



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

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

U.S. Environmental Protection Agency  
Office of Air Quality Planning and Standards  
Air Quality Assessment Division  
Research Triangle Park, NC

Washington State Department of Ecology Publication #21-02-012

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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.

## 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*.

Monitoring of the criteria pollutants O<sub>3</sub> and NO<sub>2</sub> 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 or primary quality assurance organization (PQAO); as such, approved QAPPs governing required monitoring activities will already be available. As the QA requirements for these criteria pollutants are described elsewhere, the scope of this QAPP does not include QA requirements for the measurement of ozone (O<sub>3</sub>) nor the nitrogen oxides NO, NO<sub>x</sub>, and NO<sub>y</sub>. NO and NO<sub>y</sub> are measured by monitoring agencies operating National Core (NCore) sites and will also be covered by an existing QAPP. As true NO<sub>2</sub> is a new parameter specific to PAMS (though some monitoring agencies have replaced or opted for true NO<sub>2</sub> analyzers over NO<sub>x</sub> analyzers), QA requirements for measurement of true NO<sub>2</sub> are covered for monitoring agencies that do not have authority to modify the criteria gas pollutant QAPP to include true NO<sub>2</sub> monitoring at the PAMS monitoring sites. These aspects are detailed in red highlight. Monitoring agencies that cannot refer to an existing QAPP for true NO<sub>2</sub> measurements will adopt the QA aspects of NO<sub>2</sub> monitoring listed; however, monitoring agencies which have addressed QA requirements for true NO<sub>2</sub> monitoring in another QAPP (e.g., a QAPP governing criteria pollutant monitoring) can satisfy the NO<sub>2</sub> monitoring QA requirements by referring to their specific QAPP or QAPPs in those sections highlighted red. Mention or inclusion of O<sub>3</sub> and oxides of nitrogen in this QAPP is in a manner that will not be in conflict with current EPA requirements or the monitoring organizations' approved QAPPs. EPA Regional staff will ensure the QA requirements for true NO<sub>2</sub> measurements are sufficiently covered in the PAMS monitoring QAPP or in the criteria pollutant monitoring QAPP included by reference.

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 highlight. 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 a number of 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.

**Approved by:**

Signature: \_\_\_\_\_ Date: 6/17/21  
Chris Hall, US EPA Region 10 Quality Assurance Coordinator

Signature: \_\_\_\_\_ Date: 07/07/21  
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Signature: \_\_\_\_\_ Date: 6/30/21  
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Signature: \_\_\_\_\_ Date: 6/29/21  
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Signature: \_\_\_\_\_ Date: 6/17/21  
Beth Friedman, Air Quality Program Quality Assurance Coordinator

Signatures are not available on the Internet version

**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: _____ Name: _____	Date: _____
Region 1	Signature: _____ Name: _____	Date: _____
Region 2	Signature: _____ Name: _____	Date: _____
Region 3	Signature: _____ Name: _____	Date: _____
Region 4	Signature: _____ Name: _____	Date: _____
Region 5	Signature: _____ Name: _____	Date: _____
Region 6	Signature: _____ Name: _____	Date: _____
Region 7	Signature: _____ Name: _____	Date: _____
Region 8	Signature: _____ Name: _____	Date: _____
Region 9	Signature: _____ Name: _____	Date: _____
Region 10	Signature: _____ Name: _____	Date: _____



### **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 form in Appendix A 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. The form in Appendix A can also be used for those monitoring agencies that have been delegated QAPP self-approval authority by the EPA Region.

### **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 B) 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:

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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
CCV	continuing calibration verification standard
CDOC	continuing demonstration of capability
CDS	chromatography data system
CFR	Code of Federal Regulations
COC	chain of custody
CRM	certified reference material
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
Ecology	Washington State Department of Ecology
EMP	enhanced monitoring plan
EPA	United States Environmental Protection Agency
ESMB	extraction solvent method blank
FID	flame ionization detector
FEM	Federal Equivalent Method
FEP	fluorinated ethylene propylene
FRM	Federal Reference Method
GC	gas chromatograph
HPLC	high performance liquid chromatograph
IDOC	initial demonstration of capability
IP	implementation plan

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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)
MQO	measurement quality objective
µg	microgram(s)
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 <sub>2</sub>	nitrogen dioxide
NO <sub>y</sub>	total reactive nitrogen
NWS	National Weather Service
O <sub>3</sub>	ozone molecule
OAQPS	Office of Air Quality Planning and Standards
OTR	Ozone Transport Region
PAMS	photochemical assessment monitoring station
PDMS	polydimethylsiloxane
PE	performance evaluation
PFA	perfluoroalkoxy
PGVP	Protocol Gas Verification Program
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
SRM	standard reference material
SSCV	second source calibration verification
TAD	technical assistance document
TNMOC	total non-methane organic carbon
TSA	technical systems audit
TTP	through-the-probe
UHPLC	ultra-high performance liquid chromatograph
UV	ultraviolet
VOC	volatile organic compound

### **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. 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

This plan has been distributed to the individuals currently occupying the organizational roles listed below:

Washington State Department of Ecology

- Quality Assurance Officer, Washington State Department of Ecology, Headquarters, Lacey
- Air Quality Program Deputy Manager, Headquarters, Lacey
- Technical Support Section Manager, Headquarters, Lacey
- Air Monitoring Coordinator, Headquarters, Lacey
- Air Monitoring Quality Assurance Coordinator, Headquarters, Lacey
- NWRO/SWRO & Air Quality Operations Unit Supervisor, Headquarters, Lacey
- IT & Telemetry Unit Supervisor, Headquarters, Lacey
- PAMS Operators, NWRO

