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 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 a list of makes and models for the measurement parameters listed in Section B1.

Table B2-1. List of Makes and Models of Equipment Used for the Measurement of PAMS Parameters

| Parameter | Instrument Make and Model | AQS Method Code |
|----------------------------|--|-----------------|
| Speciated VOCs by auto-GC | Agilent 7890B dual FID Auto GC/Markes CIA-Advantage KORI-XR Water Management Device and Unity Thermal Desorber | 232 |
| Carbonyl Sample Collection | ATEC 8000 Multi-Channel Sampler | 202 |
| Carbonyl Sample Analysis | Thermo Ultimate 3000 UHPLC with UV and MS detectors | |
| Mixing Height | Vaisala CL51 Ceilometer | 128 |
| Vector Wind Speed | MetOne AIO2 | 069 |
| Wind Direction, Resultant | MetOne AIO2 | 069 |
| Ambient Temperature | MetOne AIO2 | 069 |
| Relative Humidity | MetOne AIO2 | 069 |
| UV-Radiation | Eppley CUV-5 Ultra-Violet (UV) Radiometer | 011 |
| Solar Radiation | MetOne Li-200R pyranometer | 011 |
| Barometric Pressure | MetOne AIO2 | 069 |
| Precipitation | MetOne 370D Tipping Bucket Rain Gauge | 011 |

NOTE: This QAPP will refer to national SOPs developed for the PAMS Required Site Network. Monitoring agencies will follow these reference SOPs and/or specify and submit the SOP(s) they plan to use for the program during the QAPP approval process. DAQ and the LAB will follow the SOPs listed in Appendix F. DAQ and the LAB are still developing some of these SOPs and will submit the SOPs to the EPA as they are completed and approved by management.

B2.1 Chemical Parameters

This section describes ambient air sample field collection methods and automated analyzers/methods used for conducting measurements of chemical parameters in the field (i.e., in situ). These parameters are listed below in Table B2-2. Three types of chemical parameters are listed in the table: criteria pollutant gases (*italicized*), carbonyls (**bolded**), and speciated VOCs to be measured by auto-GC (remaining unitalicized and unbolded). 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, chromatographic grade stainless steel, or polytetrafluoroethylene (PTFE) or perfluoroalkoxy (PFA) Teflon[®]. Additional guidance for inlet probe siting is included in Section 3.3.1.2 of Revision 2 of the PAMS TAD. Note that Teflon[®] is not recommended for speciated VOCs inlet pathways.

Table B2-2. Priority and Optional PAMS Required Site Chemical Parameters

| Priority Chemical Parameters (Required) | AQS Parameter Code | Compound Class | Optional Chemical Parameters | AQS Parameter Code | Compound Class |
|---|--------------------|-----------------|------------------------------|--------------------|-----------------|
| 1,2,3-trimethylbenzene | 45225 | aromatic | 1,3,5-trimethylbenzene | 45207 | aromatic |
| 1,2,4-trimethylbenzene | 45208 | aromatic | 1-pentene | 43224 | olefin |
| 1-butene | 43280 | olefin | 2,2-dimethylbutane | 43244 | paraffin |
| 2,2,4-trimethylpentane | 43250 | paraffin | 2,3,4-trimethylpentane | 43252 | paraffin |
| acetaldehyde | 43503 | carbonyl | 2,3-dimethylbutane | 43284 | paraffin |
| benzene | 45201 | aromatic | 2,3-dimethylpentane | 43291 | paraffin |
| cis-2-butene | 43217 | olefin | 2,4-dimethylpentane | 43247 | paraffin |
| ethane | 43202 | paraffin | 2-methylheptane | 43960 | paraffin |
| ethylbenzene | 45203 | aromatic | 2-methylhexane | 43263 | paraffin |
| ethylene | 43203 | olefin | 2-methylpentane | 43285 | paraffin |
| formaldehyde | 43502 | carbonyl | 3-methylheptane | 43253 | paraffin |
| isobutane | 43214 | paraffin | 3-methylhexane | 43249 | paraffin |
| isopentane | 43221 | paraffin | 3-methylpentane | 43230 | paraffin |
| isoprene | 43243 | olefin | acetone₁ | 43551 | carbonyl |
| m&p-xylenes | 45109 | aromatic | acetylene | 43206 | alkyne |
| m-ethyltoluene | 45212 | aromatic | cis-2-pentene | 43227 | olefin |
| n-butane | 43212 | paraffin | cyclohexane | 43248 | paraffin |
| n-hexane | 43231 | paraffin | cyclopentane | 43242 | paraffin |
| n-pentane | 43220 | paraffin | isopropylbenzene | 45210 | aromatic |
| o-ethyltoluene | 45211 | aromatic | m-diethylbenzene | 45218 | aromatic |
| o-xylene | 45204 | aromatic | methylcyclohexane | 43261 | paraffin |
| p-ethyltoluene | 45213 | aromatic | methylcyclopentane | 43262 | paraffin |
| propane | 43204 | paraffin | n-decane | 43238 | paraffin |
| propylene | 43205 | olefin | n-heptane | 43232 | paraffin |

Table B2-2. Priority and Optional PAMS Required Site Chemical Parameters

| Priority Chemical Parameters (Required) | AQS Parameter Code | Compound Class | Optional Chemical Parameters | AQS Parameter Code | Compound Class |
|---|--------------------|-------------------------|-----------------------------------|--------------------|--------------------|
| styrene | 45220 | aromatic | n-nonane | 43235 | paraffin |
| toluene | 45202 | aromatic | n-octane | 43233 | paraffin |
| trans-2-butene | 43216 | olefin | n-propylbenzene | 45209 | aromatic |
| ozone | 44201 | criteria pollutant gas | n-undecane | 43954 | paraffin |
| true NO ₂ | 42602 | criteria pollutant gas | p-diethylbenzene | 45219 | aromatic |
| total non-methane organic carbon | 43102 | total VOCs, non-methane | trans-2-pentene | 43226 | olefin |
| | | | α-pinene ¹ | 43256 | monoterpene olefin |
| 1 – Not monitored and reported | | | β-pinene ¹ | 43257 | monoterpene olefin |
| | | | 1,3 butadiene ¹ | 43218 | olefin |
| | | | benzaldehyde | 45501 | carbonyl |
| | | | carbon tetrachloride ¹ | 43804 | halogenated |
| | | | ethanol ¹ | 43302 | alcohol |
| | | | tetrachloroethylene ¹ | 43817 | halogenated |

Sample introduction and collection guidance is included in Revision 2 of the PAMS TAD, Sections 4.2.2.1 and 5.7.2 for speciated VOCs and carbonyls, respectively. The Auto-GC and Carbonyl sampling inlet probe at the Millbrook PAMS site are dedicated to the instrument and made of chromatographic grade stainless steel with an outer diameter (OD) of 1/8 inch and 1/4 inch, respectively. The length of the inlet probes will not exceed the maximum length allowable to meet the 20 second residence time limit. Maximum length for the ATEC used for carbonyl sample collection is 67 feet, actual installed probe is approximately 40 feet. The Auto-GC inlet is composed of an inverted conical rain guard and 17 inches of 1/4-inch OD (0.21-inch inner diameter or ID) chromatographic grade stainless steel tubing coupled to a 15 micrometer (µm) particulate filter and 207 inches of 1/8-inch OD (0.085-inch ID) chromatographic grade stainless-steel tubing that is directly interfaced with the AutoGC. The total length of the inlet is 18.67 feet and with a purge rate of 100 cubic centimeters per minute (cc/min) for 2 minutes, the equipment meets the 20 second residence time requirement for PAMS sampling operations.

B2.1.1 Carbonyls by TO-11A

Sampling methods for the collection of PAMS carbonyl compounds are described in SOP# DAQ-09-002.2 ATEC 8000 Carbonyl Sampler Operator Responsibilities. The analysis of PAMS 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 bold 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 PAMS program involves collecting three consecutive 8-hour samples on a 1-in-3-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 completion of the last of the three sequential samples. Samples must be stored and transported cold ($\leq 4^{\circ}\text{C}$) and protected from light.

B2.1.2 Speciated VOCs by Auto-GC

Auto-GC systems will be used for the measurement of speciated VOCs. The auto-GC collects and preconcentrates VOCs from the sampled atmosphere and subsequently separates the VOCs for detection via a pair of flame ionization detectors (FIDs). Procedures for the installation, setup, calibration, operation, maintenance, level 1 and level 2 data review, and shut-down of the auto-GC are described in the SOP# DAQ-09-001.2 Agilent/Markes Auto-GC Analysis Operator Responsibilities.

Additional details on auto-GC sampling methods, including technical guidance regarding moisture management, are provided in Section 4.2.3 of Revision 2 of the PAMS TAD.

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:

https://www.epa.gov/sites/production/files/2020-10/documents/volume_iv_meteorological_measurements.pdf

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-07-001.2 Vaisala Ceilometer Mixing Height Sensor Operator Responsibilities,
- DAQ-07-003.1 MetOne AIO2 All-in-One Met Sensor ECB Responsibilities,
- DAQ-07-003.2 MetOne AIO2 All-in-One Met Sensor Operator Responsibilities,
- DAQ-07-004.1 MetOne 370D Tipping Bucket Rain Gauge ECB Responsibilities,
- DAQ-07-004.2 MetOne 370D Tipping Bucket Rain Gauge Operator Responsibilities,
- DAQ-07-007.1 Solar Radiation Sensor ECB Responsibilities,
- DAQ-07-007.2 Solar Radiation Sensor Operator Responsibilities,
- DAQ-07-009.1 Ultraviolet Radiation Sensor ECB Responsibilities,
- DAQ-07-009.2 Eppley CUV-5 Ultra-Violet (UV) Sensor Operator Responsibilities, and
- DAQ-15-006.5 Data Validation Standard Operating Procedures For Continuous Gaseous and Meteorological Monitors.

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 | 17 |
| Relative Humidity | 62201 | hourly average | 1 | % relative humidity | 19 |
| Barometric Pressure | 64101 | hourly average | 1 | millibar (hPa) | 16 |
| Wind Speed | 61103 | hourly average | 1 | m/s | 11 |
| Wind Direction | 61104 | hourly average | 1 | degrees compass | 14 |
| Solar Radiation | 63301 | hourly average | 1 | Watt/m ² | 79 |
| Ultraviolet Radiation | 63302 | hourly average | 1 | Watt/m ² | 79 |
| Precipitation | 65102 | hourly average | 1 | mm | 29 |
| Mixing Layer Height | 61301 | hourly average | 1 | m | 58 |

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

B3 Sample Handling and Custody

Sample handling procedures apply to chemical parameter measurements and must be consistently followed to ensure reported concentrations meet the MQOs. Chemical analysis methods for the PAMS Required Site measurements are continuous with the exception of carbonyls by TO-11A; therefore, custody requirements only apply to carbonyls sample collection, handling, and analysis.

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 considered to be in custody if it is in one's actual physical possession or stored in a secured area restricted to authorized personnel. Carbonyl sample handling and custody procedures are described in more detail in SOP# DAQ-09-002.2 ATEC 8000 PAMS Sequential 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 Carbonyls by TO-11A

DNPH cartridges are shipped at ambient temperature by the manufacturer Waters. Upon receipt by the Reedy Creek 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 certificate of analysis (COA) of background formaldehyde, acetaldehyde, and acetone contamination in µg/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], field blank, or trip blank).
- Cartridge storage areas will be free of carbonyls. Climate-controlled storage units will not 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 ($> 4^{\circ}\text{C}$).

B3.1.1 Chain of Custody

Blank cartridge media originates at the Reedy Creek Laboratory. Each cartridge, whether an ambient sample or field QC sample (such as a trip blank or field blank) will be listed on the COC form documenting the transfer of the sample cartridges from their origin, through 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 B):

- 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)

All the above parameters are covered using two forms: The Carbonyl Cartridge Chain of Custody Form (Appendix B), and the Carbonyl Cartridge Sample Information Form (Appendix C).

Note that the convention for recording custody information for the samples can include recording transfers and storage on the field collection data sheet; however, it may be more convenient to include a separate COC form for each shipment that encompasses all samples in the shipment. A separate dedicated COC form reduces the number of instances where staff transferring cartridge custody are required to sign (sample custodians need only sign one or two COC forms rather than multiple field collection forms).

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 to be employed for the PAMS Required Site Network covered by this QAPP include methods for the determination of carbonyls and speciated VOCs.

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. This method is described in the national SOPs for the collection and analysis of carbonyls for the PAMS Required Site Network. 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, necessary QC procedures, and level 1 and level 2 data review. 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 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. Alternative detectors (such as time-of-flight [TOF]) and alternative

wavelengths (e.g., 365 nm) may be employed, if method performance criteria (listed in Table B5-4) are met.

B4.2 Speciated VOCs by Auto-GC

Auto-GC systems will be used for the analysis of VOCs. The auto-GC systems collect and preconcentrate VOCs from the ambient atmosphere and subsequently separate the VOCs for detection by FID. DAQ will follow SOP # DAQ-09-001.2 which describes procedures for the installation, setup, calibration, operation, level 1 and level 2 data review, and shutdown of the Agilent/Markes Auto-GC/FID. Analysis of speciated VOCs by auto-GC is considered a continuous method, therefore there are no discrete samples collected on media which may be retained.

Additional details on auto-GC sampling methods, including technical guidance regarding moisture management, are provided in Section 4.2.3 of Revision 2 of the PAMS TAD.

B5 Quality Control

QC is the overall system of technical activities that measures the performance of an ongoing process against established standards to verify that such performance meets the stated requirements established by the data user or stakeholder. In the case of the PAMS Required Site Network, QC activities ensure that the quality objectives and criteria for measurement data, as discussed in Section A7, are maintained so that the PAMS Required Site Program 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 nonconformances occur.