EPA Region 10

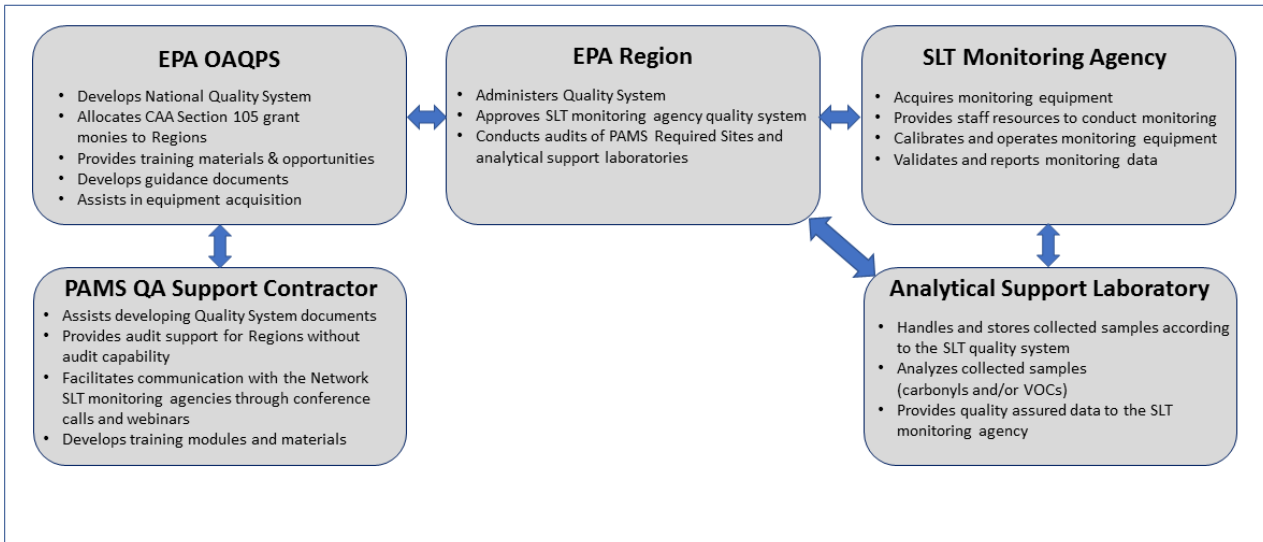
- Air Quality Assurance Coordinator
- Air Monitoring Administrator

### **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 SLT 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
- Managing the performance and PAMS contractual requirements of the National Contract ASL, including:

- Approving QAPPs and SOPs from the National Contract ASL
- Conducting TSAs of the National Contract ASL and overseeing and approving corrective actions resulting from TSAs and/or PTs
- Addressing inquiries and complaints regarding the National Contract ASL communicated by SLT monitoring agencies and/or EPA Regions

OAQPS will utilize a 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 support contractor (per discretion of specific Region)
  - Identifying and communicating audit findings to OAQPS and SLTs
  - Ensuring that SLTs and ASLs develop corrective action plans (CAPs) for audit (TSA and/or PT) findings 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**

Washington State Department of Ecology (Ecology) is responsible for acquiring equipment, providing and training 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. Ecology has the following specific responsibilities:

- Participating in the PAMS Required Site Network Workgroup
- Developing the monitoring agency's PAMS Required Site IP and submitting to the EPA Region
- Reviewing and providing input to the national PAMS QAPP, SOPs, and TAD
- Preparing waivers to PAMS requirements and submitting to the EPA Region, as needed
- Selecting and purchasing instruments to measure PAMS parameters
- Ensuring that the Ecology PQAQO identifies the independent QA personnel that will oversee the QA Program for the Ecology PAMS Required Site monitoring, including:
  - Conducting annual internal audits of field and laboratory activities  
*[note – The national contract ASL will be responsible for ensuring internal audits are conducted at the required frequency per their EPA-approved QAPP.]*
  - 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 (unless the entry is performed by a delegated entity, such as the national contract ASL).
- Developing the Ecology PAMS QAPP and submitting for EPA Regional review and approval
- Reviewing the Ecology PAMS QAPP annually and revising this document as necessary and within 5 years of previous approval
- Developing the Ecology PAMS SOPs and maintaining and revising these documents as necessary and within 5 years of previous approval
- Reviewing SOPs for ASLs that are not part of a national contract 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 ASLs, as appropriate, as negotiated between the monitoring agency and ASL or described in national contracts
- Ensuring personnel attend 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 audits (including TSAs, audits of data quality [ADQs], PEs, and PTs)
- Initiating PAMS monitoring by June 2021.

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

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#### A4.4 Analytical Support Laboratory

The ASL is responsible for analyzing the carbonyls samples the SLT monitoring agency submits. Its responsibilities include, but are not limited to:

- Complying with the PAMS Required Site SLT monitoring agency QAPP  
*[note – the national contract ASL QS will comply with the requirements in this national QAPP per contractual requirements]*
- Performing QA activities
  - Conducting internal audits (such as TSA and ADQ)
  - Participating in the PAMS PT program
- Following an approved SOP for receiving samples, extracting samples, and analyzing sample extracts
  - Notifying the SLT monitoring agency of problems with samples
  - Extracting and analyzing carbonyls samples
  - Maintaining reagents and standards for analyzing carbonyls samples
  - Ensuring instrument and supporting equipment calibrations for carbonyls extraction and analysis
  - Taking corrective action when procedural or acceptance criteria deviations occur
- Reporting sample and QC data to the SLT monitoring agency (unless contracted otherwise)
  - Verifying the laboratory data meet QA and QC acceptance criteria, are correct, are complete, and comply with monitoring agency 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 audits (TSAs, ADQs, and PTs)
- If the ASL is part of the national analytical support laboratory contract (i.e., which typically also serves as the National Air Toxics Trends Stations [NATTS] ASL), developing the laboratory QAPP governing PAMS carbonyls ASL support (which must comply with the requirements in this national model QAPP) and submitting to the OAQPS for approval in a timely manner, implementing the approved QAPP and SOPs, validating data, and reporting required data to AQS per arrangement with Ecology.

#### 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 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 2019 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.<sup>1</sup> The following are the highlights of the changes that occurred to the PAMS program as a result 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 O<sub>3</sub> 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.<sup>2</sup>
- 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 Ozone<sup>1</sup>

**Table A5-1. Required Sites in CBSAs with a Population Greater than 1,000,000<sup>2</sup>**

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

**Table A5-1 (continued). Required Sites in CBSAs with a Population Greater than 1,000,000**

Region	State	AQS ID	CBSA	Population	Existing PAMS?
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
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 so as to increase the likelihood that ozone concentrations will come into attainment with the ozone NAAQS.

**A5.1 Monitoring Agency PAMS Required Site(s)**

This QAPP covers the required PAMS Sites listed in Table A5-2.

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

Site AQS ID	Site Name	Site Location (Address)	County
53-033-0080	Seattle-Beacon Hill	4130 Beacon Ave S Seattle, WA	King
53-033-0057 (solar and UV radiation)	Seattle-Duwamish	4700 East Marginal Way Seattle, WA	King

## **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 F. 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-3day schedule (refer to Table B1-2), or hourly averaged formaldehyde;
- Hourly averaged concentrations of O<sub>3</sub> (not covered in this QAPP);
- Hourly averaged concentrations of nitrogen oxide (NO), “true” nitrogen dioxide (NO<sub>2</sub>), and total reactive nitrogen (NO<sub>y</sub>) (NO and NO<sub>y</sub> are not covered in this QAPP);
- 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 F 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	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  ASL will require an high performance liquid chromatograph (HPLC) or ultra-high performance liquid chromatograph (UHPLC) as described in Method TO-11A and in PAMS TAD Revision 2 Section 5.0
Ozone	Federal Reference Method/Federal Equivalent Method (FRM/FEM) ozone analyzer <sup>a</sup>
True NO <sub>2</sub>	FRM/FEM True NO <sub>2</sub> analyzer – photolytic conversion with chemiluminescent detection or by cavity attenuated phase shift spectroscopy
NO/NO <sub>y</sub>	NO <sub>y</sub> analyzer <sup>a</sup>
Ambient Temperature	thermometer or thermistor
Wind Direction	cup and vane, propeller and vane, or sonic anemometer
Wind Speed	cup and vane, propeller and vane, or sonic anemometer
Atmospheric Pressure	aneroid barometer, pressure transducer
Relative Humidity	hygrometer
Precipitation	tipping bucket
Mixing Layer Height	ceilometer
Solar Radiation	pyranometer
Ultraviolet Radiation	pyranometer