B5.1 Quality Control for Field Activities

QC for field activities relate to carbonyls sample collection, speciated VOC analysis, 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 the carbonyls sample collection SOP, field blanks 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 nonconformances are observed. When clock setting deviations are noted, the clock should be reset, and the offset should be applied to the sample start and stop times. 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 and subtract seven minutes from the sample start and stop times recorded 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 field blank, trip blank, or collocated or duplicate sampling criteria failures will not be apparent until analysis results are completed. Root-cause analysis will be performed as soon as possible for field QC sample nonconformances, 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 (zero air challenge) | Collection of an 8-hour sample of ambient air scrubbed through an activated charcoal filter and humidified to investigate contamination contributed by the sampler | Prior to the beginning of every PAMS season following instrument maintenance (ozone denuder recharge/ replacement, particulate filter change, etc.) | All target compounds < 0.20 µg/cartridge greater than co-collected reference sample for acetaldehyde and formaldehyde | Repeat bias challenge following further cleaning which could include flushing with humidified zero air, replacement of flow path components, etc. |
| Mass Flow Controller Calibration | Establishment of the MFC slope and intercept by comparison to a flow transfer standard | At the beginning of each PAMS season and when flow verification checks fail criteria | Flow verification immediately following calibration must be within ±10% of flow transfer standard | Recalibrate flow controller. If problem persists, investigate for leaks, blockage in flow path, etc. May require replacement of MFC or other instrument parts. |
| Mass Flow Controller Calibration Verification | Verify sampling flow of each channel at the sampling flow setting | Minimally every 30 days during PAMS season. | Within ±10% of flow transfer standard | Recalibrate flow controller and verify within proper specification. Qualify all previous samples since the last acceptable flow check or calibration as “W” and “LK” (reported concentration biased high for flow verification results biased low) or “LL” (reported concentration biased low for flow verification results biased high) as appropriate in AQS. |

Table B5-1. Carbonyls Field Quality Control Parameters

| QC Parameter | Detail | Required Frequency | Acceptance Criteria | Recommended Corrective Action |
|------------------------------|---|---|--|--|
| Clock Accuracy | Verify clock accuracy against a known accurate time standard | Each sampling event | Within ± 5 minutes of the true reference time | Reset clock to correct time. Apply offset to sample start/stop times. |
| Field Blank | Blank cartridge installed in a sampling channel for five to ten minutes | Twice monthly (approximately every 14 days) during PAMS season | 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. Qualify associated field collected samples as "FB" in AQS. Associated samples are those in the shipment with the field blank and since the most recent acceptable field blank. |
| Trip Blank | blank cartridge accompanying collected samples to and from the field site | Used for corrective action purposes only when field blank 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. Qualify associated field collected samples as "TB" in AQS. Associated samples are those in the shipment with the trip blank. |
| 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 3 rd sequential sample (whose sampling is nominally completed at 4:00 a.m.) | Qualify associated data as "HT" in AQS. |
| Duplicate Sample Collection | collection of a separate cartridge through a common inlet probe concurrently with a primary 8-hour sample | Optional – 10% of primary sampling events – DAQ will not be collecting duplicate samples | Relative percent difference $\leq 20\%$ for compounds ≥ 0.5 $\mu\text{g}/\text{cartridge}$ | Qualify both samples as estimated "QX" in AQS. |
| Collocated Sample Collection | collection of a separate cartridge through an independent inlet probe concurrently with a primary 8-hour sample | Optional – 10% of primary sampling events - DAQ will not be collecting collocated samples | Relative percent difference $\leq 20\%$ for compounds ≥ 0.5 $\mu\text{g}/\text{cartridge}$ | Qualify both samples as estimated "QX" in AQS. |

B5.1.2 Quality Control for Speciated VOCs Collection and Analysis

QC processes for speciated VOC collection and analysis, as described in Table B5-2 and replicated in the speciated VOCs measurement SOP, are designed to demonstrate that the instrument is sufficiently free of contamination and interferences; to establish the carbon response calibration of

the two FIDs within the instrument; to independently verify the calibration for compounds representing the molecular weight range of the PAMS priority VOCs; and to confirm that the instrument's performance is acceptable on an ongoing basis. System performance QC checks involve verifying the bias criteria are met for representative compounds across the molecular weight range and ensuring that instrument contamination and carryover are sufficiently low. PAMS VOCs in ambient air are typically measured at concentrations less than 2 ppbC, therefore, it is important for the calibration to include a low concentration level (approximately 1 ppbC) to properly characterize the instrument response at such low concentration. The next highest concentration will be approximately 5 ppbC. While approximately 25 ppbC should be sufficient to capture the majority of measured PAMS VOCs, agencies have latitude to select the concentration of the high calibration standard. While FID response has been established to be linear over large concentration ranges, instrument preconcentration capture and desorption of the target compounds do not behave linearly at low and high concentrations, particularly for very volatile (e.g., ethane, ethylene) compounds and those with higher boiling points (1,2,4-trimethylbenzene, dodecane). Nonlinear performance may be more pronounced when trap materials have aged. For this reason, the daily CCV will include a suite of compounds representing the molecular weight range (C₂ to C₁₀). Several analytes are known to be problematic (recovered less than 70% of the theoretical concentration) with the carbon-response calibration method. Acetylene, alpha-pinene, and beta-pinene are known to exhibit degradation in standard cylinders and/or suffer poor preconcentration performance.

Table B5-2. Speciated VOCs Field Quality Control Parameters

| QC Parameter | Description | Required Frequency | Acceptance Criteria | Recommended Corrective Action |
|----------------------------|--|--|---|---|
| Initial calibration (ICAL) | Multi-point calibration of the auto-GC with minimally a representative hydrocarbon for each GC column-FID combination (e.g. propane and benzene). Minimum of three concentrations covering approximately 1.0 to 25 ppbC. | Initially at the beginning of PAMS season, after maintenance (such that response is impacted), following failing calibration checks, and at the conclusion of monitoring each PAMS season. Agencies may analyze the primary calibration standard weekly as an additional check to monitor system performance – not required. | Linear regression with non-zero y-intercept must show r^2 of ≥ 0.99 . Also $ \text{intercept/slope} \leq 0.5$ ppbC or $\leq \text{MDL}$, whichever is lower. Each standard level evaluated against the calibration curve must be within 20% of the nominal concentration. If all of the above criteria (r^2 , $ \text{y-intercept/slope} $, RF RSD, and standard $\pm 20\%$ of nominal) are met, the calibration may utilize the average RF. Measurements exceeding the calibration range will be qualified as "EH". | Prepare new calibration if possible . It may be necessary to investigate for system contamination or interferences resulting in suppression or enhancement of analytes. System leaks and trap degradation may impede a proper calibration as well as carryover from samples or standards. Improperly conditioned traps may contribute chromatographic artifacts. If preparing a new calibration curve is not possible, minimally qualify as "QX" in AQS for affected compounds until a new ICAL curve is generated and passes criteria. Invalidation as "AT" may be required at analyst discretion if compound recovery is exceptionally high or low or if multiple ICAL curve acceptance criteria are not met. |

Table B5-2. Speciated VOCs Field Quality Control Parameters

| QC Parameter | Description | Required Frequency | Acceptance Criteria | Recommended Corrective Action |
|---|--|--|--|--|
| System Blank (SB) | Analysis of humidified zero air to ensure the system is sufficiently clean for continued analysis. | Prior to ICAL, and every 24 ± 4 hours of operation following or preceding the CCV (preference is to follow the CCV to ensure absence of carryover before analyzing ambient samples). | All target VOCs must be ≤ the determined MDL or 0.5 ppbC, whichever is lower. | Analyze another blank, if possible, to investigate potential carryover from high concentration sample. Investigate system for contamination. Unless technical justification is provided to explain nonconformance, qualify as “LB” in AQS for affected compounds since the last passing SB. |
| Second Source Calibration Verification (SSCV) | Analysis of a known standard prepared from a stock gas that is at least a different lot number than the lot number of stock gas used for preparing the ICAL standards. | Immediately following ICAL and minimally weekly thereafter – The SSCV may also serve as the retention time standard | All target VOCs must recover within ±30% of the expected nominal concentration | Analysis cannot commence if propane (or butane) or benzene fail in the SSCV immediately following the ICAL. Investigate for discrepancy between ICAL and SSCV. Investigate chromatogram for retention time shifts which may result in peak misidentification. Investigate for instrument contamination resulting in coeluting peaks. Investigate for system leaks or trap malfunction resulting in low recovery. Unless technical justification is provided to explain nonconformance, minimally qualify as “QX” in AQS for affected compounds since the most recent passing SSCV. Invalidation as “ST” may be required at analyst discretion if compound recovery is exceptionally high or low. |
| Clock Accuracy | Verify clock accuracy against a known accurate time standard | Weekly, recommended to check each site visit. | Within ±5 minutes of the time standard | Ensure adjusted sampling start times are no earlier than 10 minutes before the hour and no later than 30 minutes after the hour. Invalidate compounds detected in sample hours that do not conform. Apply null code “AG”. |

Table B5-2. Speciated VOCs Field Quality Control Parameters

| QC Parameter | Description | Required Frequency | Acceptance Criteria | Recommended Corrective Action |
|---|--|---------------------------------|---|--|
| Continuing Calibration Verification (CCV) | Analysis of a known standard containing compounds representing the molecular weight range & prepared within the calibration curve to demonstrate the instrument calibration remains within tolerance. Concentration of CCV should be approximately 2-5 ppbC for target analytes. | Every 24 ± 4 hours of operation | All target VOCs must recover within ±30% of the expected nominal concentration. | Investigate chromatogram for retention time shifts which may result in peak misidentification. Investigate for instrument contamination resulting in coeluting peaks. Investigate for system leaks or trap malfunction resulting in low recovery. Unless technical justification is provided to explain nonconformance, qualify as “QX” in AQS for affected compounds since the most recent passing CCV. Invalidation as “ST” may be required at analyst discretion if compound recovery is exceptionally high or low. |
| Retention Time Standard (RTS) | Separate analysis of the SSCV standard mix | Minimally weekly | All target VOCs must be within the established retention time windows. | Review previous week’s ambient and QC check sample data to evaluate events resulting in retention time shift. May require reassignment or adjustment of retention time windows and reprocessing of data collected since the most recent CCV or RTS. Unless technical justification is provided to explain nonconformance, associated ambient sample data will be invalidated as “BH” for compounds whose identities cannot be confirmed. |
| Precision check | Replicate analysis of the CCV or replicate analysis of the SSCV to evaluate the reproducibility of the analysis – replicates are analyzed sequentially (back to back) | Weekly | Absolute relative percent difference for each target VOC must be ≤ 25% | Investigate system for carryover, contamination, leaks, or suppression, as indicated by trends in compound behavior. Qualify ambient sample data for affected compounds since the last passing precision check as “QX” in AQS. |

Styrene is known to show poor correlation with the certified concentration in standard cylinders. Instrument operators need not take stringent corrective action if QC samples exhibit low

recovery for these four compounds. The agency will document the low recovery of these compounds and will qualify the associated ambient concentration data when reporting to AQS.

B5.1.3 Quality Control for Meteorology

Meteorological instruments require minimal intervention and maintenance once configured and calibrated, therefore it is anticipated that meteorology parameters will be measured at each PAMS Required Site year-round. QC procedures for meteorology measurements consist of the initial calibration and an annual calibration check. These calibration checks and the associated acceptance criteria are shown in Table B5-3, which are replicated in the appropriate SLT monitoring agency SOPs. For all measurements, if the indicated acceptance criteria are exceeded, the instrument calibration will be adjusted to match the reference standard.

Table B5-3. Quality Control Parameters for Meteorology Measurements

| Meteorology Parameter | Calibration Check Standard | Required Frequency | Acceptance Criteria | Recommended Corrective Action |
|-----------------------|---|--------------------|--|---|
| Ambient Temperature | Separately calibrated AIO2 sensor, designated the audit sensor. | Semi-annually | The average difference, or bias, must be $\leq \pm 0.5^{\circ}\text{C}$ for a minimum of 48, valid CTS audit pairs covering at least two diurnal cycles. | Inspect instrument for damage or worn components. Correct data where possible (e.g. wind direction). Recalibrate instrument. Qualify all collected data since the most recent calibration or acceptable calibration check as "3" in AQS, as applicable. |
| Relative Humidity | Separately calibrated AIO2 sensor, designated the audit sensor | | The average difference, or bias, must be $\leq \pm 5\%$ RH for a minimum of 48, valid CTS audit pairs covering at least two diurnal cycles. | |
| Barometric Pressure | Separately calibrated AIO2 sensor, designated the audit sensor | | The average difference, or bias, must be $\leq \pm 2$ hPa for a minimum of 48, valid CTS audit pairs covering at least two diurnal cycles. | |
| Wind Speed | Separately calibrated AIO2 sensor, designated the audit sensor | | The average difference, or bias, must be $\leq \pm 1.0$ m/s for a minimum of 48, valid CTS audit pairs covering at least two diurnal cycles. | |
| Wind Direction | Separately calibrated AIO2 sensor, designated the audit sensor | | The average difference, or bias, must be $\leq \pm 10^{\circ}$ for a minimum of 48, valid CTS audit pairs covering at least two diurnal cycles. | |
| Solar Radiation | Compared to a NIST-traceable pyranometer | | The average difference, or bias, must be $\leq \pm 5\%$ for a minimum of 48, valid CTS audit pairs covering at least four diurnal cycles. | |
| UV Radiation | Compared to a NIST-traceable radiometer | | The average difference, or bias, must be $\leq \pm 5\%$ for a minimum of 48, valid CTS audit pairs covering at least four diurnal cycles | |
| Precipitation | Add water at a constant rate such that the gauge tips every 15 seconds and measure output with a graduated cylinder | | $\leq \pm 10\%$ of input volume | |
| Mixing Height | An optical termination hood is used to determine the instrument "zero" bias.) | | Visually verified as minimum backscatter. See figure 6 in section 4.3 in SOP# DAQ-07-001.2 | |

Associated data since the most recent acceptable calibration or calibration verification will be minimally qualified and may potentially be invalidated if the deviation is deemed significant.

B5.2 Quality Control for Laboratory Activities

QC procedures for laboratory activities cover laboratory extraction and analysis of carbonyls cartridges as identified in Table B5-4, which are replicated 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] **(not performed routinely but instead is used as a corrective action response when three or more consecutive MB cartridges fail acceptance criteria)** 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, 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 B5-4. Carbonyls Laboratory Quality Control Parameters

| QC Parameter | Detail | Required Frequency | Acceptance Criteria | Recommend Corrective Action |
|--|---|--|---|--|
| Solvent Blank (SB) | 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 _{sp} | Analyze several SBs and pump mobile phase to flush system. If contamination or interference persists, further investigation of source of contamination is necessary. |
| Initial Calibration (ICAL) | Analysis of five or more different calibration standard solutions covering the concentration range of interest | Prior to PAMS season, after failed continuing calibration verification, and after changing instrument components or maintenance which impacts calibration response | $r \geq 0.999$, back calculated concentration of each standard level within $\pm 20\%$ of nominal, $ \text{intercept/slope} \leq$ MDL _{sp} | Review chromatography for co-eluting peaks or improper integration. If problem is not found, repeat calibration. If still unable to meet criteria, prepare new calibration standards and reanalyze. If still unable to meet criteria, apply null code "AT" prior to reporting data to AQS and the null code must be applied to all injections processed using the calibration curve. |
| Second Source Calibration Verification (SSCV) also known as the HL-QA | Analysis of a known standard prepared from a stock solution sourced from a vendor independent of the primary calibration stock standard or may be the same source as the primary calibration stock standard but is at least a different lot number than the stock used for instrument calibration; verifies the quality of the ICAL | Immediately following ICAL and may also serve as the CCV. | Target analyte concentrations within $\pm 15\%$ of nominal | Review preparation records, calculations, procedures, and chromatography to investigate discrepancy with ICAL. If root cause not found, prepare new SSCV and/or ICAL, if possible , and reanalyze extracts analyzed since the last passing SSCV. Analysis should not commence until SSCV following ICAL meets criteria or at minimum, apply null code "AS" to affected compounds since the last passing SSCV. |

Table B5-4. Carbonyls Laboratory Quality Control Parameters

| QC Parameter | Detail | Required Frequency | Acceptance Criteria | Recommend Corrective Action |
|---|---|--|--|--|
| Continuing Calibration Verification (CCV) also known as the HL-QA | Analysis of a known standard solution to verify the instrument calibration remains valid | At the beginning of each day's analysis when an ICAL is not performed and after every 12 hours of analysis | Target analyte concentrations within $\pm 15\%$ of nominal | Review chromatography for co-eluting peaks or improper integration. If problem is not found, establish new ICAL, if possible, and reanalyze extracts analyzed since the last passing CCV. If associated samples cannot be reanalyzed, apply null code "AS" to affected compounds since the last passing SSCV in AQS. |
| Holding Times | Maximum duration from end of sample collection for sample extraction Maximum duration from sample extraction to analysis | all field-collected and laboratory QC cartridges | 14 days from end of sample collection to extraction 30 days from sample extraction to analysis | Qualify samples exceeding holding times as "HT" in 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 | measured mass per cartridge ($\mu\text{g}/\text{cartridge}$): - acetaldehyde ≤ 0.10 - formaldehyde ≤ 0.15 - acetone ≤ 0.30 - other individual compounds ≤ 0.10 | Reject media lot and return to vendor. If media must be used, qualify results for compounds with exceedances as "LB" in AQS. |
| Method Blank (MB) also known as the 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 \leq MDL | Review preparation records, chromatography, and procedures for sources of contamination. Unless technical justification is provided to explain nonconformance, qualify all sample results in the extraction batch as "LB" in AQS. |
| Laboratory Control Sample (LCS) also known as the cartridge spike | Blank cartridge spiked with a known amount of target analytes and extracted | Minimally twice quarterly, recommended each extraction batch of 20 or fewer field-collected samples | Formaldehyde recovery within 80 to 120%, all other target analytes recovery within 70 to 130% | Review preparation records, chromatography, and procedures for sources of contamination or suppression. Unless technical justification is provided to explain nonconformance, qualify sample results in the extraction batch as "QX" in AQS. |
| Laboratory Control Sample Duplicate (LCS D) also known as the cartridge spike duplicate | Duplicate blank cartridge spiked with a known amount of target analytes and extracted to assess precision of the extraction and analysis method | Minimally twice quarterly, recommended each extraction batch of 20 or fewer field-collected samples | Formaldehyde recovery within 80 to 120%, all other target analytes recovery within 70 to 130%; precision with LCS as RPD $\leq 20\%$ | Review preparation records, chromatography, and procedures for sources of contamination or suppression. Unless technical justification is provided to explain nonconformance, qualify sample results in the extraction batch as "QX" in AQS. |

Table B5-4. Carbonyls Laboratory Quality Control Parameters

| QC Parameter | Detail | Required Frequency | Acceptance Criteria | Recommend Corrective Action |
|--|--|--|--|--|
| Extraction Solvent Method Blank (ESMB) | Aliquot of solvent lot used for extraction contained within a volumetric flask used for extraction | One per extraction batch of 20 or fewer field-collected samples. | Target analyte concentrations \leq MDL _{sp} | Review preparation records, chromatography, and procedures for sources of contamination. Qualify sample results in the extraction batch as "LB" in AQS. |
| Replicate Analysis | Repeat analysis of a routine sample extract | One each day of analysis | Relative percent difference \leq 10% for compounds \geq 0.5 μ g/cartridge | Reanalyze extracts to confirm disparate results. If confirmed, qualify sample results in the analysis batch as "4" in AQS. |
| Field Blank | Blank cartridge installed in a sampling channel for five to ten minutes | As submitted to the laboratory by field site(s) | measured mass per cartridge (μ g/cartridge): - acetaldehyde \leq 0.40 - formaldehyde \leq 0.30 - acetone \leq 0.75 - sum of other compounds \leq 7.0 | Investigate sources of contamination in handling and transport. Unless technical justification is provided to explain nonconformance, qualify associated field collected samples as "FB" in AQS. Associated samples are those in the shipment with the field blank and the samples since the most recent acceptable field blank. |
| Trip Blank | Blank cartridge accompanying collected samples to and from the field site | Trip blanks are not performed regularly. Instead, this QC sample is used as part of corrective action investigations to find sources of contamination in the event of systemic field blank failures of priority compounds (Formaldehyde and Acetaldehyde). | measured mass per cartridge (μ g/cartridge): - acetaldehyde \leq 0.10 - formaldehyde \leq 0.15 - acetone \leq 0.30 - other individual compounds \leq 0.10 | Investigate sources of contamination in handling and transport. Unless technical justification is provided to explain nonconformance, qualify associated field collected samples as "TB" in AQS. Associated samples are those in the shipment with the trip blank. |
| Sample Storage | Cartridges stored refrigerated and protected from light | All samples | Storage in foil pouch at \leq 4°C | If temperature is exceeded, qualify results as "TT" in AQS. |
| Extract Storage | Sample extracts stored refrigerated and protected from light | All extracts | Storage in amber vials at \leq 4°C | If temperature is exceeded, qualify results as "TT" in AQS. |
| Duplicate Sample Analysis | Analysis of a separate sample cartridge collected concurrently with a primary 8-hour sample through a common inlet probe | DAQ does not collect duplicate samples. | Relative percent difference \leq 20% of the associated primary cartridge for compounds \geq 0.5 μ g/cartridge | Unless technical justification is provided to explain nonconformance, qualify both samples as "QX" in AQS. |

Table B5-4. Carbonyls Laboratory Quality Control Parameters

| QC Parameter | Detail | Required Frequency | Acceptance Criteria | Recommend Corrective Action |
|----------------------------|--|--|---|--|
| Collocated Sample Analysis | Analysis of a separate sample cartridge collected concurrently with a primary 8-hour sample through an independent inlet probe | DAQ does not collect collocated samples. | Relative percent difference $\leq 20\%$ of the associated primary cartridge for compounds $\geq 0.5 \mu\text{g}/\text{cartridge}$ | Unless technical justification is provided to explain nonconformance, qualify both samples as "QX" in AQS. |

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

Instrumentation used to conduct PAMS measurements or to calibrate PAMS 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

Monitoring equipment (e.g., auto-GCs, carbonyls samplers, and ceilometers) necessary to outfit the PAMS Required Site will be selected and purchased to ensure sufficient time to receive, inspect, install, calibrate, and become familiar with the operation of the instruments. While training on instrument use will continue after the beginning of PAMS season, monitoring agencies will plan for site operators and auditors to attend training sessions, when available, in the months leading up to PAMS season.

B6.2 Instrument Acceptance Testing and Shakedown

The instruments and support equipment for PAMS monitoring are complex and typically require a testing, conditioning, and shakedown period of minimally several weeks 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. Depending on instrument installation status, the monitoring agency will plan to perform instrument conditioning and shakedown with sufficient time prior to the start of each PAMS season to ensure instruments are functioning properly and are calibrated. During this shakedown period, site operators will treat the data as a "dry run" for generating PAMS measurement data to work out instrument and data transformation problems and become accustomed to the instrument operation and data outputs. Each monitoring agency will conduct a shakedown assessment (a TSA) prior to the first PAMS Required Site monitoring season and annually thereafter prior to PAMS season (unless the instruments are operated year-round). Monitoring agencies will not report data to AQS during the shakedown period.

B6.2.1 Initial Instrument Acceptance and Shakedown

Once monitoring instruments and equipment are purchased and have been received, the instruments and equipment will be inspected within one month of receipt (earlier if possible) to ensure they are in good condition and include the necessary components required for installation. Vendors will be contacted immediately if 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 monitoring agencies 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
- Performing leak checks on the instrument

Once proper instrument operation has been confirmed, site operators will calibrate or verify the calibration of the instruments, as appropriate, as part of the instrument shakedown. Known aspects of instrument and support equipment operation which require several days to weeks to complete include, but are not limited to, the purging and conditioning of zero air generators (for auto-GC use); passivation and conditioning of calibration standard gas regulators, lines, and calibrators; and flow calibration of carbonyls sampling instruments.

This initial shakedown and testing period will occur minimally three months prior to the 2021 PAMS season, preferably earlier, to ensure that problems and related troubleshooting and corrective actions can be resolved prior to beginning required monitoring.

B6.2.2 Annual Instrument Shakedown

The monitoring agency may elect to operate all or some of the instruments year-round. In such case, the maintenance schedule prescribed for each instrument is to be followed and suitability for each measurement will be evidenced by the QC procedures and checks required for PAMS Required Site measurements. If, however, the monitoring agency opts to shutdown PAMS monitoring at the conclusion of PAMS season, instruments will go through shakedown such that the instruments are online, calibrated, and stable minimally four weeks prior to the start of PAMS season and in sufficient time to demonstrate proper operation as evidenced by acceptable performance in PTs. *Note that auto-GCs and supporting equipment are typically less prone to operational problems when operated year-round.*

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) must be inspected monthly to ensure conditions do not adversely affect instrument operation or data integrity.
- Data collection and data quality 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.
- Equipment will be inspected during site visits to ensure instruments are in appropriate working order. Site visit checklists or instructions on how to document site visits and equipment inspections are provided in the SOPs.

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 PAMS instrument SOPs. Additional information on instrument maintenance can be found in Revision 2 of the PAMS TAD. PAMS instrument and support equipment maintenance activities will be performed per the frequency detailed in Table B6-1.

Monitoring agencies 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 |
|---------------------------------|---|--|
| Agilent/Markes Auto-GC | Maintenance activities are prescribed in SOP# DAQ-09-001.2. They include replacing preconcentrator trap(s), servicing the Kori-XR, and Unity-XR instrument components. Calibrating standard dilution measurement equipment is prescribed in SOP DAQ-03-006.1. | Performed annually prior to PAMS season |
| ATEC 8000 Carbonyls Sampler | Maintenance activities are prescribed in SOP# DAQ-09-002.1. They include recharging/replacing the ozone denuder, replacing the particulate filter, performing positive bias challenge, and flow controller calibration. | Performed annually prior to PAMS season |
| Precipitation Gauge | Tipping Bucket Gauge: Visually inspect and clean apparatus of dirt and debris, as needed. Manually tip bucket 10 times and verify that 10 tips were recorded by the instrument. | Visually inspect each site visit, perform operational check weekly |
| Wind Speed/Direction Instrument | Cleaning and lubricating per manufacturer recommendations | Annually during calibration verification |
| Thermometer | Inspect and clean radiation shield. Verify paint reflective integrity. | Minimally every six months or more frequently depending on |

Table B6-1. Routine Instrument Maintenance Activities

| Instrument | Maintenance Activity | Frequency |
|-----------------------------|---|---|
| | | site conditions |
| Barometer | Inspect wiring integrity and instrument housing for proper ventilation – remove dust from indoor sensors | Each site visit |
| Hygrometer | Inspect and clean radiation shield. Verify paint reflective integrity. Replace screen as needed | Minimally every six months or more frequently depending on site conditions |
| Radiometer (pyranometer) | Clean dome lens, verify level, and review data to verify diurnal pattern, inspect and replace desiccant – realign after servicing | Clean lens and inspect level, unit and data each site visit - replace desiccant monthly |
| Ceilometer | Maintenance activities are prescribed in SOP# DAQ-07-001.2 . Check for alarms and warnings, clean laser window, check window blower operation, check and clean (as needed) door gasket. | Each site visit |
| HPLC for carbonyls analysis | Maintenance activities are prescribed in SOP# DAQ-03-004.2 . Such includes 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 |

Prior to each PAMS season, monitoring agencies will complete maintenance on the instruments and support equipment necessary for PAMS measurements. Monitoring agencies will replace worn items as needed, verify proper operation, and calibrate instruments such that the instruments are readied for collecting and reporting PAMS measurements starting no later than June 1 of each year. Note that for auto-GCs or continuous gaseous monitors, these instruments may need to be readied several weeks in advance to accommodate PT sample analysis or through-the-probe (TTP) audits as arranged with the EPA Regional representative or EPA's QA contractor.

PAMS 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). **Site checklists or instructions on documenting site visits are provided in the SOPs.** These checklists are valuable data inputs for data verification and validation. Agencies may choose to prepare their own checklist to capture different or additional aspects of monitoring when operators are on site. Operators should pay particular attention to instruments outdoors, such as meteorology instruments. A visual inspection will include verifying that instruments temperature shields are present, free of damage, and not blocked (such as with a bird nest, insect nest, etc.). Mechanical wind instruments should be verified to be operational if the wind is blowing and precipitation gauges should be inspected for debris. 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 PAMS Required Network Sites will be calibrated prior to use and according to the schedule/frequency described within this section, which are duplicated in the PAMS TAD and national 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 re-calibration, of the instrument or monitor.

Instrument calibrations will be documented in logbooks dedicated to the instrument. The 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 will not be used past their expiration date.

B7.1 Instrument Calibration

Instrument calibration instructions are specified for the beginning of and conclusion (shutdown) of PAMS season in the applicable SOPs.

B7.1.1 *Carbonyls Instrument Calibration*

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

B7.1.1.1 *Carbonyls Field Sampling Instrument Calibration and Calibration Verification*

Carbonyls sampling unit flow controller(s) will be calibrated initially prior to the beginning of PAMS season and the flow calibration verified minimally monthly thereafter. Flow calibration verification will be within $\pm 10\%$ of the flow indicated at standard conditions of 760 mmHg and 25°C against a NIST-traceably certified flow transfer standard.

B7.1.1.2 *Carbonyls Laboratory Instrument Calibration and Calibration Verification*

Initially, following maintenance or repair that would reasonably impact the instrument response, and following failure of CCV or SSCV, the HPLC or UHPLC will be calibrated for the target compounds by analysis of a minimum of five concentration levels covering the concentration range expected to bracket the concentrations of carbonyls in the cartridge extracts. Instruments that are not operated continually (e.g., those shut down for several months at a time) will be calibrated when returned to online status. Calibration will be verified immediately following the ICAL by analysis of an independent SSCV and every 12 hours of analysis thereafter by analysis of a CCV. The SSCV and CCV will be within $\pm 15\%$ of the nominal concentration or corrective

action must be taken.

B7.1.2 Calibration and Calibration Verification for Speciated VOCs by Auto-GC

Auto-GCs for measuring speciated VOCs will be calibrated as part of initial set-up and shakedown, minimally at the start of the PAMS season, and when maintenance to the instrument is reasonably expected to alter its calibration. Auto-GC calibration is described in more detail in SOP # DAQ-09-001.2 and is established by analysis of minimally three concentration levels (0.25ppbv, 2ppbv, and 10ppbv) which contains a mixture of all PAMS VOC compounds monitored and reported as detailed in Table B2-2. These concentrations can change at the discretion of the AutoGC operator. 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 at 2ppbv containing the sample mixture of PAMS VOC compounds representing the molecular weight range (C₂ to C₁₂). This SSCV is to be analyzed minimally weekly thereafter and must be within ± 30% of the nominal concentration for the target compounds.

B7.1.3 Calibration and Calibration Verification for Meteorology Instruments

Meteorological instruments require calibration initially prior to placement into service. Instrument calibration will then be verified minimally 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 listed in Table B5-3 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 PAMS measurement instruments includes, but is not limited to, flow transfer standards, reference thermometers, reference barometers, volumetric labware, and mass flow controllers. Calibration and calibration verifications will be performed by comparison to such 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. The certification provider, primary standards of comparison, and approved method or SOP for each appropriate support instrument are provided in the SOPs listed in Table B7-1. Some of these SOPs are still under development at the time of this QAPP submittal.