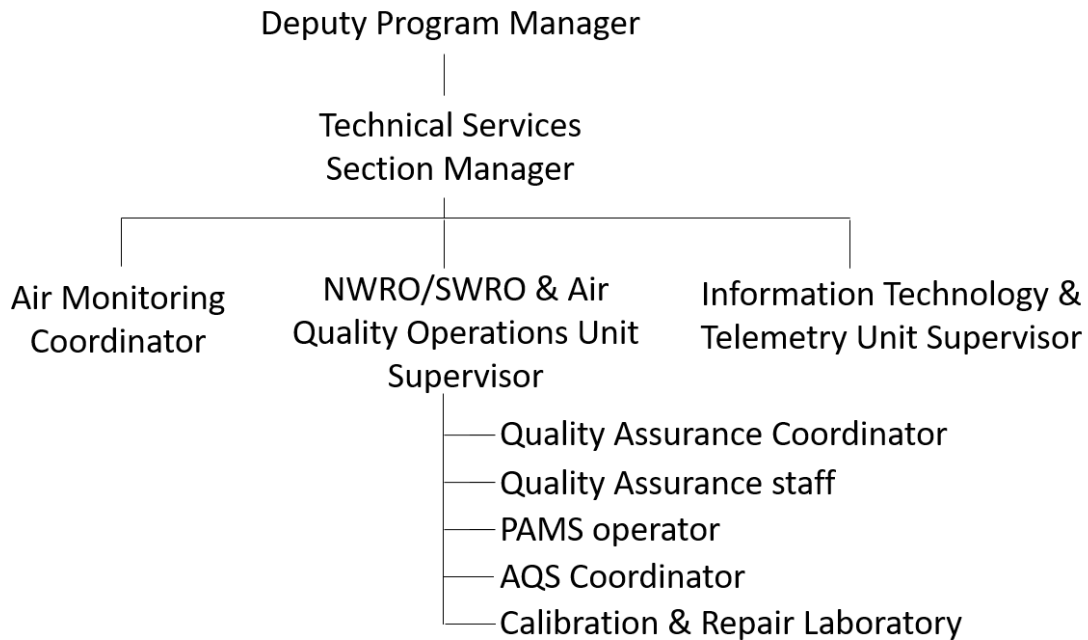
<sup>a</sup> Ozone and NO/NO<sub>y</sub> are described in the appropriate monitoring agency criteria pollutant monitoring QAPP.

## A6.2 Personnel to Accomplish Tasks

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. An organization chart should be included that delineates the reporting structure.

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

The organization structure of the Air Quality Program to implement PAMS is shown below. Note that the PAMS program is implemented by a subset of Air Quality Program personnel. Duties and responsibilities are listed below.



**Figure A6-1. Ecology PAMS Monitoring Organizational Chart**

**Deputy Program Manager**

- Assures Ecology AQP policies are in place and effective to achieve state and federal clean air objectives
- Responsible for overall program leadership and strategic direction
- Supervises the Technical Services Section Manager

**TSS Section Manager**

- Supervises the Air Monitoring Coordinator, the IT & Telemetry Unit supervisor, and the NWRO/SWRO & Air Quality Operations Unit supervisor
- Ensures there are sufficient resources to conduct PAMS measurements and supporting data processing activities

**Air Monitoring Coordinator**

- Project Manager for PAMS
- Identifies air monitoring equipment needs and recommends equipment purchases

**NWRO/SWRO & Air Quality Operations Unit Supervisor**

- Supervises PAMS operators, Quality Assurance staff, and Calibration & Repair Laboratory staff
- Oversees PAMS site operation and maintenance

**IT & Telemetry Unit Supervisor**

- Supervises IT & Telemetry staff
- Oversees telemetry system operation and maintenance

#### Quality Assurance Coordinator

- Responsible for the PAMS Quality Assurance Project Plan
- Oversees implementation of AQP's quality system

#### Quality Assurance Staff

- Conducts independent performance audits on PAMS parameters
- Responsible for data validation of PAMS parameters

#### PAMS Operators

- Maintains and operates parameters at the PAMS required sites
- Performs initial data verification of PAMS parameters

#### AQS Coordinator

- Submits PAMS data (with the exception of carbonyls data) to EPA's Air Quality System

#### Calibration and Repair Laboratory

- Provides PAMS site installation, equipment calibration, and maintenance support.

**Analytical Support Laboratory (ASL):** ASL staff will comply with the portions of this QAPP which apply to the laboratory analysis of carbonyls and/or speciated VOCs in canisters. 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.

Eastern Research Group (ERG) is the ASL responsible for the laboratory analysis of carbonyl samples. ERG is approved by EPA to perform the following tasks in support of the PAMS program:

- Writes laboratory quality assurance policies, plans, and procedures
- Prepares, certifies, and ships carbonyl sampling tubes to monitoring sites
- Analyzes carbonyl samples
- Assesses and reports data quality
- Validates analytical data
- Conducts inter- and intra-laboratory testing



- Stores and archives laboratory data and documentation
- Delivers periodic electronic data results to key personnel
- Reports results (valid, flagged, and suspect data) to AQS

### **A6.3 Schedule for PAMS Required Site Activity Milestones**

Ecology will conduct the PAMS Required Site activities to meet the milestones as described in Table A6-2. Ecology plans to follow the standard three-month PAMS season (June 1 to August 31).

**Table A6-2. PAMS Required Site Activity Annual Milestones**

<b>Activity</b>	<b>Start Date</b>	<b>Completion Due Date</b>	<b>Details</b>
Pre-sampling Season Instrument and Support Equipment Maintenance	As needed to ensure completion by March 1 annually	March 1 annually – prior to PAMS season for sites monitoring earlier than March 1	Complete annually prior to beginning annual monitoring - Preventive maintenance for measurement instruments, sample collection instruments, support equipment
Reference Standards Acquisition, Certification, or Recertification	As needed to ensure instruments are calibrated prior to March 1 annually	March 1 annually – prior to PAMS season for sites monitoring earlier than March 1	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	March 1 annually for auto-GCs, April 15 for other measurement systems	April 15 each year (to be completed prior to receipt of PTs for speciated VOCs and carbonyls)	Shakedown period for each instrument to ensure stable and accurate instrument performance by the start of PAMS season on June 1 – particularly important for sites operating instruments only for PAMS season
Quality Systems Review and Revision	Once data are validated and reported to AQS from the previous year, approximately March 31, if not earlier	April 15 annually	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
Demonstration of Capability	As convenient to ensure completion and approval by April 15 – or earlier if PAMS monitoring begins prior to beginning monitoring for the calendar year	April 15 – or earlier if PAMS monitoring begins prior to beginning monitoring for the calendar year	Approval by monitoring agency management (i.e., immediate supervisor) of the instrument operators, data validators, and auditors to perform their assigned duties – staff will complete training and management will approve by signature (Refer to example training form in Appendix D)
Shakedown Audit	April 15 annually, when performed	May 15 annually, when performed – prior to PAMS season for sites monitoring earlier than March 1	Readiness assessment to determine areas requiring resources or correction to ensure systems are online and calibrated prior to commencing PAMS monitoring
Proficiency Test (PT) for Speciated VOCs and Carbonyls— Phase 1	Phase 1 - April 15 annually (for VOCs)	May 1 annually (for VOCs)	Sample with concentrations of target speciated VOCs and carbonyls blind to the site operator and/or support laboratory – VOCs conducted prior to and toward the end of each PAMS season. Carbonyls conducted prior to PAMS seasons.

Activity	Start Date	Completion Due Date	Details
Proficiency Test (PT) for Speciated VOCs and Carbonyls— Phase 2	Phase 2 - August 15 annually (for VOCs)	August 31 annually (for VOCs)	Sample with concentrations of target speciated VOCs and carbonyls blind to the site operator and/or support laboratory – VOCs conducted prior to and toward the end of each PAMS season. Carbonyls conducted prior to PAMS seasons.
PAMS Monitoring	June 1 annually	August 31 annually	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

**Table A6-2 (continued). PAMS Required Site Activity Annual Milestones**

Activity	Start Date	Completion Due Date	Details
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
Performance Evaluation (PE) for True NO <sub>2</sub>	June 1 annually	August 31 annually	Conduct of the PE will occur during active true NO <sub>2</sub> monitoring for agencies conducting monitoring beyond June 1 to August 31  Challenge of the true NO <sub>2</sub> measurement system through the probe (TTP) with known standard NO <sub>2</sub> concentrations – conducted by monitoring agency QA or independent PQAO staff
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

Activity	Start Date	Completion Due Date	Details
Data Verification and Validation	June 8 annually	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

Ecology Quality Assurance staff will assess the performance of the PAMS Required Site activities by conducting independent assessments. The monitoring agency and ASL QA staff will perform these 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) to meet the project outcomes within a 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 O<sub>3</sub> and NO<sub>2</sub> 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. Note that an MQO for precision is not specified for meteorology measurements. Precision for meteorology would involve either measuring the same event with two separate instruments (collocation) or measuring a standard condition in replicate. It is not practical to operate a full-time collocated meteorology station due to the additional expense and logistics required to install a separate meteorology tower, and challenging the meteorology instruments in situ to acquire replicate measurements of a controlled meteorology condition is impractical. 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				
	Representativeness (Sampling Frequency) <sup>a</sup>	Bias (%)	Precision (%)	Sensitivity (Detection Limit)	Completeness (%)
Auto-GC speciated VOCs	Continuous, hourly average	≤ 25 <sup>b</sup>	≤ 25 <sup>c</sup>	≤ 0.5 ppbC	≥ 75
True NO <sub>2</sub> and NO/NO <sub>y</sub>	Continuous, hourly average	< ±15.1% or ± 1.5 ppb <sup>d</sup> whichever is greater	< 15.1% or 1.5 ppb <sup>c</sup> whichever is greater	≤ 0.001 ppm	≥ 75
Ozone	Continuous, hourly average	< ± 7.1% or ± 1.5 ppb <sup>d</sup> whichever is greater	< 7.1% or 1.5 ppb <sup>c</sup> whichever is greater	≤ 0.002 ppm	> 90% (avg) daily max available in O <sub>3</sub> season with min of 75% in any 1 year <sup>i</sup>
TO-11A (carbonyls)	Three sequential 8-hour samples every 3 <sup>rd</sup> day <sup>e, f</sup>	≤ 25 <sup>g</sup>	≤ 15 <sup>h</sup>	≤ 0.25 µg/m <sup>3</sup>	≥ 85
Meteorology	Representativeness (Sampling Frequency) <sup>a</sup>	Bias	Precision	Sensitivity (Resolution)	Completeness (%)
Ambient Temperature	Continuous, hourly average	≤ ± 0.5 °C	not specified	≤ 0.1 °C	≥ 75
Relative Humidity	Continuous, hourly average	≤ ± 5% RH	not specified	≤ 0.5% RH	≥ 75
Barometric Pressure	Continuous, hourly average	≤ ± 3 hPa	not specified	≤ 0.1 hPa	≥ 75
Wind Speed	Continuous, hourly average	≤ ± 0.2 m/s or ± 5%, whichever is greater	not specified	≤ 0.1 m/s	≥ 75
Wind Direction	Continuous, hourly average	≤ ± 5 degrees	not specified	≤ 1 degree	≥ 75
Solar Radiation	Continuous, hourly average	≤ ± 5%	not specified	≤ 1 Watt/m <sup>2</sup>	≥ 75
UV Radiation	Continuous, hourly average	≤ ± 5%	not specified	≤ 0.01 Watt/m <sup>2</sup>	≥ 75
Precipitation	Continuous, hourly average	≤ ± 10%	not specified	≤ 0.25 mm/hr	≥ 75
Mixing Layer Height	Continuous, hourly average	≤ ± 5 m or ± 1%, whichever is greater	not specified	≤ 10 m	≥ 75

<sup>a</sup> Spatial representativeness is addressed in monitor siting as specified in Section A7.3.1.2.

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**Table A7-1 (continued). PAMS DQIs and Associated MQOs**

<sup>b</sup> 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.

<sup>c</sup> 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.

<sup>d</sup> 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.

<sup>e</sup> 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.

<sup>f</sup> 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://www3.epa.gov/ttn/amtic/calendar.html>

<sup>g</sup> Assessed with twice-annual PT samples.

<sup>h</sup> 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>

<sup>i</sup> Refer to 40 CFR Part 50 Appendix U, Section 4

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 – though the period at a given site when ozone production becomes problematic may be extended to begin before June 1 and end after August 31), the sampling frequency for each of the required parameters is prescribed as follows. The sampling frequency for ozone, true NO<sub>2</sub>, NO<sub>y</sub>, speciated VOCs, and meteorological parameters is for sampling to occur continuously daily and the collected data averaged for each hour. Ozone and NO/NO<sub>y</sub> measurements at the PAMS Required Site will be described in and comply with the monitoring agency QAPP governing the NCore measurements of criteria pollutants at the site.