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 SOP# DAQ-13-001.1 and SOP# DAQ-03-009.4 | ≤ 2% of NIST-traceable standard across its range of flow rates | Calibration of flow controllers for carbonyls sampling units and mass flow controllers in gas calibrators | Annual per manufacturer specifications | Calibration check not required |
| Mechanical Pipette | Minimum pipette volume: Accuracy must be < 8.0% and precision (CV) must be < 3.0% Maximum pipette volume: Accuracy must be < 2.0% and precision (CV) must be < 1.0% | Delivery of five known liquid volumes – preparation of carbonyls calibration standards | Initially and when calibration verification checks demonstrate an out of tolerance condition | Once per calendar quarter |
| Class A Volumetric Labware | Meets Class A tolerances specific to the labware designated volume | Measuring final volume of standard solution preparation | 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 and site storage unit monitoring for carbonyls sample and extract storage – temperature monitoring of monitoring shelter – <u>note this is not a thermometer for reporting meteorological data</u> | Initially and when calibration verification checks demonstrate an out of tolerance condition | Annual calibration verification 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 $\pm 2\%$ of nominal weight | Laboratory – Weighing of mobile phase components, verification of pipettes | Annually or when calibration checks demonstrate an out of tolerance condition | Once per calendar quarter with certified calibration check weights bracketing the balance load; Must cover the range of use |
| Certified Weights | Tolerances within those assigned to the class of weights | Laboratory – Calibration verification of balances | Annual or as required by the manufacturer | Annual calibration is sufficient |
| Pressure Gauges or Transducers SOP# DAQ-03-006.1 | Within ± 0.5 psi or manufacturer-specified tolerance, whichever is smaller | Field and Laboratory – Measure canister pressure/vacuum for standards preparation; precise metering of standard and diluent gases for calibration of monitoring instruments | Annually, must cover the range of use or calibrated according to manufacturer procedures. | Annual calibration is sufficient |
| Mass Flow Controller – Gas Calibrator SOP# DAQ-09-002.1 | Within $\pm 2\%$ of certified flow transfer standard | Field – precise metering of sampled air for calculation of volume sampled | Annual or when calibration checks demonstrate flows are out of tolerance | Minimally quarterly (before and at the end of PAMS season), monthly recommended |

^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 gas standards, particulate filters for inlets and instruments, stainless steel tubing, high pressure cylinder regulators, auto-GC preconcentrator traps, ozone photometer lamps, 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 following SOPs as it pertains to the specific piece of equipment used for PAMS monitoring:

- DAQ-07-003.1 MetOne AIO2 All-in-One Met Sensor ECB Responsibilities
- DAQ-07-004.1 MetOne 370D Tipping Bucket Rain Gauge ECB Responsibilities
- DAQ-07-008.1 Solar Radiation Sensor ECB Responsibilities
- DAQ-07-009.1 Ultraviolet Radiation Sensor ECB Responsibilities
- DAQ-09-001.2 Markes-Agilent AutoGC Analysis Operator Responsibilities
- DAQ-09-002.1 ATEC 8000 PAMS Sequential Carbonyl Sampler ECB Responsibilities
- DAQ-03-004.2 Thermo Ultimate 3000 Ultra High-Performance Liquid Chromatography by Ultra-Violet Radiation and Mass Spectrometry (UAT and PAMS Carbonyl Analysis) Operator Responsibilities

B8.1 Acceptance of Standard Materials

On an annual basis PAMS monitoring agencies 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 PAMS analyzers 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 certificate of analysis stating the purity (for neat materials or pure gases) or certified concentration with associated uncertainty for each component as well as the expiration.

Note that EPA employs a national contract laboratory to independently verify the concentration of propane and benzene in speciated VOCs retention time standard (RTS) cylinders against a NIST-certified standard. The verification laboratory provides a certificate of analysis for the verification of each individual RTS cylinder, listing the average measured concentration of each compound. The average of the concentrations measured by the verification laboratory must be within $\pm 10\%$ of the value listed on the gas vendor certificate of analysis. The verification laboratory values indicate the cylinder concentrations are accurate to within the vendor-listed tolerance; however, these values do not indicate the measurement uncertainty or expiration and will not be referenced for determining concentrations of calibration standards or calibration verification standards. Rather, the concentrations and expiration date listed on the gas vendor certificates of analysis 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 Regional Representative.

Certificates of analysis will be maintained by the monitoring agency or laboratory and be available for inspection during TSAs. Gas 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. **The vendor certification of the PAMS AutoGC VOC standards is valid for two years.** Recertification of standard gases may be more cost effective than purchasing new standards and can be performed during the non-sampling season (as applicable to the specific PAMS Required Site).

Prior to acceptance or use of a standard material for calibration, particularly for custom-ordered materials, the certificate of analysis will be inspected to ensure the correct compounds are included, that their concentrations are as requested and within requested tolerances, and that listed impurities are acceptably low. The new stock standards will be analyzed against a known acceptable instrument calibration and known stable (acetylene, styrene, and pinene isomers are not considered to be stable) compounds such as propane, benzene, toluene, ethylbenzene, and xylenes will be within the method bias specification.

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 monitoring agencies are 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. It is expected that the **LAB** will perform this lot blank analysis for each lot of media for use at supported sites.

If the criteria in the table are not met, the lot will not be used for sampling and will be returned to the vendor. **If the lot of contaminated cartridges is not accepted by the manufacturer or must be used for routine sampling to prevent missing excessive amounts of scheduled sample events, the failing lot of cartridges may be used for routine sample events, but all carbonyls failing lot blank criteria must be appropriately qualified in AQS.**

Table B8-1. DNPH Cartridge Lot Blank Acceptance Criteria

| Carbonyl Compound | Acceptance Limit (µg/cartridge) |
|---|---------------------------------|
| Acetaldehyde | ≤ 0.10 |
| Formaldehyde | ≤ 0.15 |
| Acetone ^a | ≤ 0.30 |
| All Other Carbonyl Compounds ^b | ≤ 0.10 |

^aAcetone is not monitored or reported for PAMS analyses.

^bcartridge vendor (Waters) 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.

B9 Non-direct Measurements

Non-direct measurement data will be used to support data validation activities, as described in Section 10 of Revision 2 of the PAMS TAD on data verification and validation. Such data may include historical PAMS data or reported concentrations and meteorological measurements from other monitoring sites. Data acquired from non-direct measurements may also include site operator observations.

B9.1 Historical PAMS Data and Supplemental Measurement Data from Other Monitoring Sites

PAMS data may be compared, for the purposes of verification and validation, to measurement data from other monitoring sites including other PAMS sites, air toxics sampling sites, meteorology stations, etc., and to historical PAMS data. While the data undergoing verification and validation may be subjected to further scrutiny, adjusted by the addition of qualifiers, or invalidated due to comparison with historical and/or other supplemental data, the monitoring agency will not perform assessment (e.g., further validation) on the historical and/or supplemental data. Adjustment or validation of such data is outside the scope of this QAPP. General guidelines for data validation are given in the PAMS TAD Revision 2 Section 10 and it is recommended that users of any such data confirm the data's fitness for the intended purpose of comparison prior to use.

B10 Data Management

The monitoring agency will ensure that data are recorded, verified, validated, reported, managed, and archived in a manner that permits reconstruction of activities throughout the data lifecycle.

Data management practices for the meteorological parameters (wind speed, wind direction, ambient temperature, relative humidity, barometric pressure, solar radiation, ultraviolet radiation, rain, mixing layer height) and chemical parameters (carbonyls and speciated VOCs) are covered in the following SOPs:

Meteorological Parameters:

- Sections 5, 6, 7, and 8 in SOP# DAQ-07-003.1 AIO2 All-in-one Met Sensor, ECB Responsibilities
- Sections 5, 6, 7, and 8 in SOP# DAQ-07-003.2/3 AIO2 All-in-one Met Sensor, Operator/Coordinator Responsibilities
- Sections 5, 6, 7, and 8 in SOP# DAQ-07-008.1 Solar Radiation Sensor, ECB Responsibilities
- Sections 5, 6, 7, and 8 in SOP# DAQ-07-008.2/3 Solar Radiation Sensor, Operator/Coordinator Responsibilities
- Sections 5, 6, 7, and 8 in SOP# DAQ-07-009.1 Ultraviolet Radiation Sensor, ECB Responsibilities
- Sections 5, 6, 7, and 8 in SOP# DAQ-07-009.2/3 Eppley CUV-5 Ultra-violet (UV) Sensor, Operator and Coordinator Responsibilities
- Sections 5, 6, 7, and 8 in SOP# DAQ-07-004.1 MetOne 370D Rain Gauge, ECB Responsibilities
- Sections 5, 6, 7, and 8 in SOP# DAQ-07-004.2/3 MetOne 370D Rain Gauge, Operator and Coordinator Responsibilities

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- Section 5.5 in SOP# DAQ-15-006.5 Data Verification and Validation for Continuous Gaseous Pollutants
 - Sections 4, 5, 6, 7, and 8 in SOP# DAQ-05-001.5 Ambient Monitoring Section Database Manager
 - Sections 5, 6, 7, and 8 in SOP# DAQ-07-001.2 Vaisala CL-51 Ceilometer, Operator Responsibilities

Carbonyl Parameters:

- Sections 5, 6, 7, and 8 in SOP# DAQ-09-002.1 ATEC 8000 PAMS Sequential Carbonyl Sampler, ECB Responsibilities
- Sections 5, 6, 7, and 8 in SOP# DAQ-09-002.2 ATEC 8000 PAMS Sequential Carbonyl Sampler, Operator Responsibilities
- Sections 5, 6, 7, and 8 in 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 in SOP# DAQ-03-004.5 Thermo Ultimate 3000 UHPLC-UV-MS (UAT and PAMS Carbonyl Analysis), RCO Responsibilities

Speciated VOC Parameters:

- Sections 4, 5, 6, 7, and 8 in SOP# DAQ-09-001.2 Markes-Agilent Automated Gas Chromatograph, Operator Responsibilities
- Sections 5, 6, 7, and 8 in SOP# DAQ-03-005.1 Entech 3100A Canister Cleaner, ECB Responsibilities
- Sections 5, 6, 7, and 8 in SOP# DAQ-03-005.2 Entech 3100A Canister Cleaner, Operator Responsibilities
- Sections 5, 6, 7, and 8 in SOP# DAQ-03-006.1 Entech 4700 Precision Diluter, ECB Responsibilities
- Sections 5, 6, 7, and 8 in SOP# DAQ-03-006.2 Entech 4700 Precision Diluter, Operator Responsibilities

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 PAMS data are of sufficient quality and quantity to meet the Required Site Network DQOs. Site operators and laboratory staff have the responsibility to prevent nonconformances 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 nonconformances before the quality of PAMS data is compromised. Nonconformances impacting data quality will be reported to the appropriate monitoring agency manager 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 PAMS Required Site Network QS, the following types of assessments will be conducted to ensure that the resulting data quality meets the PAMS 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%201_17.pdf

Staff conducting assessments (auditors) will be independent of staff performing the functions and will have authority to inform management of nonconformances to approved, established procedures and policies. These staff members should be organized under the monitoring agency quality assurance unit (QAU) as described in Section A6.2. Auditors will have authority to suggest to management to stop work activities if nonconformances 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 PAMS Required Site assessments.

Table C1-1. PAMS Required Site Assessments

| Assessment | Description | Responsible Party Conducting Assessment | Frequency |
|------------------------------------|---|---|---|
| Shakedown Audit (TSA and IPA) | Evaluation of PAMS Required Site readiness | Monitoring agency QAU | The DAQ goal is to conduct this audit before the start of each PAMS season |
| Technical Systems Audit (TSA) | Review of compliance with PAMS Required Site Program requirements, QAPP, SOPs, and best practices | Monitoring agency QAU | Annually during active PAMS monitoring |
| | | 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 PAMS monitoring |
| Instrument Performance Audit (IPA) | Measurement of carbonyls sampling unit flow with a certified flow transfer standard independent of that used for instrument calibration or verification | Monitoring agency QAU | Annually during active PAMS monitoring or at completion of active PAMS monitoring |
| | Comparison of meteorological instrument measurements by comparison with a known certified standard independent of that used for instrument calibration or verification | Monitoring agency QAU | Annually during active monitoring – during PAMS season if meteorological measurements are not made year-round |
| 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 | Monitoring agency QAU and LAB QAU | Annually during active PAMS monitoring or at completion of active PAMS monitoring and before or just after submittal of a site's PAMS data to AQS – Monitoring agencies are encouraged to perform the ADQ as early in the monitoring season as practical to catch issues to minimize impact on data |
| Proficiency Test (PT) | Analysis of a sample with target analytes at concentrations blind to the monitoring agency and LAB for both speciated VOCs and carbonyls analysis | EPA through QA support contractor | Twice annually, once prior to PAMS season and once just prior to the end of the PAMS season or twice annually as provided by approved EPA support contractor |

C1.1.1 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 monitoring agency QAU will conduct IPAs at PAMS Required Sites at least once per PAMS monitoring season for instruments operated only during PAMS season. Monitoring agencies are encouraged to conduct IPAs during PAMS season, however, are provided latitude to conduct IPAs during active monitoring. The EPA Regional Representative or delegate may conduct IPAs of the pollutant and meteorology instruments, as equipment and capabilities permit, during the triennial TSA.

C1.1.1.1 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 (assumed to be once per PAMS season unless the PAMS carbonyls monitoring is conducted at the site outside of the June 1 to August 31 PAMS season), an individual from the monitoring agency QA group 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 PAMS 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 for each of the flow channels utilized for sampling. The assessor will notify the site operator in the event of a nonconformance; corrective action will be required (mass flow controller calibration, flow obstruction removed, etc.) before cartridge 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. Corrective action is also recommended for flow calibration assessments that indicate flows are approaching, but not exceeding the appropriate flow acceptance criterion.

C1.1.1.2 Meteorology Instrument Performance Audits

Typically, meteorological instruments will be operating year-round and can be audited during the year when convenient for the monitoring agency QAU. For instruments operating year-round, it is recommended that meteorological audits occur approximately six months after the annual calibration check. Each meteorological instrument will be audited by comparison to a reference standard. When possible, such IPAs are best conducted with the instrument in-situ, as removal of the instrument for audit may eliminate the ability to capture specific aspects of monitoring such as wind-direction, for which the mounting position and compass alignment are critical. It may be impractical to perform in-situ IPAs if instruments must be removed for assessment, such as temperature probes which are submerged in a water bath for assessment. Meteorological IPAs will meet the acceptance criteria listed in Table B5-3. **The processes DAQ will use for**

conducting performance audits on the meteorological equipment are detailed in the following SOPs:

- SOP# DAQ-07-001.2 Vaisala Ceilometer Mixing Height Sensor Operator Responsibilities
- DAQ-07-003.1 MetOne AIO2 All-in-One Met Sensor ECB Responsibilities
- DAQ-07-004.1 MetOne 370D Tipping Bucket Rain Gauge ECB Responsibilities
- DAQ-07-008.1 Solar Radiation Sensors ECB Responsibilities
- DAQ-07-009.1 Ultraviolet Radiation Sensor ECB Responsibilities

C1.1.2 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.

To increase the uniformity of TSAs, EPA has developed checklists for the PAMS Required Site program for both monitoring agency and LAB operations, incorporating elements from the PAMS Required Network TAD and national QAPP and SOPs. 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). Monitoring agency QA staff will perform a TSA annually during active PAMS monitoring (this will be between the June 1 and August 31 PAMS season unless the monitoring site is monitoring outside of this period) and TSA reports will be submitted to monitoring agency management and a copy sent to the EPA Regional Representative. As an option, QA staff may also elect to perform an annual pre-PAMS season shakedown/readiness audit, as described in the section below.

DAQ will utilize a designated PAMS TSA audit team that will perform a TSA on the carbonyls sample handling, extraction, and analysis procedures annually. Laboratory TSAs will focus on QSs, compliance with QS documents, performance of analytical methods, sample handling and custody, and data review, verification, and reporting. The PAMS TSA audit team will distribute the TSA report to the LAB and DAQ management. The LAB will notify DAQ management of corrective actions, root cause analysis, and demonstrate return to conformance for audit findings deemed to impact data quality. Such reports will identify the affected data. DAQ will subsequently notify EPA Region 4 of the outcomes of the annual PAMS TSA, including any corrective actions taken by DAQ. DAQ SOP DAQ-15-004.5 PAMS Shakedown Audits and TSAs, currently under development, describes the audit procedures the DAQ PAMS TSA audit team will follow.

Following program implementation, EPA will conduct a TSA at each PAMS Required Site every three years. The Regional Representative will conduct the triennial TSA or may delegate audit conduct to the National QA Support Contractor. Since not every site will have its own laboratory, laboratories supporting multiple PAMS sites will be subject to audit in the calendar year that the supported PAMS sites are audited but will not be audited more than once every

three years unless major audit findings suggest more frequent auditing is necessary. As much as possible, PAMS TSAs will be scheduled in conjunction with NCore, NATTS, or other monitoring program audits at the site or laboratory to reduce the burden on monitoring agencies 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.