Due to the labor-intensive aspects of manual sample collection 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 (note that the QA requirements have not been established for continuous formaldehyde measurements).

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.

Hourly speciated VOCs and PAMS carbonyls (three sequential eight hour samples on a 1 in 3 schedule) will be measured only during the PAMS season (June 1 – August 31). Ozone, true NO<sub>2</sub>, NO/NO<sub>y</sub>, and meteorological measurements 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.

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 degrees. 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.

**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
True NO <sub>2</sub>	2 to 15 m AGL (neighborhood or larger spatial scale)

**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 O<sub>3</sub> or NO<sub>2</sub> 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, and should preferably be 20 meters when measuring NO<sub>2</sub>, 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 <sup>a</sup> (meters)	Minimum distance <sup>a</sup> (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

<sup>a</sup> 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.<sup>4,6,7</sup> 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.<sup>4,7</sup> 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.

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.<sup>6</sup> 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 un-watered short grass or, in areas which lack a vegetation cover, natural earth. Concrete, asphalt, and oil-soaked surfaces and other similar surfaces must be avoided to the extent possible. The sensor will be at least 30 m horizontally from any such paved area. If these siting criteria (open ground and distance from paved surfaces) cannot be achieved, it will be identified in site characterization documentation. Other areas to avoid include extraneous energy sources (subway entrances, rooftops, electrical transmission equipment), large industrial heat sources, 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.<sup>8</sup>

**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 degrees. 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.

**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.

### *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 barring extenuating circumstances such as equipment failure or if the sampling event is the last of the season, etc. Make-up samples will be collected according to the following:

1. Before the next scheduled sampling date
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

### *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 of Ozone and NO<sub>y</sub>:** Precision assessments for NO<sub>y</sub> and ozone are addressed in the monitoring agency NCore or State and Local Monitoring Stations (SLAMS) QAPP for criteria pollutant monitoring.

**Precision for Continuous Measurements of true NO<sub>2</sub>:** Precision for true NO<sub>2</sub> is assessed by calculating the upper 90% confidence limit (CL) for the coefficient of variation (CV) across all single-point QC checks measured annually (or during PAMS monitoring if NO<sub>2</sub> monitoring is limited to PAMS season). For functional form of the calculation, see 40 CFR 58 Appendix A Section 4.1.2, Equation 2.

**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  $\leq 25\%$  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:** As discussed in Section A7.3, precision for meteorological measurements is not practical and will not be assessed for the PAMS Required Site Program.

**Precision for Carbonyls:** Field sampling precision must be assessed for carbonyls at minimally 10% of the PAMS Required Network 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  $\geq 0.5 \mu\text{g}/\text{cartridge}$ . 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 ASL 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 ASL 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 ASL 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 at 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/NATTS20112012QAARfinal.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.

Bias of continuous chemical analysis parameters is evaluated by challenging the instruments with a known standard on a frequent basis, daily for VOCs and minimally every 14 days for NO<sub>2</sub>, typically during nighttime hours when ambient concentrations of the target analytes are lower and the measurements are less critical in predicting ozone levels for the following day. The known standard is analyzed to demonstrate the instrument calibration remains within tolerance and is typically followed by a blank or “zero” immediately following the calibration check to demonstrate that the instrument signal returns to background levels in the absence of target analyte. 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 and true NO<sub>2</sub> analysis are described in Sections B5.1.2 and B5.1.3, respectively.

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 HPLC 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 carbonyls field sample collection SOP. The positive bias verification procedure will be described in the agency carbonyls field sample collection SOP and must demonstrate that the sampling unit contribution for each target carbonyl is < 0.2 µg/cartridge. This is evidenced by measurement of target compounds on a challenge cartridge collected with humidified zero air being ≤ 0.2 µg/cartridge greater than the co-collected reference cartridge for each individual target carbonyl compound. 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 µg/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 ± 10% of the flow transfer standard. If the flow is not within ±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 ±15% of the original response. If this criterion is exceeded, corrective action will be performed to demonstrate appropriate

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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 annually just prior to PAMS season and VOCs will also be assessed toward the end of PAMS season through analysis of PT samples. Bias of speciated VOCs 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 true NO<sub>2</sub> measurements will be independently assessed by conducting an annual performance evaluation (PE) described in 40 CFR Part 58 Appendix A, Section 3.1.2. Additional PE assessments will be conducted minimally every 5 years by EPA as part of the National Performance Audit Program (NPAP) as described in 40 CFR Part 58 Appendix A, Section 2.4.

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. Note that this calibration verification is separate from the annual instrument performance audit described in Section C1.1.1.2. Bias assessment for meteorological instruments is described below:

- Wind anemometers – bias is assessed for mechanical instruments by rotating the anemometer shaft at several known rotational speeds and verifying the instrument output is within the tolerance specified by the instrument manufacturer. The bias of sonic anemometers is determined by wind tunnel test comparison to a calibrated reference device at multiple representative wind speeds and directions. Measurement bias will be maintained to within  $\pm 0.2$  m/s or  $\pm 5\%$ , whichever is greater.
- Wind vanes – bias is assessed by ensuring the orientation pin is set within specification to the compass azimuth of true north and that instrument outputs for several orientations around the 360° compass are within  $\pm 3^\circ$  of the true setting; this requires determining true north to within  $\pm 1^\circ$  accuracy. The combined error in the system must be kept to  $\leq 5^\circ$ . True north can be determined by referencing the current magnetic declination. The National Oceanic and Atmospheric Administration offers a current magnetic declination calculator at the following website:

<https://www.ngdc.noaa.gov/geomag-web/>

- Temperature probes – bias is assessed by comparison to a NIST-traceably certified thermometer or thermistor. The calibration check is performed at three different temperatures spaced across the range of expected temperatures experienced at the site.

The temperature probe is to be within  $\pm 0.5^{\circ}\text{C}$  from the certified reference standard at each comparison level.

- 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 is 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  $\text{RH} < 40\%$ .
- Pyranometers/Radiometers – bias is assessed by comparison of the pyranometer/radiometer to a NIST-traceably certified pyranometer/radiometer for one diurnal cycle and must be within  $\pm 5\%$  of the reference standard for both solar radiation and UV radiation.
- Barometers – bias is assessed by comparison of the barometer to a NIST-traceably certified barometer or pressure transducer over the course of several consecutive hours. The average measurements from the barometer over the comparison period must be within  $\pm 3$  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  $\pm 5$  m or  $\pm 1\%$  of the known distance, whichever is greater. A hard target test is not feasible at the Seattle-Beacon Hill PAMS site. Ecology plans on following alternative guidance provided by EPA.