C1.1.2.1 Shakedown Audits

Prior to the June 1, 2021 implementation of the PAMS Required Site program and each spring thereafter, the monitoring agency will conduct a shakedown audit of the PAMS monitoring program to evaluate readiness for the upcoming PAMS season. This shakedown audit will consist of a TSA and include an IPA of the carbonyls sampling instrument(s). The shakedown audit will focus on the readiness of the site operators and data reviewers, the adequacy of their training, the availability of all required QS documents (QAPP, SOPs, field collection forms, COCs) and the suitability and readiness status of the instruments for officially beginning PAMS monitoring.

Shakedown audits are intended as a tool to identify compliance gaps and areas where additional resources are required such that data of sufficient quality and quantity may be generated as of startup on June 1, 2021 (and the beginning of each subsequent PAMS season). Formal corrective action is not required because of shakedown audits. The shakedown audit is inherently different than an independent audit (TSA and/or IPA) conducted during monitoring season to assess the compliance of the PAMS operations with the monitoring agency's QS.

C1.1.3 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 monitoring agency 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

DAQ and LAB QA staff will conduct ADQs for PAMS minimally annually and prior to entering data into AQS for speciated VOCs, carbonyls, and meteorology parameters, for those aspects of data collection and reporting for which they are responsible. Results of the ADQ will be reported to the EPA Regional Representative. Monitoring agencies are encouraged to conduct the annual

ADQ as early in the monitoring season as possible to catch issues early where their impact to subsequent data is minimized.

C1.1.4 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 site or laboratory.

The PT program will evaluate the Millbrook PAMS Site and the LAB for measurement bias, specifically for speciated VOCs and carbonyls. An EPA contractor will prepare VOCs and carbonyls samples for shipment to either the field site (VOCs) or to the LAB (carbonyls) on a biannual basis, both prior to and near the end of PAMS season. Samples are spiked with target analytes at concentrations blind to the sites and laboratories. The Millbrook Site or the LAB will analyze the PT sample(s) on the auto-GC (VOCs) or via DAQ's TO-11A method (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 PAMS Required Network mean (with statistical outliers removed).

Auto-GC results for VOCs PT samples must be within $\pm 25\%$ of the assigned target value for each evaluated target compound. For carbonyls, the LAB must demonstrate PT analysis results which are 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 Millbrook Site or the LAB 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 necessity will be based on the number of parameters and the severity of the unacceptable evaluations as well as other details of the PT as provided by the PT provider for interpretation of the results. These details are described in study-specific summary interpretations based on the circumstances of each PT study.

C1.2 Corrective Actions

The monitoring agency will have a corrective action process in place that is executed upon discovery of nonconformances to the monitoring agency PAMS QAPP and/or applicable PAMS SOPs. Each monitoring agency will have a corrective action tracking procedure so that corrective actions are available in a single location (e.g., binder, database, etc.) and may be readily referenced. The DAQ corrective action process is described in SOP DAQ-15-002 Corrective Action Process.

For each nonconformance, a corrective action report (CAR) 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

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- 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 monitoring agency director and QA unit

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

- Repeated calibration failure
- Incorrect sample storage conditions
- Persistent blank contamination
- Incorrect procedures followed
- Repeated QC acceptance criteria failures
- Unacceptable PT results

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. Monitoring agencies are encouraged to seek assistance from EPA Regions, EPA OAQPS, or instrument manufacturers in instances in which a root cause is not evident.

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 and/or support contractor; however, the responsibility of implementing corrective actions lies with the monitoring agency. A CAP generally addressed 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 nonconformances elsewhere in the QS

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- corrective actions to preclude recurrence of the specific and similar nonconformances
 - 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 monitoring agency sites or the LAB do not meet PT acceptance criteria, the Regions and monitoring agency 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 reported to the Regions and to OAQPS so that lessons learned may be shared and the PAMS program may be continuously improved.

C2 Reports to Management

Monitoring agency management will be apprised of the results of all independent assessments conducted on their sites and labs operating in support of the PAMS Required Site program. Monitoring agency QA staff will report assessment outcomes to management in a timely manner. **Assessments that do not pass are reported to management as described in SOP DAQ-15-002 Corrective Action Process.** Network summary reports will be generated minimally at the completion of data entry to AQS for each PAMS season and will be submitted to management.

C2.1 Assessment Reports

Monitoring agency QA staff will forward assessment reports 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). Reports resulting from internal QA activities (e.g., TSA, IPA, ADQ, PTs, etc.) will identify operational and data quality nonconformances, resource needs (e.g., staff training, equipment), and results from relevant external assessments.

C2.2 Annual Network Summary Reports

Monitoring agency staff will run a dedicated AQS report (AMPXXX – yet to be developed) detailing the site(s) performance (attainment of the MQOs) for the DQIs of bias, precision, sensitivity, and completeness. This report will include information for the specific site and may also include aggregated data from the PAMS Required Site Network as a whole. This report will be generated after the completion of the PAMS season's validated data upload to AQS, will inform the monitoring agency of their performance in the network, and will identify areas for improvement.

D. DATA VALIDATION AND USABILITY

D1 Data Review, Verification, and Validation Requirements

The verification and validation process 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 at PAMS Required Sites and the LAB will undergo verification and validation prior to reporting to AQS. Data verification is the process of evaluating the completeness, correctness, and conformance/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 quality goals established during the planning phase have been achieved;¹¹ for example, to determine if season-long 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 verified and validated can a DQA be performed to determine if it is fit for its intended purpose,¹² which for PAMS is to assist in the development and refinement of predictive models for the formation of ground-level O₃.

To meet the DQO for supporting ozone modeling efforts, data must meet the MQOs and will have been verified and validated as described in Section 10 of Revision 2 of the PAMS TAD which addresses data verification and validation. Data verification and validation are described briefly in the next several sections.

D1.1 Data Verification and Validation Responsibilities

Verification and validation of data for the PAMS Required Site Network is the responsibility of the monitoring agencies that operate the field component of the program, with input from the carbonyls LAB analyst. The LAB will minimally verify the carbonyls data reported to ensure the data are correct and comply with the established laboratory QAPP and SOP(s).

The process DAQ will use for review of carbonyl sampling and analysis data are detailed in SOP# DAQ-03-004.2. The process DAQ will use for review of the PAMS VOCs are detailed in SOP# DAQ-09-001.2

The processes DAQ will use for verification of carbonyl sampling and analysis data are detailed in SOP DAQ-03-004.2. The process DAQ will use for verification of PAMS VOCs are detailed in SOP# DAQ-09-001.2

The processes DAQ will use for validation of carbonyl sampling and analysis data are detailed in SOP DAQ-03-004.5. The process DAQ will use for validation of PAMS VOCs are detailed in Eastern Research Group (ERG) data validation procedures. Recall, DAQ will send Level 1 and

Level 2 reviewed AutoGC VOC data to ERG for final validation. ERG will send the validated results to DAQ and DAQ will report the validated results to AQS.

Personnel performing data verification and validation activities will:

- Be familiar with typical diurnal concentration variations (e.g., the time daily maximum concentrations occur and the interrelationship of pollutants.) For example, benzene, toluene, and xylene concentrations usually increase and decrease together due to these being attributed to mobile sources, whereas ozone typically follows a diurnal cycle with a peak during the afternoon hours.
- Be familiar with the types of instrument malfunctions that cause characteristic irregularities in reported data.
- Recognize that cyclical or repetitive variations (at the same time each day or at periodic intervals during the day) in continuous measurements may be caused by excessive line voltage or temperature variations. Emissions from nearby sources can also cause erroneous or non-representative measurements.

D1.2 Data Verification

In the data verification process, PAMS 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. PAMS data verification applies to activities in the field as well as in the LAB performing carbonyl cartridge extraction and analysis. Data verification includes routine (self) review of collected data by the instrument operator and subsequent technical (peer) review.

D1.2.1 Routine (Self) Review

The instrument operator(s) will perform the initial steps of routine (self) review portion of data verification which include reviewing recorded data to ensure the records are complete and comply with the acceptance criteria in the monitoring agency 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 that minimizes the loss of data should errors or conditions be 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. For example, if the site instrument operator has configured the true NO₂ instrument to automatically analyze a calibration check standard every week but

does not take the time to review the weekly check for several weeks, such a delay in reviewing the collected data risks losing a week or more of sampling data in the event the instrument lamp fails and the calibration check standard does not meet acceptance criteria. Ideally depending on the measurement system, the individual will conduct a cursory review daily when data are generated, preferably in the morning (verifying nightly QC checks met criteria), to provide a status of instrument's present performance.

Table D1-1. Routine Review Activities and Associated Frequency

| Verification Activity | Frequency |
|---|------------------------------------|
| Measurements did not exceed the alarm limits set in the DAS | Daily ^a |
| The rate of change observed for the analyte is consistent with ambient data trends (specific to high frequency measurements – e.g. minute data) | Daily ^a |
| Measurement data that exceed the instrument calibration range | Daily ^a |
| Measurement data are complete (sample collection and COC forms are not missing information, expected electronic files are recorded, and logbook entries are complete) | Daily ^a |
| Samples/data were collected in accordance with the sample design and approved SOP | Weekly |
| Sample collection and handling procedures were followed correctly | Weekly |
| Data files are properly identified | Weekly |
| Computer file entries match hand entered data sheets | Weekly |
| Analytical procedures used to generate data were implemented as specified | Weekly |
| 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) | Weekly, as applicable |
| QC check criteria were met and corrective actions are taken when criteria are not met | Daily ^a , as applicable |
| Chromatography is acceptable (stable baseline, adequate peak separation, etc.) and that analyte identification is appropriate based on the established RT windows | Daily ^a |
| Carbonyls sample holding times were met and the analysis laboratory reviewed and verified carbonyl analysis data | When carbonyls data are reviewed |
| Deviations from stated procedures or acceptance criteria are documented and impacted data are flagged or invalidated per monitoring agency policy | Weekly |
| Measurements that are known to be invalid because of instrument malfunctions are invalidated as per monitoring agency policy | Weekly |
| Data are substituted from a backup in the event of failure of the primary data acquisition system | Weekly |
| Corrections and changes to the data records are documented | Continuously |

^a Daily on normal business days when staff are on duty.

Once the data has 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 (mass flow controllers, 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 sample holding times were met and the LAB reviewed and verified carbonyl analysis data
 - Deviations from stated procedures or acceptance criteria are documented and impacted data are flagged or invalidated per monitoring agency policy
 - Measurements that are known to be invalid because of instrument malfunctions are invalidated as per monitoring agency 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

D1.3 Data Validation

Data validation is a process that investigates the individual data points within the context of other co-collected data, historical 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. Only after a given dataset has been verified and validated can a DQA be performed to address the PAMS-specific DQO.

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 in DAS as an initial review of data. DAS programs may include programmed qualifiers that are applied when a parameter rate of change or upper range limit is exceeded. These are various evaluations that monitoring agency 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 by the use of 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, timeseries

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 monitoring agency, to identify systematic bias.

Levels 2 and 3 data validation will be performed when historical data at the site or nearby comparable sites are 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 a QA staff member may recreate the validation as part of the annual ADQ. Data will be validated in portions of time consisting of one to four weeks' worth of data, depending on the volume of data to be validated, so that the dataset is manageable. For example, speciated VOCs data will be validated in one-week portions that include the bracketing weekly precision QC checks. Validating four weeks of speciated VOCs data in one dataset is unwieldy and is more appropriate for carbonyls 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 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 |
|----------------|---|
| Speciated VOCs | One week's worth – to include bracketing weekly QC checks |
| Carbonyls | Two to four weeks' worth – ensure concurrent speciated VOCs data are available for validation |
| Meteorology | Two to four weeks' worth – ensure concurrent pollution data to prepare pollution roses |

D1.4 Reporting of Validated Data to AQS

After the data validation has been completed minimally through Level 1, measurement data may be uploaded to AQS. Data will be uploaded to AQS within 180 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. Chemical measurements for speciated VOCs and carbonyls will include the associated MDL in the AQS coded data. Monitoring agencies are 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, the monitoring agency 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.

D1.4.1 Reporting Values Below Method Detection Limits (Chemical Parameters)

Instrument sensitivity for chemical parameters for the PAMS Required Sites is characterized by determining the MDL as described in Section 3.3.5.1 of Revision 2 of the PAMS TAD. 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.** Alarms may be set in the DAS to alert users when low values are recorded; however, the DAS will be configured to permit all data values to be recorded from the instruments and will not censor data.

For speciated 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

DAQ will employ a combination of software tools such as instrument control software, DART, Envista ARM, Envistas Ultimate, and excel macros to perform data review, verification, and validation steps. Specific level 1 data review procedures including the identity of software tools DAQ will use are described in more detail in the following SOPs:

Level 1 Data Review SOPs:

- DAQ-03-004.2 Thermo Ultimate 3000 UHPLC/UV/MS UAT and PAMS Carbonyl Analysis, Operator Responsibilities
- DAQ-07-001.2 Vaisala Ceilometer Mixing Height Sensor, Operator Responsibilities
- DAQ-07-003.2 MetOne AIO2 All-in-One Met Sensor, Operator Responsibilities
- DAQ-07-004.2 MetOne 370D Tipping Bucket Rain Gauge, Operator Responsibilities

- DAQ-07-008.2 Solar Radiation Sensor, Operator Responsibilities
- DAQ-07-009.2 Ultraviolet Radiation Sensor, Operator Responsibilities
- DAQ-09-001.2 Agilent/Markes Auto-GC/FID PAMS Analysis, Operator Responsibilities

D2.1 Data Verification Methods

Instrument operators and technical 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 routine reviews and technical reviews will include examining data manually and using automated tools to verify the data. Manual methods include, for example, direct examination of chromatography data for auto-GCs, 1-minute data for continuous monitoring methods (meteorology and certain chemical parameters), hand-transcribed data, hand calculation of calibration data, and site and maintenance logs. Automated methods include generation and review of summary reports for auto-GC, DAS summary reports and alarm reports, data completeness reports, and similar reports that provide an aggregation of data to provide efficient confirmation that data meet criteria for bias, precision, completeness, and sensitivity.

Data verification activities are tailored to the specific parameter being verified. Specific details for each parameter type are discussed in detail in Section 10 of Revision 2 of the PAMS TAD. Monitoring agencies will describe the data verification activities, procedures, and tools in an SOP or combination of SOPs to ensure that data are correct, complete, and meet technical acceptance criteria, and when data integrity are impacted, the data are invalidated or flagged to indicate the deficient aspects. The monitoring agency will create checklists to ensure that critical data verification elements are reviewed, and their review documented during routine reviews and technical reviews. Checklists will indicate whether the critical element was satisfied. Such checklists will be included in the data verification and validation SOP(s) specified in this QAPP. DAQ data verification procedures are described in more detail in the following SOPs:

Level 2 Data Verification SOPs:

- DAQ-03-004.2 Thermo Ultimate 3000 UHPLC/UV/MS UAT and PAMS Carbonyl Analysis, Operator Responsibilities
- DAQ-07-001.2 Vaisala Ceilometer Mixing Height Sensor, Operator Responsibilities
- DAQ-07-003.2 MetOne AIO2 All-in-One Met Sensor, Operator Responsibilities
- DAQ-07-004.2 MetOne 370D Tipping Bucket Rain Gauge, Operator Responsibilities
- DAQ-07-008.2 Solar Radiation Sensor, Operator Responsibilities
- DAQ-07-009.2 Ultraviolet Radiation Sensor, Operator Responsibilities
- DAQ-09-001.2 Agilent/Markes Auto-GC/FID PAMS Analysis, Operator Responsibilities

D2.2 Data Validation Methods

This section describes general tools for conducting data validation for PAMS Required Site data. These tools are useful in identifying anomalous data and increasing confidence in datasets; however, validators will use a combination of such tools to validate data, and not rely on one specific tool to confirm or nullify data validity. As mentioned previously, each monitoring agency will describe the PAMS Required Site data validation process and tools in an SOP or similar controlled document. DAQ data validation procedures are described in more detail in the following SOPs:

Level 3 Data Validation SOPs:

- DAQ-03-004.5 Thermo Ultimate 3000 UHPLC/UV/MS UAT and PAMS Carbonyl Analysis, RCO Responsibilities
- DAQ-15-006.5 Data Validation Standard Operating Procedures For Continuous Gaseous and Meteorological Monitors
- DAQ-07-001.5 Vaisala Ceilometer Mixing Height Sensor, RCO Responsibilities, currently under development;
- DAQ-09-001.5 Agilent/Markes Auto-GC/FID PAMS Analysis, RCO Responsibilities, currently under development.

D2.2.1 Data Visualization Methods

Graphical techniques permit comparison of concentrations of each PAMS 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 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

More information on these tools and methods is available in Section 10 of Revision 2 of the PAMS TAD. PAMS monitoring agencies will incorporate these tools and methods, as appropriate, in their data validation procedures and specify the checks and comparisons applicable to the given parameter type(s). The processes DAQ will use for data visualization, comparison and validation are detailed in the SOPs listed in section D2.2 above.

D2.2.2 *Statistical Methods*

A critical part in validating data within a dataset and against external (historical and spatial) datasets is to generate simple statistics. As with data visualization tools, DART and DAS software packages include automated screening checks and statistical tools that aid in identifying data that exceed user-defined criteria. Screening checks include performing comparisons of related pairs or groups of parameters and identifying situations where criteria such as ratios, sums, and presence or absence of parameters deviate from expected relationships or conditions.

D2.2.3 *Examination of Supporting Data*

Comprehensive 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. As part of Level 1 validation activities, validators will review these supporting data sources and verify compromised data are appropriately flagged or invalidated, as appropriate:

Technical Systems Audit Reports: TSAs may uncover nonconformances 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 speciated VOCs data impacted during that time period would likely be invalidated. 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 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 or reprocess data, or if the error cannot be corrected, to invalidate the affected data. For example, an ADQ may identify that the nominal concentration was incorrectly input as 3.91 instead of 3.19 ppbC input to generate calibration standards for benzene. Such a situation could probably be corrected, and the data reprocessed with an updated calibration curve for the parameters on the higher molecular weight hydrocarbon channel (PDMS column) of the auto-GC.

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, and may qualify or invalidate affected data based on the severity and scope of the nonconformance. For example, an IPA identifies a flow rate 15% higher than the flow transfer standard for a carbonyls sampling unit. After further evaluation, if the audit proves to be valid, and the sampler flow rate is beyond the acceptance criterion, the monitoring agency would either estimate the associated results with a QA qualifier or invalidate measurement data back to the most recent passing flow check and invalidate the sample data from that sampling unit when reporting to AQS.

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 pairs will be minimally qualified when precision acceptance criteria are exceeded, unless a technically justifiable rationale is determined and documented (such as one of the two cartridges became disconnected during the sampling event). If a systemic problem is found to be the root cause, affected data may be qualified or invalidated. For example, if collocated carbonyls samples exceed precision acceptance criteria and corrective action uncovers a leak in the primary sampling unit inlet, the data from the primary samples would be invalidated back to the most recent acceptable precision pair.

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. The monitoring agency will use its best judgment about the impact of site conditions on the acceptability of the data and may consult with the EPA PAMS Regional Representative.

Corrective Action Reports: Data validators will review corrective action reports, 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 the monitoring agency to correct the data where possible (e.g., if a wind direction sensor is installed 180° out of phase), 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, the monitoring agency will identify compromised data within AQS by addition of a qualifier or combination of qualifiers. Qualifiers associated with PAMS 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 B5-4 for carbonyls and B5-2 for speciated 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. If reported to AQS, data generated from routine QC checks (except auto-GC system blanks), calibration, determination of MDLs, or instrument troubleshooting for continuous measurement methods will be coded with a Null qualifier to ensure it is not inadvertently reported as ambient data. Invalid data are reported to AQS with a Null (NULL) Code Qualifier which eliminates the associated measurement parameter 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 PAMS

| Qualifier Code | Qualifier Description | Qualifier Type | Comment |
|----------------|--|----------------|---|
| 1 | Deviation from a CFR/Critical Criteria Requirement | QA | substitute a more descriptive QA qualifier where possible |
| 2 | Operational Deviation | QA | substitute a more descriptive QA qualifier where possible |
| 3 | Field Issue | QA | substitute a more descriptive QA qualifier where possible |

| Qualifier Code | Qualifier Description | Qualifier Type | Comment |
|----------------|--|----------------|---|
| 4 | Lab Issue | QA | substitute a more descriptive QA qualifier where possible |
| 5 | Outlier | QA | |
| 7 | Below Lowest Calibration Level | QA | |
| DI | Sample was diluted for analysis | QA | applies to carbonyls only |
| EH | Estimated; Exceeds Upper Range | QA | |
| FB | Field Blank Value Above Acceptable Limit | QA | |
| HT | Sample pick-up hold time exceeded | QA | applies to carbonyls only |
| LB | Lab blank value above acceptable limit | QA | applies to carbonyls only |
| LJ | Identification Of Analyte Is Acceptable; Reported Value Is An Estimate | QA | most common qualifier when an estimate is needed |
| 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 | rare – in most situations such data should be invalidated |
| QX | Does not meet QC criteria | QA | |
| SQ | Values Between SQL and MDL | QA | |
| SS | Value substituted from secondary monitor | QA | rare – most sites will not have collocated instruments |
| SX | Does Not Meet Siting Criteria | QA | should require invalidation, but no associated null code exists |
| TB | Trip Blank Value Above Acceptable Limit | QA | applies to carbonyls only |
| TT | Transport Temperature is Out of Specs. | QA | applies to carbonyls only |
| V | Validated Value | QA | |
| VB | Value below normal; no reason to invalidate | QA | |
| AC | Construction/Repairs in Area | NULL | |
| AD | Shelter Storm Damage | NULL | |
| AE | Shelter Temperature Outside Limits | 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 | should be used in situations where the 75% of the hour is not met or the sampling period for VOCs is not 40 minutes |
| AM | Miscellaneous Void | NULL | substitute a more descriptive code where possible |
| AN | Machine Malfunction | NULL | |
| AP | Vandalism | NULL | |
| AQ | Collection Error | NULL | |
| AR | Lab Error | NULL | |
| AS | Poor Quality Assurance Results | NULL | substitute a more descriptive QA qualifier where possible |
| 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 | used for analysis of the VOCs PT sample & TTP audit for ozone & NO ₂ |

| Qualifier Code | Qualifier Description | Qualifier Type | Comment |
|----------------|--|----------------|--|
| BA | Maintenance/Routine Repairs | NULL | |
| BB | Unable to Reach Site | NULL | |
| BE | Building/Site Repair | NULL | |
| BH | Interference/co-elution/misidentification | NULL | applies to auto-GC parameters only |
| BI | Lost or damaged in transit | NULL | applies to carbonyls only |
| 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 | applies to carbonyls only |
| SC | Sampler Contamination | NULL | |
| TC | Component Check & Retention Time Standard | NULL | |
| TS | Holding Time Or Transport Temperature Is Out Of Specs. | NULL | recommend use of "HT" QA qualifier instead |
| XX | Experimental Data | NULL | used for troubleshooting, instrument conditioning, MDL determination, etc. |
| IC | Chem. Spills & Indust Accidents | INFORM | rare |
| ID | Cleanup After a Major Disaster | INFORM | rare |
| IE | Demolition | INFORM | rare |
| IH | Fireworks | INFORM | rare |
| II | High Pollen Count | INFORM | rare |
| IJ | High Winds | INFORM | rare, may apply to wind speed and direction data |
| IK | Infrequent Large Gatherings | INFORM | rare |
| IM | Prescribed Fire | INFORM | rare |
| IP | Structural Fire | INFORM | rare |
| IQ | Terrorist Act | INFORM | rare |
| IR | Unique Traffic Disruption | INFORM | rare |
| IS | Volcanic Eruptions | INFORM | rare |
| IT | Wildfire-U. S. | INFORM | rare |
| J | Construction | INFORM | rare |

D2.2.4.2 [Corrective Action Process](#)

The monitoring agency'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.

D2.2.4.3 [Notification of EPA or Other Stakeholders](#)

For serious or systematic problems impacting data, individuals within the monitoring agency responsible for determining the impact of the data and determining the validation status of the data will be notified. Stakeholders and users of the data that might be impacted by the validation status will also be notified. Monitoring agencies will contact the EPA PAMS Regional Representative who may themselves notify or may instruct the monitoring agency to notify the PAMS Program and EPA PAMS QA Leads to provide documentation of corrective actions affecting the status of a significant amount of reportable data. Such would be the case if the data impacted represented 10% of the season's data or jeopardized the ability to meet the completeness MQO. These stakeholders will also be notified when corrective actions have been

completed and return to conformance has been demonstrated. Monitoring agencies will include significant problems in their annual QA reports to management.

D3 Reconciliation with User Requirements

D3.1 Reconciling Results with DQOs

The DQOs and intended uses for the PAMS Required Site Network data are discussed in Section A7.1. The DQO for the PAMS Required Site Network is to provide a database of ozone precursors and associated meteorology data that modelers can use to evaluate ozone prediction models. The MQOs listed in Section A7.3 were established to provide the expected data quality modelers need. Following the first year of PAMS Required Site measurement data collection, it is expected that EPA modelers will evaluate the quality and suitability of the data and may request revisions to the MQOs which may involve increasing sensitivity, decreasing bias, or increasing precision, for example. Any such adjustments will be communicated to the PAMS Required Site Network stakeholders.

After the first full year of PAMS Required Site data collection, EPA will perform a DQA to assess and characterize the overall network data quality. EPA will prepare a report aggregating the PAMS QA/QC data for the year which may be combined with EPA modelers' data quality and suitability evaluation. The report will attempt to determine whether the PAMS Required Site DQOs are being achieved and whether revisions to the program and QS are needed. Monitoring agencies will perform a DQA for each of their PAMS sites to evaluate the site's attainment of the specified MQOs. Monitoring agencies will include a description of their DQA and the outcomes in the annual QA report described in Section D2.2.4.3.

D3.2 Interim Corrective Actions

EPA may review PAMS QA/QC data and collected measurements during the first year of the PAMS Required Site network operation. If such an interim assessment indicates that the stated MQOs need to be adjusted to meet the intended use, EPA may revise the sampling design for the PAMS Required Site Network, which may include revising site selection, sampling frequency, QC measurements frequency and acceptance criteria, and equipment maintenance frequency. Changes in MQOs may result in the need to adjust PAMS monitoring procedures during implementation of the program.

REVISION HISTORY

1. Revision 0 – **BDV** 03/12/2021 Initial Publication and Adaptation
2. Revision 1 – **SJW** 12/7/2022 Modifications detailed in green highlighted text throughout the document. Also, the document headers were re-formatted and re-organized to make the document read easier.

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<http://www3.epa.gov/ttn/naaqs/standards/ozone/data/20150925cavender.pdf>
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<https://www3.epa.gov/ttnamti1/pamsguidance.html>

APPENDIX A

EXAMPLE QUALITY BULLETIN FORM

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 bulletin until further notice | <input type="checkbox"/> |
| Discard this bulletin after noting contents | <input type="checkbox"/> |
| This bulletin 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

LAB DNPH CARTRIDGE CHAIN-OF-CUSTODY FORM

DNPB CARTRIDGE SAMPLE CHAIN OF CUSTODY FORM FOR NATTS and PAMS REQUIRED SITES

| Sample ID | Pre-sample Storage | Sample Type | Sample Start (Date and Time) | Sample Stop (Date and time) | Sample Shipment Method | Sample Storage at Laboratory |
|-----------|--------------------|-------------|------------------------------|-----------------------------|------------------------|------------------------------|
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| Relinquished by: | Date/Time: | Received by: | Date/Time: |
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Form # DAQ-16-008
 Revision 0
 Effective Date: 01-01-2021

APPENDIX C

UAT and PAMS DNPH CARTRIDGE SAMPLER INFORMATION FORM

| North Carolina Division of Air Quality Laboratory Analysis Branch | | | | | |
|--|--|--------------------------|--|--|--------------------|
| Cartridge Chain of Custody Form | | | | | |
| NC DAQ Laboratory Analysis Branch: 4403 Reedy Creek Road, Raleigh, NC 27607 Phone: (919)-733-9777 | | | | | |
| Revision 0, Effective: 5/1/2020 | | | | | |
| Laboratory Setup Information | | | | | |
| 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 CATRIDGE LOT BLANK | | | | | |
| Sampling Site: | | | Sample # | | |
| DNPH Cartridge Lot#: | | | Scheduled Sampling Date: | | |
| Lab setup by (initial & date): | | | | | |
| Field Setup Information | | | | | |
| Sampler SN or FAS#: | | | Site Operator (initials, date & time of setup): | | |
| Sampler Expiration Date: | | | NIST Device Date and Time: | | |
| As Found Sampler Display Date & Time: | | | AS Left Sampler Display Date, Time: (if adjustment made) | | |
| Time Difference (mins): | Time Difference >5 minutes? Yes No | | | | |
| NIST Flow Standard (Type, SN, Exp. Date): | | | Measured Pre Sample Flow Rate (L/min): | Acceptable Range (0.9 L/min - 1.1 L/min) | |
| DNPH "Sample" Cartridge Scheduled Sampling Date/Time: | | | Leak Check Pass? (Circle One): | Yes No | Leak Rate (L/min): |
| Acceptable Range (< 0.01 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 Device (SN / Exp. Date): | | | Measured Post Sample Flow Rate (L/min): | | |
| Field Comments: | | | | | |
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| Laboratory Receipt/Login Information | | | | | |
| Sample Received by: | | | Sample Receipt Temperature (°C): | | |
| Date and Time Sample Received: | | | | | |
| Laboratory Comments: | | | | | |
| | | | | | |
| Extraction Date: | | Extracted by (initials): | | Extraction Manifold Port Number: | |

APPENDIX D

DAQ Forms DAQ-16-004, DAQ-16-022, DAQ-16-019, and DAQ-16-007

PAMS Required Site Training Form (DAQ-16-004) page 1 of 2

DAQ-16-004: DAQ PAMS REQUIRED SITE TRAINING FORM

Revision 2 4/08/21

Staff Member _____

The staff member has read the following PAMS Required Site quality system documents:

| Document | Version and Effective Date | Date Read/Initials | Version and Effective Date | Date Read/Initials |
|---|----------------------------|--------------------|----------------------------|--------------------|
| DAQ-01-007: Monitoring Agency PAMS Required Site QAPP | | | | |
| DAQ-09-001.2: Agilent/Marke's Auto-GC/FID PAMS Analysis Operator Responsibilities | | | | |
| DAQ-09-002.1: ATEC 8000 PAMS Aldehyde Sampler ECB Responsibilities | | | | |
| DAQ-09-002.2: ATEC 8000 PAMS Aldehyde Sampler Operator Responsibilities | | | | |
| DAQ-09-001.5: Agilent/Marke's Auto-GC/FID PAMS Analysis Data Validation | | | | |
| DAQ-08-001.1: Model T500U Nitrogen Dioxide (NO ₂) Monitoring System ECB Responsibilities | | | | |
| DAQ-08-001.2: Model T500U Nitrogen Dioxide (NO ₂) Monitoring System Operator Responsibilities | | | | |
| DAQ-07-001.1: Vaisala Ceilometer Mixing Height Sensor ECB Responsibilities | | | | |
| DAQ-07-001.2: Vaisala Ceilometer Mixing Height Sensor Operator Responsibilities | | | | |
| DAQ-07-001.5: Vaisala Ceilometer Mixing Height Sensor RCO Responsibilities | | | | |
| DAQ-07-003.1: MetOne AIO2 All-in-One Met Sensor ECB Responsibilities | | | | |
| DAQ-07-003.2: MetOne AIO2 All-in-One Met Sensor Operator Responsibilities | | | | |
| DAQ-07-008.1: Solar Radiation Sensors ECB Responsibilities | | | | |
| DAQ-07-008.2: Solar Radiation Sensors Operator Responsibilities | | | | |
| DAQ-07-009.1: Kipp & Zonen CUV-5 UV Sensor ECB Responsibilities | | | | |
| DAQ-07-009.2: Kipp & Zonen CUV-5 UV Sensor Operator Responsibilities | | | | |
| DAQ-07-004.1: MetOne 370D Tipping Bucket Rain Gauge ECB Responsibilities | | | | |
| DAQ-07-004.2: MetOne 370D Tipping Bucket Rain Gauge Operator Responsibilities | | | | |
| DAQ-05-001.5 Envista Database Management Procedures | | | | |
| DAQ-03-004.2: Thermo Ultimate 3000 UHPLC/UV/MS NATTS and PAMS Aldehyde Analysis Operator Responsibilities | | | | |