Acceptably low bias in the measurements from each of the individual meteorological instruments will be verified as described in Section B5.1.4.

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). For true  $\text{NO}_2$ , there are limitations in the ability to properly generate suitable concentration standards for monitoring agencies to experimentally determine the MDL; however, monitoring agencies are encouraged to experimentally determine the MDL when feasible. 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, 5.6, and 6.2.9 for speciated VOCs, carbonyls, and true  $\text{NO}_2$ , respectively; the procedure is described briefly below.



MDLs are determined according 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. Determined 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. Management, by way of signature approval of training records, or equivalent, must verify that staff are competent to conduct all such activities.

New Ecology air monitoring personnel are required to complete training that will prepare them for their specific Washington Network job duties. An example training plan for an air monitoring operator can be found in the Washington State Ambient Air Monitoring Quality Assurance Plan as well as Ecology's Quality Report to Management (2019); typically training plans for new Ecology air monitoring personnel must be completed within the first calendar year. Unit supervisors are responsible for ensuring new Ecology air monitoring personnel meet all training requirements and review required and recommended training during annual performance evaluations. Unit supervisors also document and keep copies of completed training plans, as well as review transcripts in Ecology's Learning Management System. Ecology has a training and development team that manages the Learning Management System and required and recommended training courses.

Air monitoring personnel must be capable of performing the following basic functions independently with limited assistance from Ecology staff:

- Installing, operating, and maintaining of environmental monitoring/sampling equipment
- Calibrating environmental monitoring/sampling equipment, in accordance with manufacturer specifications and standard operating procedures
- Performing basic sampling data review to ensure data validity
- Operating a computer and using typical office software products
- Reviewing monitoring plans for technical accuracy
- Conducting routine sampling and testing
- Analyzing, evaluating, and interpreting data, writing reports
- Ability to use environmental spreadsheets and databases in support of monitoring projects

In addition to the base training as an Ecology air monitoring operator, PAMS program-specific air monitoring training is also required. At a minimum, Ecology PAMS personnel are required to:

- Read the most current version of the EPA's PAMS Technical Assistance Document
- Read this Quality Assurance Project Plan
- Read Ecology's Washington State Ambient Air Monitoring Quality Assurance Plan
- Read SOPs pertinent to PAMS parameters

Specialized training for air monitoring staff consists of Ecology-provided training, external training, conferences and professional organizations, and vendor training. Ecology Calibration & Repair Laboratory, Quality Assurance, and air monitoring personnel provide periodic training on the proper calibration, operation, quality control, and maintenance activities for instruments used in the Washington Network. To the extent possible, Ecology provides training to all monitoring operators for any monitoring equipment that has not been previously used in the Washington Network. PAMS personnel are highly encouraged to take advantage of external training, including Air Pollution Training Institute courses and training from vendors. Vendor training is especially recommended for operating the auto-GC and validating the auto-GC data.

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 refamiliarize 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. The approval must be completed before data collection activities may begin. A member of management (supervisor or similar) and/or QA unit will observe the site operator performing the procedures as described in the applicable SOP as part of the annual TSA to evaluate continued competence. An example training form is 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 in prior to and including the PAMS 2021 season 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 Analytical Support Laboratory Analyst Training**

Once the ASL 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 at least 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 ( $\pm 15\%$  of nominal). The observer will document the acceptable performance and laboratory management will approve the analyst to independently perform the analysis by approval signature on the IDOC (checklist, approval form, or similar).

Once the IDOC is completed, the analyst will demonstrate continued proficiency with the method on an annual basis by performing a CDOC. The CDOC will be met by the analyst in one of three ways: achieving recovery within the method bias specification ( $\pm 15\%$  of nominal) for analysis of an LCS (spiked cartridge) whose concentration of target analytes is blind to the analyst; acceptable performance on all target analytes for a PT sample; or achieving recovery

within method bias specification ( $\pm 15\%$  of nominal) for all target analytes on four consecutive LCSs. Laboratory management will approve the analyst CDOC by approval signature.

## 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. Ecology’s documentation and records procedures are detailed in the Washington State Ambient Air Monitoring Quality Assurance Plan. Information is included about electronic and manual records, Ecology’s data acquisition system and Site Information Management System, Standard operating procedures, and record retention.

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. Ecology’s SOPs for PAMS parameters describe routine instrument operation, maintenance activities, sample collection, data validation and reporting, corrective action, training, and data management. The parameter-specific SOPs include information on required instrumentation, calibration equipment, quality control activities and acceptance criteria, and corrective actions for nonconformances. Ecology’s SOPs, quality control documents, and quality assurance documents are version-controlled to ensure that only the most up-to-date procedures are conducted. Previous versions of documents are archived in order to ensure that the measurement data are traceable to the policies and procedures in place at the time of data collection.

**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

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, incl. 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

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. In order 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 B) 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, Ecology’s air monitoring documentation and records are detailed in Section 7 of the Washington State Ambient Air Monitoring Quality Assurance Plan.

#### ***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.<sup>9</sup> 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 in order to ensure modifications to electronic records are recorded and that the original data are not overwritten.

With the exception of the auto-GC, carbonyl, and ceilometer data, the Air Quality Program utilizes Envitech Ltd./DR DAS (Envidas) software products for electronic data collection, review, verification, validation and submittal to AQS. All collected data utilizing Envidas is stored in an Envidas database on a Microsoft SQL platform physically located at Ecology's Headquarters building in Lacey, WA, and managed by the Air Quality Program's Information Technology staff. Ceilometer data is interfaced, stored, and backed up with the University of Maryland Baltimore County Ceilometer Network. Auto-GC data is stored on an on-site computer and backed up to an external drive.

#### **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. Ecology COC procedures can be found in the Air Toxics SOP as well as the Air Toxics Monitoring Quality Assurance Project Plan.

COC procedures and requirements are detailed in Section B3.1.1. An example COC form (specific to PAMS carbonyls samples) is included in Appendix C.

### **A9.3 QA/QC Records**

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

- Instrument maintenance, calibration, and calibration verification
- Standards certification, recertification, or calibration
- IPAs
- TSAs
- ADQs
- PEs
- 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.<sup>10</sup> 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.

PAMS Required Site Network QAPPs and supporting SOPs will be archived for minimally 10 years following the date that they are superseded. Electronic data are stored in databases, shared network drives, and other locations. Raw and edited ambient air quality and most quality control data are securely stored in a SQL database backed up daily at the Washington State Data Center and accessible by Ecology's Air Quality Information Technology team. The State Data Center as well as Ecology follow best Information Technology practices for the security of data and systems. One-hour ambient air monitoring data are kept in perpetuity and backups of stored data are conducted daily.

### **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 are validated and approved or the 30-day extract holding time has been exceeded. Expired extracts are of little value; however, in the event expired extracts are analyzed, results reported from such expired extracts require qualification as “QX” when reported to AQS. Extracts will not be archived and will be disposed properly according to hazardous waste procedures established by the laboratory.

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## 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. Ecology has obtained a waiver from EPA Region 10 to collect solar and UV radiation measurements at an alternative site in Seattle. The waiver is included in Appendix F.

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 NO<sub>2</sub>**
- NO/NO<sub>y</sub>
- ozone

NO/NO<sub>y</sub> and ozone are described simply for convenience; however, the QS for these criteria pollutant gases is covered under the Washington Ambient Air Monitoring Network Quality Assurance Plan 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. 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 in below in Table B1-1.

Continuous instrument measurements (meteorology, speciated VOCs, O<sub>3</sub>, true NO<sub>2</sub>, and NO/NO<sub>y</sub>) 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 routine 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 <sup>a</sup>	Continuously, daily	Hourly average
True NO <sub>2</sub>	Continuously, daily	Hourly average
NO/NO <sub>y</sub> <sup>a</sup>	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) <sup>b</sup>	Continuously, daily	Hourly average
Meteorological Parameters	Continuously, daily	Hourly average

<sup>a</sup> Monitoring for ozone and NO/NO<sub>y</sub> are not covered in this QAPP. Please refer to the Washington State Ambient Air Monitoring Quality Assurance Plan.

<sup>b</sup> Continuous formaldehyde monitoring with hourly average concentration reporting can be substituted for the carbonyl sequential collection of three 8-hour samples every 3<sup>rd</sup> 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-11A<sup>b</sup>***

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**

<b>Sequential Sample</b>	<b>Collection Start Time (local standard time)</b>	<b>Collection End Time (local standard time)</b>
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.

Target carbonyls analytes are those identified in bold and noted as “carbonyls” in Table B2-1. 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). 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

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<sup>b</sup> 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.

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 B2-1 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. All optional compounds listed in Table B2-1 will be measured and reported.

### ***B1.1.3 Continuous Measurement Methods***

Data collection for continuous true NO<sub>2</sub> and meteorological methods will include minimally 45 minutes of ambient data collection during the respective hour (75% of the hour) to be valid. Hours with fewer than 45 minutes of data collection will not be considered valid hours for data reporting.

#### ***B1.1.3.1 True NO<sub>2</sub>***

Ambient true NO<sub>2</sub> will be measured continuously except when the NO<sub>2</sub> analyzer is undergoing periodic QC checks (span/zero/precision checks), maintenance, and performance audits. During these periods, the instrument may be taken offline or data may be flagged to indicate that the measurements must not be reported as ambient measurement data.

#### ***B1.1.3.2 Meteorological Instruments***

Meteorological instruments will record ambient measurements continuously except when an instrument is undergoing QC checks, maintenance, or performance audits, for which the instrument will be taken offline or data may be flagged to indicate the measurements must not be reported as ambient measurement data. QC checks or performance audits for which the instrument is left in situ and continues to measure ambient conditions may be reported as valid data; however, if a probe's conditions are altered from the typical measurement configuration, the measurements will be invalidated.

## **B1.2 Quality Control Measurements**

QC samples are collected and/or analyzed for the chemical measurement parameters (carbonyls, speciated VOCs, and true NO<sub>2</sub>), 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 and precision 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, B5-4, and B5-5 for carbonyls field sample collection, speciated VOCs, true NO<sub>2</sub>, meteorology, and carbonyls laboratory analysis, respectively.

SLT monitoring agencies and ASLs are encouraged to 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.

A list of makes and models and applicable SOPs for the measurement parameters listed in Section B1 is shown in Table B2-1:

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

Parameter	Instrument	Ecology SOP
Carbonyls	ATEC 8000-3 Cartridge Sampler	Air Toxics Standard Operating Procedure, currently under revision
Ambient Temperature	RM Young 41342VF	Meteorological Monitoring Procedure
Wind Direction and Wind Speed	Vaisala WMT 700 Series Sonic Sensor	Meteorological Monitoring Procedure
Atmospheric Pressure	RM Young 61202V	Meteorological Monitoring Procedure
Relative Humidity	Rotronics HC2A-S3	Meteorological Monitoring Procedure
Precipitation	RM Young 52202	Meteorological Monitoring Procedure
Mixing Layer Height	Vaisala CL51	Ceilometer Standard Operating Procedure, currently under development
Solar Radiation	Kipp & Zonen SMP6	Meteorological Monitoring Procedure
UV Radiation	Kipp & Zonen SUV5	Meteorological Monitoring Procedure
True NO <sub>2</sub>	Teledyne-API T500U CAPS	Gaseous Pollutant Monitoring Standard Operating Procedure

Parameter	Instrument	Ecology SOP
NO/NO <sub>y</sub>	Teledyne T200U	Gaseous Pollutant Monitoring Standard Operating Procedure
Ozone	Teledyne-API T400	Ozone Monitoring Operating Procedure
Speciated VOCs	Markes-Agilent (FID)	Auto-GC Standard Operating Procedure, currently under development

*NOTE: Ecology will follow the SOPs listed in Table B2-1.*

## **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 B2-1. 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 one or more inlet probes. The materials comprising, the siting of, and the configuration of the inlet probe will comply with 40 CFR Part 58 Appendix E and Section A7.3.1.2 of this QAPP to ensure the sampled atmosphere is representative of the ambient air in the geographic area intended to be represented by the site. Briefly, the inlet probe(s) will be constructed of borosilicate glass or polytetrafluoroethylene (PTFE) or perfluoralkoxy (PFA) Teflon<sup>®</sup> for criteria pollutant gases. For carbonyls and VOCs, inlet probe(s) will be of borosilicate glass or chromatographic grade stainless steel, or their equivalent. FEP Teflon<sup>®</sup> is prohibited as a probe material in 40 CFR Part 58 Appendix E Section 9(b); however, PTFE and PFA Teflon are not specifically prohibited and are permitted for carbonyls sample collection. Monitoring agencies are strongly discouraged from employing Teflon<sup>®</sup> in their sampling inlet pathways for speciated VOCs. Additional guidance for inlet probe siting is included in Section 3.3.1.2 of Revision 2 of the PAMS TAD.

The air monitoring instrument inlet can be connected to an inlet probe dedicated to the instrument or can be connected to an inlet manifold with connections for multiple instruments. Consideration will be given to the length of the sampling inlet pathway (including the manifold, if so equipped) and flow rate such that the sample residence time is kept to 20 seconds or less. Consideration will also be given to minimize intrusion of particulate matter (PM) and condensed water into the sampling inlet; one method for controlling the latter is by inverting the terminus of the inlet and installing a rain shield (such as inverted funnel) on the inlet probe. Air monitors may be connected to any port on a manifold. Additional sample introduction and collection guidance is included in Revision 2 of the PAMS TAD, Sections 4.2.2.1, 5.7.2, and 6.2.8 for speciated VOCs, carbonyls and true NO<sub>2</sub>, respectively. The inlet composition and configuration for speciated VOCs, carbonyls, and True NO<sub>2</sub> is detailed in the Auto-GC SOP, Air Toxics SOP, and Gaseous Pollutant Monitoring SOP, respectively.