PAMS Required Site Training Form (DAQ-16-004) page 2 of 2

DAQ-16-004: DAQ PAMS REQUIRED SITE TRAINING FORM **Revision 2 4/08/21**

Staff Member _____

The staff member has read the following PAMS Required Site quality system documents:

| Document | Version and Effective Date | Date Read/Initials | Version and Effective Date | Date Read/Initials |
|---|-----------------------------------|---------------------------|-----------------------------------|---------------------------|
| DAQ-03-004.5: Thermo Ultimate 3000 UHPLC/UV/MS NATTS and PAMS Aldehyde Analysis Data Validation | | | | |
| 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 Diluter ECB Responsibilities | | | | |
| DAQ-03-006.2: Entech 4700 Precision Diluter Operator Responsibilities | | | | |
| DAQ-13-001.1: BGI TetraCal Flow Transfer Standards ECB Responsibilities | | | | |
| DAQ-13-002.1: DryWell 3101 Temperature Generator ECB Responsibilities | | | | |
| DAQ-14-001.5 SOP on Preparing SOPs | | | | |
| DAQ-14-002.5 SOP and QAPP Tracking Database | | | | |
| DAQ-14-003 Records Retention and Archival Policies | | | | |
| DAQ-15-002: Corrective Action Process | | | | |
| DAQ-15-003: Training | | | | |
| DAQ-15-004.5 PAMS Shakedown Audits and TSAs | | | | |
| DAQ-15-006.5 Data Validation Standard Operating Procedures for Continuous Gaseous and Meteorological Monitors | | | | |
| Other SOPs as defined by the monitoring agency: | | | | |
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DAQ Continuing Demonstration of Capability (DAQ-16-019)

DAQ-16-019: DAQ CONTINUING DEMONSTRATION OF CAPABILITY

Trainee _____ Trainer _____

Once the IDOC is completed, the trainee will read the current version of the SOP governing the procedure(s) and complete a continuing demonstration of capability (CDOC) which will include performance of the procedure(s) independently under the observation of a QA staff member, supervisor, or other trained staff member (i.e., the Trainer).

| Procedure (list the SOP or a description of the activity) | Date Trainee Performed Procedure(s) Independently Under Observation | Approval by Trainer to Perform Procedure Independently |
|---|---|--|
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Revision 1

1/21/2022

APPENDIX E

GUIDANCE FOR PAMS MONITORING AGENCIES TO INCORPORATE PAMS REQUIREMENTS INTO ANNUAL MONITORING NETWORK PLANS

Guidance for 1) Photochemical Assessment Monitoring Stations (PAMS) Required Network Implementation Plans (and waivers), and 2) Enhanced Monitoring Plans (EMPs).

This guidance and the following two attachments represent templates for consideration for implementation plans for the (1) Required Monitoring Network PAMS site (at certain NCore sites) and (2) for the EMPs required for moderate or higher nonattainment areas (NA) and states within the Ozone Transport Region (OTR). These templates should help in the development of implementation plans that should be included in the annual monitoring network plan as required by 40 CFR 58.10.

For higher population NCore sites (i.e., those in Core Based Statistical Areas (CBSAs) greater than 1,000,000), the Required Monitoring Network Implementation Plan must include the final site location, the types of instruments to be installed, and frequency of measurements that will be made. The Required Monitoring Network Implementation Plans should state the methods and procedures that will be followed as stipulated in the final PAMS rule, national PAMS Quality Assurance Program Plans (QAPP), and the PAMS Technical Assistance Document (TAD). The expected auto gas chromatograph (GC) monitoring systems will require a level of expertise which may not be currently available to monitoring agencies. Early planning is crucial to meeting deployment and measurement deadlines.

The final ozone national ambient air quality standards (NAAQS) rule has waiver provisions which allow monitoring organizations which have low concentrations of ozone (as defined in the rule) to request a waiver from implementing PAMS at an otherwise required NCore site entirelyⁱ, or to make PAMS measurements at alternative locations such as existing PAMS sites or existing National Air Toxics Trends Station (NATTS) sitesⁱⁱ. In addition, while it is expected that auto GCs will be used for VOC measurements in order to report hourly measurements, there is an opportunity to seek a waiver and instead collect three 8-hour canister samples, once every three daysⁱⁱⁱ. In addition, a monitoring organization may request that it utilize data from a nearby meteorological station rather than establish its own^{iv}. Monitoring organizations must request a waiver from any deviation described above. The waivers will be in the form of a one- or two-page technical memo that describes the need and rationale for the waiver, and any other requisite supporting information including alternative locations (such as existing PAMS sites), and/or proposed alternative measurement procedures (see end notes to this memo in this regard). The waiver will be submitted to the EPA Regional Administrator for review and approval. Waivers may be submitted with the required Annual Monitoring Network Implementation Plan or as a standalone document, if agreed to by the local EPA Regional Office.

- Monitoring organizations should submit the draft Implementation Plan for required PAMS locations and any waivers to EPA Regional Offices by May 1, 2017, along with their draft Annual Monitoring Network Plan (AMNP). This will ensure that a 30 day public notice is provided, and EPA may provide comments during that time. Final Implementation Plans should be submitted by July 1, 2017, along with the AMNP.

NOTE: The regulation requires that the draft Implementation Plans be submitted by July 1, 2018; however, in order to be operational by June 1, 2021, it is recommended that the organizations submit their Implementation Plans by May 1, 2017.

- As with all AMNPs, the EPA Regions will have 120 days to review the waivers and the proposed PAMS Implementation Plans, and provide a formal response to the state's plan (and waiver if proposed), no later than October 31, 2017 (Based on the submission of the final AMNP by July 1, 2017).

All O₃ moderate (and worse) NA areas and states in the OTR must develop and implement EMPs. These EMPs must include the final site location, the types of instruments to be installed, and the frequency of measurements that will be made at the site. They should also identify the rationale for proposed measurements, and in the case of EMP sites within the OTR, must take into account interstate and interregional transport of ozone and ozone precursors.

- Monitoring organizations should submit the draft EMPs for areas in the OTR and moderate NAs to EPA Regional Offices by May 1, 2018, along with their draft AMNP. This will ensure that a 30-day public notice is provided, and the EPA can provide comments during that time. Final EMPs should be submitted by July 1, 2018, along with the AMNP.

NOTE: The regulation requires these EMPs be submitted by October 1, 2019 (or two years following the effective date of a designation to a classification of Moderate or above O₃ NA whichever is later). We recognize that some areas may not know if they are moderate nonattainment areas until after that date, and the dates described here may need to be pushed back by exactly one year to accommodate that possibility. However, for areas in the OTR, to ensure (possible) continuity of existing measurements, and for a variety of other logistical and programmatic considerations, we recommend this earlier submittal date of July 1, 2018.

- As with all AMNPs, the EPA Regions will have 120 days to review the proposed EMPs, and provide a formal response to the state's plan, no later than October 31, 2018. (Based on the submission of the final AMNP by July 1, 2018).

While not a comprehensive list, EMP may include: additional O₃ sites; additional NO_x or NO_y sites; additional VOC/carbonyl measurements (different time periods, different locations and different precursors); or enhanced upper air measurements. EPA encourages that all EMPs be developed in consideration of and in coordination with other nearby PAMS/ EMPs. In the OTR, EPA intends that this coordination should occur and include all states in the OTR. For the states in the OTR, EPA encourages a comprehensive EMP with well-defined objectives.

References

ⁱ Appendix D of 40 CFR Part 58, 5(f) allows an otherwise required NCore site from implementing PAMS if the ozone design value is less than 85% of the NAAQS, and the area is not considered important regarding upwind or downwind nonattainment areas. States/ locals which have such an area should consult with the local EPA Regional Office. Such an area would need to submit a request to the EPA Regional Administrator and include a discussion of design values in the area, and all areas nearby- including a discussion of the closest ozone nonattainment area(s), and its relationship (or lack thereof) to air quality in the area seeking a waiver. That request should be part of the AMNP described above, and EPA would approve (or disapprove) the request when it acts on the AMNP. Any alternative method of seeking such a waiver should be agreed with the appropriate EPA Regional Office.

ⁱⁱ Appendix D of 40 CFR Part 58, 5(c) allows for the collection for required PAMS measurements at an alternative location. For areas considering such a request, it must be demonstrated that the alternate location will provide representative and useful data for regional or national tracking of trends in ozone precursors. For example, it may be a nearby location that has measured PAMS compounds in the past, and could be beneficial from a trends perspective. Any request should meet the specific requirements of the rule, be included in the AMNP, and to be acceptable, be approved by the EPA Regional Administrator.

ⁱⁱⁱ Appendix D of 40 CFR Part 58, 5(d) provides that the EPA Regional Administrator may grant a waiver from continuous VOC measurements to allow for speciated VOC measurement as three- 8 hour averages on every third day during the ozone season. EPA will consider waivers where precursor concentrations are low, or for other logistical or programmatic constraints. In considering approval of a waiver, the EPA Regional Administrator will consider the ability to compare and utilize other nearby PAMS (and EMP) locations to ensure the data collected can be used in a useful manner. Any request should meet the specific requirements of the rule, be included in the AMNP, and to be acceptable, be approved by the EPA Regional Administrator.

^{iv} Appendix D of 40 CFR Part 58, 5(e) provides that the EPA Regional Administrator may grant a waiver allowing representative meteorological data from nearby monitoring stations to be used to meet the meteorological measurements required. To be acceptable, a request must provide for the location of the alternative measurements, a detailed description of the appropriateness and representativeness of the location relative to PAMS location, assurance that the data will always be available, and ensure that the data meet appropriate EPA quality assurance requirement for those measurements. Any request should meet the specific requirements of the rule, be included in the AMNP, and to be acceptable, be approved by the EPA Regional Administrator.

PAMS Monitoring Implementation Network Plan

Example Monitoring Organizations Required to Operate at NCore Sites

(Insert monitoring organization) formerly operated two Photochemical Assessment Monitoring Stations (PAMS) sites in the air monitoring network in 2015, at the *(Insert Location)* and *(Insert Location)* sites. However, the recently revised monitoring rule (80 FR 65292; October 26, 2015) requires PAMS measurements June 1 through August 31 at NCore sites that are located in Core-Based Statistical Areas (CBSAs) with populations of 1,000,000 or more.

Network Decision

- The NCore site located at *(Insert Location)* will serve as the location of the required PAMS site and will measure the following parameters described below. An Inventory of equipment used at the site(s) is provided in attachment 2
- We request a waiver from implementing PAMS at an otherwise required NCore site entirely, or to make PAMS measurements at alternative locations such as existing PAMS sites or existing NATTS sites. Rationale for this waiver is provided in Waiver attachment

Auto GC Decision

Volatile organic compounds (VOCs) – A complete list of the targeted compounds are found in Table 1.

- We will measure hourly speciated VOC measurements with an auto-gas chromatograph (GC) using *(insert manufacturer)*.
- We request a waiver to allow three 8-hour samples every third day as an alternative to daily hourly speciated VOC measurements at locations *(insert locations)*. Rationale for this waiver is provided in Waiver Attachment

Meteorology Measurements Decision – Note: EPA is suggesting the use of ceilometers for determining mixing height, however other types of meteorological equipment that provide for an indication of mixing height can be proposed

- Will measure wind direction, wind speed, temperature, humidity, atmospheric pressure, precipitation, solar radiation, UV radiation, and mixing height. We have elected to use the following instrumentation to measure the parameters described above: *(insert equipment models and manufacturer)* .
- We request a waiver to allow meteorological measurements to be obtained from other nearby sites. Rationale for this waiver is provided in Waiver attachment

Other Required Measurements

Carbonyls - Carbonyl sampling at a frequency of three 8-hour samples on a one-in-three day basis (~90 samples per PAMS sampling season) using (*insert sampler and analytical manufacturer*). Sites will be required to measure and report formaldehyde and acetaldehyde and are encouraged to measure and report acetone and benzaldehyde. The TO-11A test method, as used in the National Air Toxics Trends (NATTS) program² will be used.

Nitrogen Oxides – Will monitor for NO and NO_y (total oxides of nitrogen) in addition to true NO₂. The true NO₂ is required to be measured with a direct reading NO₂ analyzer, cavity attenuated phase shift (CAPS) spectroscopy or photolytic-converter NO_x analyzer. We are currently using a Teledyne-Advanced Pollution Instruments T200UP for the true NO₂ measurement. We plan to replace it with a Teledyne Model T500U. NO and NO_y will be measured using a Thermo Electron/ Thermo Environmental Instruments Model 42i-Y.

Table 1 PAMS Target Speciated VOCs List

| Priority Compounds | | Optional Compounds | |
|-------------------------------------|--|------------------------|-----------------------------------|
| 1,2,3-trimethylbenzene ^a | m-ethyltoluene ^a | 1,3,5-trimethylbenzene | isopropylbenzene ^b |
| 1,2,4-trimethylbenzene ^a | n-butane | 1-pentene | m-diethylbenzene |
| 1-butene | n-hexane ^b | 2,2-dimethylbutane | methylcyclohexane |
| 2,2,4-trimethylpentane ^b | n-pentane | 2,3,4-trimethylpentane | methylcyclopentane |
| benzene ^{a,b} | o-ethyltoluene ^a | 2,3-dimethylbutane | n-decane |
| cis-2-butene | o-xylene ^{a,b} | 2,3-dimethylpentane | n-heptane |
| ethane ^c | p-ethyltoluene | 2,4-dimethylpentane | n-nonane |
| ethylbenzene ^{a,b} | propane | 2-methylheptane | n-octane |
| ethylene | propylene | 2-methylhexane | n-propylbenzene ^a |
| isobutane | styrene ^{a,b} | 2-methylpentane | n-undecane |
| isopentane | toluene ^{a,b} | 3-methylheptane | p-diethylbenzene |
| isoprene | trans-2-butene | 3-methylhexane | trans-2-pentene |
| m&p-xylenes ^{a,b} | total non-methane organic carbon (TNMOC) | 3-methylpentane | α/β-pinene |
| | | acetylene | 1,3 butadiene ^b |
| | | cis-2-pentene | carbon tetrachloride ^b |
| | | cyclohexane | ethanol |
| | | cyclopentane | tetrachloroethylene ^b |

Source: Revisions to the Photochemical Assessment Monitoring Stations Compound Target List. U.S. EPA, November 20, 2013

^a Important SOAP (Secondary Organic Aerosols Precursor) Compounds

^b HAP (Hazardous Air Pollutant) Compounds

^c Non-reactive compounds, not considered to be VOC for regulatory purposes

² See NATTS Technical Assistance Document for TO-11A method.

PAMS Monitoring Implementation Network Plan

Example Monitoring Organizations Not Required To Operate At NCore Sites

(Insert monitoring organization) formerly operated (*x#*) Photochemical Assessment Monitoring Stations (PAMS) sites in its air monitoring network in 2015, at the *(Insert Location)* and *(Insert Location)* sites. The recent revised ozone NAAQS rule¹ requires PAMS measurements at NCore sites that are located in Core-Based Statistical Areas (CBSAs) with populations of 1,000,000 or more. Since *(Insert monitoring organization)* NCore sites are located in CBSAs with populations less than one million, this requirement does not apply *(insert monitoring organization)*. (In some cases, a State may have an NCore site that requires PAMS measurements, but additional “Enhanced Monitoring” sites are necessary to adequately characterize the problem.) States with moderate or above ozone non-attainment areas and states within the Ozone Transport Region (OTR) are required to develop and implement Enhanced Monitoring Plans (EMPs). These EMPs are intended to provide monitoring organizations with the flexibility to implement additional monitoring to suit the needs of their area such as, additional ozone, ozone precursor and/or meteorological monitoring activities. (For an area in the OTR- include the following: In developing this plan, we have coordinated with all other States (and DC) in the OTR and EPA Regions 1, 2, and 3. As a contiguous area of interregional transport, we have agreed to the spatial distribution of these monitoring locations, as well as the type and frequency of the air quality (and other measurements) to include.)

(Insert monitoring organization) has determined the EMP measurement options will include (but are not limited to) additional ozone air measurement at *(insert location)*, upper air measurements *(insert location)*, measurements of total VOC or enhanced/reduced amount of VOCs/carbonyl species *(identify)*, additional nitrogen dioxide monitoring *(insert location)*, and additional meteorology/boundary layer measurements. This required EMP reflects local needs within the context of interstate, interregional transport of ozone and ozone precursors.

¹80 FR 65292; October 26, 2015

Attachment 1 Waiver Requests and Rationale

Waiver from implementing PAMS at an otherwise required NCore site (waiver could be either in its entirety, or to be at a different location)

Rationale for this waiver

Auto GC Waiver Request

We request a waiver to allow three 8-hour samples every third day as an alternative to daily hourly speciated VOC measurements at locations (insert locations).

Rationale for this waiver

Meteorological Waiver Request

We request a waiver to allow meteorological measurements to be obtained from other nearby sites.

Rationale for Waiver

Attachment 2 Equipment Inventory

| Region | 4 | |
|---------------------|---|----------------------------|
| State | North Carolina | |
| AQS ID | 37-183-0014 | |
| CBSA | Raleigh-Cary | |
| | | |
| | | |
| Parameter | Category | Detail |
| Site | Is the AQS site ID listed above the expected PAMS Core site location? | Yes |
| | What is the status of the decision for the expected PAMS Core site location (not started, draft, or final)? | Final |
| | Is there an alternate PAMS Core site location selected? | No |
| | Identify type of alternative site (existing PAMS, NATTS, etc) Alternate site AQS ID (if known) | |
| Mixing Height | Is there an existing functional ceilometer or others similar instrument available for use? | No |
| | current location (at future PAMS Core site, at other site, not applicable) | |
| | instrument type (ceilometer, radar profiler, etc) | Ceilometer |
| | manufacturer | Vaisala |
| | model | CL51 |
| | date purchased | 2020 |
| | comments | |
| Auto GC | Is there an existing Auto GC available for use? | Yes |
| | current location (at future PAMS Core site, at other site, not applicable) | At Site |
| | manufacturer | Agilent/Marke |
| | model | 7890B dual FID Unity TD |
| | date purchased | 2017 |
| | Does it have a service contract? | Yes |
| | comments | |
| True NO2 | Is there an existing true NO2 instrument available for use? | Yes |
| | current location (at future PAMS Core site, at other site, not applicable) | |
| | instrument type (photolytic conversion, cavity ringdown, CAPS, etc) | CAPS |
| | manufacturer | API Teledyne |
| | model | T500IT |
| | date purchased | 2020 |
| | comments | |
| Carbonyls Sampling | Is there an existing sequential carbonyls sampling unit or similar instrument available for use? | Yes |
| | current location (at future PAMS Core site, at other site, not applicable) | Installed at PAMS site |
| | manufacturer | Atek |
| | model | 8000 |
| | date purchased | 2020 |
| | comments | |
| Carbonyls Analysis | Does the site currently have a support laboratory for carbonyls or plans to use a support laboratory? | Yes, in house |
| | laboratory name | Laboratory Analysis Branch |
| | comments | Thermo Ultimate 3000 UHPLC |
| Barometric Pressure | instrument type (aneroid barometer, etc) | Piezoresistive silicon |
| | manufacturer | MetOne |
| | model | AIO2 |
| | date purchased | 2020 |
| | comments | |
| UV Radiation | instrument type (UV radiometer, etc) | UV Radiometer |
| | manufacturer | Kipp & Zonana |
| | model | CUV-5 |
| | date purchased | 2020 |
| | comments | |
| Solar Radiation | instrument type (pyranometer, etc) | pyranometer |
| | manufacturer | MetOne |
| | model | Li-200R |
| | date purchased | |
| | comments | |
| Precipitation | instrument type (tipping bucket, weighing, etc) | Tipping Bucket Rain Gauge |
| | manufacturer | MetOne |
| | model | 370D |
| | date purchased | |
| | comments | |

APPENDIX F

LIST OF DAQ STANDARD OPERATING PROCEDURES

Table F-1. List of Standard Operating Procedures Used for PAMS Monitoring

| DAQ Document Number | SOP Title | Brief Summary |
|---------------------|--|---|
| DAQ-09-001.2 | Agilent/Marke's Auto-GC/FID PAMS Analysis Operator Responsibilities | Instrument Installation, Calibration, Operation, Data Entry, and Level 1 and 2 Data Review |
| DAQ-09-002.1 | ATEC 8000 PAMS Sequential Carbonyl Sampler ECB Responsibilities | Sampler Installation, Calibration, and Certification |
| DAQ-09-002.2 | ATEC 8000 PAMS Sequential Carbonyl Sampler Operator Responsibilities | Sampler Operation, COC form completion |
| DAQ-03-004.2 | Thermo Ultimate 3000 Ultra High-Performance Liquid Chromatography by Ultra-Violet Radiation and Mass Spectrometry (UAT and PAMS Carbonyl Analyses) Operator Responsibilities | Instrument Operation, Calibration, Cartridge Handling, Cartridge COC, Cartridge Extraction, Data Entry, and Level 1 and 2 Data Review |
| DAQ-03-004.5 | Thermo Ultimate 3000 UHPLC-UV-MS Urban Air Toxics (UAT) and Photochemical Assessment Monitoring Station (PAMS) Carbonyl Analysis Instrument | Level 3 Data Validation |
| DAQ-03-005.1 | Entech 3100A Canister Cleaning System | Installation and maintenance of the Entech 3100A Canister Cleaner used to clean 6-L Silco-treated Summa canisters used to Make ICAL and QC standards for the PAMS VOC Analytical Instrument |
| DAQ-03-005.2 | Entech 3100A Canister Cleaning System | Canister Cleaning of Silco Canister Used to Make ICAL and QC standards for the PAMS VOC Analytical Instrument |
| DAQ-03-006.1 | Entech 4700 Static Dilution System | Installation and maintenance of the Entech 4700 Precision Diluter used to make ICAL and QC standards for the PAMS Agilent/ Marke's Auto-GC/FID Analytical Instrument |
| DAQ-03-006.2 | Entech 4700 Static Dilution System | Operation of equipment used to make ICAL and QC standards for the PAMS Agilent/ Marke's Auto-GC/FID Analytical Instrument |
| DAQ-05-001.5 | Envista Database Management Procedures | Handling of the Envista database by the database manager |
| DAQ-07-001.2 | Vaisala Ceilometer Mixing Height Sensor Operator Responsibilities | Instrument Operation, Data Entry, and Level 1 and 2 Data Review |

Table F-1. List of Standard Operating Procedures Used for PAMS Monitoring

| DAQ Document Number | SOP Title | Brief Summary |
|---------------------|---|--|
| DAQ-07-003.1 | MetOne AIO2 All-in-One Met Sensor ECB Responsibilities | Instrument Certification, Installation, CTS Auditing, Mfg. Calibration |
| DAQ-07-003.2 | MetOne AIO2 All-in-One Met Sensor Operator Responsibilities | Instrument Operation, Data Entry, and Level 1 and 2 Data Review |
| DAQ-07-004.1 | MetOne 370D Tipping Bucket Rain Gauge ECB Responsibilities | Instrument Certification, Installation, Auditing/Calibration |
| DAQ-07-004.2 | MetOne 370D Tipping Bucket Rain Gauge Operator Responsibilities | Instrument Operation, Data Entry, and Level 1 and 2 Data Review |
| DAQ-07-008.1 | Solar Radiation Sensors ECB Responsibilities | Instrument Certification, Installation, Auditing, Mfg. Calibration |
| DAQ-07-008.2 | Solar Radiation Sensors Operator Responsibilities | Instrument Operation, Data Entry, and Level 1 and 2 Data Review |
| DAQ-07-009.1 | Ultraviolet Radiation Sensor ECB Responsibilities | Instrument Certification, Installation, Auditing, Mfg. Calibration |
| DAQ-07-009.2/3 | Eppley CUV-5 Ultra-Violet (UV) Sensor Operator/Coordinator Responsibilities | Instrument Operation, Data Entry, and Level 1 and 2 Data Review |
| DAQ-13-001.1 | BGI TetraCal Flow Transfer Standards ECB Responsibilities | Instrument Calibration and Certification |
| DAQ-13-002.1 | DryWell 3101 Temperature Generator ECB Responsibilities | Instrument Calibration and Certification |
| DAQ-14-001 | SOP on Preparing SOPs | Procedures on how to develop DAQ SOPs |
| DAQ-14-002.5 | QAPP and SOP 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 | DAQ process for conducting and documenting training |
| DAQ-15-004.5 | PAMS Shakedown Audits and TSAs | DAQ process for conducting PAMS annual shakedown audits and internal technical systems audits |
| DAQ-15-006.5 | Data Validation Standard Operating Procedures For Continuous Gaseous and Meteorological Monitors | DAQ process for validating data from gaseous monitors and meteorological sensors that operate continuously |

APPENDIX G 2021 COLLOCATED TRANSFER STATION (CTS) AUDIT RESULTS (AIO2 vs. AIO2 vs. AIO2)

Initial CTS audits results and initial acceptance limits (bias and precision) applied to 2021 CTS audit between three AIO2 sensors collecting meteorological data in triplicate at the Millbrook PAMS site.

Millbrook Test AIO2 sensor VS. MillbrookCTS AIO2 sensor. Date range of meteorological data used (8/16/2021 to 8/23/2021). All data for AT, RH, and BP were hourly average values. All data for WS and WD were hourly vector average values.

| MillbrookTest AIO2 - MillbrookCTS AIO2 8/16/2021 12:00 AM-8/23/2021 11:00 PM Type: AVG 1 Hr. | | | | | | |
|--|---------|-------------|---------|---------|---------|---------|
| Comment | WD Diff | WD corrDiff | WS Diff | AT Diff | RH Diff | BP Diff |
| Parameter = | NA | WD | WS | AT | RH | BP |
| # of Data Points (must be > 48) = | | 74 | 74 | 74 | 74 | 74 |
| Measured Bias (AVG Difference) = | NA | 9.55 | -0.03 | 0.17 | -2.70 | 0.26 |
| Measured Precision (Standard deviation) = | NA | 6.85 | 0.22 | 0.05 | 0.31 | 0.29 |
| Unit = | | degrees | m/s | °C | % | mb |
| Bias Limits (+/-) = | NA | 10.00 | 1.00 | 1.00 | 10.00 | 2.00 |
| Precision Limits (+/-) = | NA | 5.00 | 0.50 | 0.50 | 5.00 | 1.00 |
| | | | | | | |

MLLBRK2 AIO2 sensor VS. MillbrookCTS AIO2 sensor. Date range of meteorological data used (8/16/2021 to 8/23/2021). All data for AT, RH, and BP were hourly average values. All data for WS and WD were hourly vector average values.

| MLLBRK2 AIO2 - MillbrookCTS AIO2 8/16/2021 12:00 AM-8/23/2021 11:00 PM Type: AVG 1 Hr. | | | | | | |
|--|---------|-------------|---------|---------|---------|---------|
| Comment | WD Diff | WD corrDiff | WS Diff | AT Diff | RH Diff | BP Diff |
| Parameter = | NA | WD | WS | AT | RH | BP |
| # of Data Points (must be ≥ 48) = | | 80 | 80 | 80 | 80 | 80 |
| Measured Bias (AVG Difference) = | NA | 9.88 | 0.09 | -0.20 | 1.23 | 0.25 |
| Measured Precision (Standard deviation) = | NA | 6.32 | 0.18 | 0.11 | 0.75 | 0.30 |
| Unit = | | degrees | m/s | °C | % | mb |
| Bias Limits (+/-) = | NA | 10.00 | 1.00 | 1.00 | 10.00 | 2.00 |
| Precision Limits (+/-) = | NA | 5.00 | 0.50 | 0.50 | 5.00 | 1.00 |
| | | | | | | |

MLLBRK2 AIO2 sensor VS. **Millbrook Test AIO2** sensor. Date range of meteorological data used (8/16/2021 to 8/23/2021). All data for AT, RH, and BP were hourly average values. All data for WS and WD were hourly vector average values.

| MLLBRK2 AIO2 - MillbrookTest AIO2 8/16/2021 12:00 AM-8/23/2021 11:00 PM Type: AVG 1 Hr. | | | | | | |
|---|---------|-------------|---------|---------|---------|---------|
| Comment | WD Diff | WD corrDiff | WS Diff | AT Diff | RH Diff | BP Diff |
| Parameter = | NA | WD | WS | AT | RH | BP |
| # of Data Points (must be ≥ 48) = | | 74 | 74 | 74 | 74 | 74 |
| Measured Bias (AVG Difference) = | NA | 5.89 | 0.08 | -0.36 | 3.95 | -0.01 |
| Measured Precision (Standard deviation) = | NA | 8.63 | 0.29 | 0.13 | 0.65 | 0.05 |
| Unit = | | degrees | m/s | °C | % | mb |
| Bias Limits (+/-) = | NA | 10.00 | 1.00 | 1.00 | 10.00 | 2.00 |
| Precision Limits (+/-) = | NA | 5.00 | 0.50 | 0.50 | 5.00 | 1.00 |
| | | | | | | |

APPENDIX H 2022 CTS AUDIT RESULTS (AIO2 vs AIO2)

| Site Sensor vs. CTS Sensor | | Limit | Results | PASS/FAIL |
|----------------------------|--------------------|----------|---------|-----------|
| Wind speed | Average | ±1.0 m/s | 0 | PASS |
| | Standard Deviation | ±0.5 m/s | 0.1 | PASS |
| Wind Direction | Average | ±10.0° | 3.7 | PASS |
| | Standard Deviation | ±10.0° | 4.8 | PASS |
| Ambient Temperature | Average | ±0.50°C | -0.04 | PASS |
| | Standard Deviation | ±0.25°C | 0.06 | PASS |
| Barometric Pressure | Average | ±2.0 hPa | -0.8 | PASS |
| | Standard Deviation | ±1.0 hPa | 0.2 | PASS |
| Relative Humidity | Average | ±5.0% | 2.4 | PASS |
| | Standard Deviation | ±2.5% | 0.4 | PASS |

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