### ***B2.1.1 Carbonyls by TO-11A***

Sampling methods for the collection and analysis of carbonyl compounds by TO-11A are described in detail in the national PAMS SOPs. 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 setup, calibration, operation, maintenance, and shut-down of auto-GCs are described in the following national PAMS SOPs, which are intended to provide instruction for properly trained instrument operators:

- SOP for the Analysis of PAMS VOCs in Ambient Air via the Consolidated Analytical Systems/Chromatotec AirmOzone Auto-GC-FID
- SOP for the Analysis of PAMS VOCs in Ambient Air via the Markes Unity-XR Thermal Desorber with Agilent 7890B Auto-GC-FID
- SOP for the Analysis of PAMS VOCs in Ambient Air via the PerkinElmer TurboMatrix TD300 Thermal Desorber with Clarus 580 Auto-GC-FID

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.



**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
<b>Acetaldehyde</b>	<b>43503</b>	<b>carbonyl</b>	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
<b>Formaldehyde</b>	<b>43502</b>	<b>carbonyl</b>	3-methylheptane	43253	Paraffin
Isobutene	43214	paraffin	3-methylhexane	43249	Paraffin
Isopentane	43221	paraffin	3-methylpentane	43230	Paraffin
Isoprene	43243	olefin	<b>acetone</b>	<b>43551</b>	<b>Carbonyl</b>
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
Styrene	45220	aromatic	n-nonane	43235	Paraffin
Toluene	45202	aromatic	n-octane	43233	Paraffin
trans-2-butene	43216	olefin	n-propylbenzene	45209	Aromatic
<i>Ozone</i>	<i>44201</i>	<i>criteria pollutant gas</i>	n-undecane	43954	Paraffin
<i>true NO<sub>2</sub></i>	<i>42602</i>	<i>criteria pollutant gas</i>	p-diethylbenzene	45219	Aromatic
total non-methane organic carbon	43102	total VOCs, non-methane	trans-2-pentene	43226	Olefin
			$\alpha$ -pinene	43256	monoterpene olefin
			$\beta$ -pinene	43257	monoterpene olefin
			1,3 butadiene	43218	Olefin
			<b>benzaldehyde</b>	<b>45501</b>	<b>Carbonyl</b>
			carbon tetrachloride	43804	Halogenated
			Ethanol	43302	Alcohol
			tetrachloroethylene	43817	Halogenated

**B2.1.3 True NO<sub>2</sub> by CAPS or Photolytic Conversion to NO with Chemiluminescent Detection**

An FRM/FEM analyzer will be employed for measurement of true NO<sub>2</sub> per the PAMS National SOP:

- Standard Operating Procedure for the Analysis of True Nitrogen Dioxide (NO<sub>2</sub>) in Ambient Air for the Photochemical Assessment Monitoring Stations (PAMS) Network

EPA has designated the following instrument methods as FEMs for NO<sub>2</sub> analysis:

- FEM EQNA-0514-212 - Teledyne Advanced Pollution Instruments (API) Model T500U CAPS NO<sub>2</sub> Analyzer
- FEM EQNA-1013-210 - Environnement S.A. AS32M CAPS NO<sub>2</sub> Analyzer
- FEM EQNA-0217-242 - Ecotech Serinus 60 CAPS NO<sub>2</sub> Analyzer
- FEM designation available from supplier - Aerodyne Research, Inc. CAPS NO<sub>2</sub> Monitor
- FEM EQNA-0320-256 - Teledyne API Model N500 CAPS NO<sub>2</sub>/NO<sub>x</sub>/NO Analyzer
- FEM EQNA-0512-200 - Teledyne API Model T200UP Photolytic Conversion NO<sub>2</sub> Analyzer

The CAPS true NO<sub>2</sub> analyzer ingests a sampled air parcel and using a specific wavelength of light, determines the concentration of NO<sub>2</sub> in the air parcel relative to the loss of signal in the instrument optical cell. For photolytic conversion instruments, the instrument employs two channels, one channel that converts NO<sub>2</sub> to NO at a precise wavelength of light efficient for converting NO<sub>2</sub> to NO with few interferences, and one channel without conversion, and measures the concentration of NO<sub>2</sub> by difference using a chemiluminescent detector.

**B2.2 Meteorology**

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

**Table B2-3. Meteorological Parameters**

Parameter	AQS Parameter Code	Duration	AQS Duration Code	Example Reported Unit <sup>a</sup>	AQS Unit Code <sup>a</sup>
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 <sup>2</sup>	79
Ultraviolet Radiation	63302	hourly average	1	Watt/m <sup>2</sup>	79
Precipitation	65102	hourly average	1	mm	29
Mixing Layer Height	61301	hourly average	1	m	58

<sup>a</sup>. 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.

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://www3.epa.gov/ttnamti1/files/ambient/met/Volume\\_IV\\_Meteorological\\_Measurements.pdf](https://www3.epa.gov/ttnamti1/files/ambient/met/Volume_IV_Meteorological_Measurements.pdf)

Results will be measured continuously and reported as the hourly average.

### **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. Sample handling and custody procedures for carbonyls samples are detailed in the Air Toxics Monitoring Quality Assurance Project Plan and the Air Toxics SOP.

#### **B3.1 Carbonyls by TO-11A**

New cartridges will be stored at  $\leq 4^{\circ}\text{C}$  upon receipt. New Waters cartridges are typically shipped at ambient temperature and Supelco cartridges are typically shipped at sub-ambient temperatures. Both cartridge types are typically provided sealed individually in a foil pouch. 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. Moreover:

- Cartridges will only be handled with gloved hands (chemicals from hand sanitizers, lotions, etc., can contaminate sample cartridges).
- Markers containing volatile solvents (e.g., permanent markers such as Sharpie<sup>®</sup>, which emit solvents such as acetone) will not be used for marking on foil storage pouches. Ball-point pens or printed stick-on labels are preferred.
- 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 may originate at the analysis laboratory; therefore, COC procedures may be prescribed by the ASL. Regardless of the origin of the new cartridge media, each cartridge, whether an ambient sample or field QC sample (such as a trip blank or field blank) will be listed on a 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 C):

- 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)

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, speciated VOCs, and true NO<sub>2</sub>.

### **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 B5-5. This method is described in the national SOPs for the collection and analysis of carbonyls for the PAMS Required Site Network, which describe the procedures for solvent extraction of derivatized carbonyl-hydrazones collected on the DNPH cartridge samples, analysis of these extracts by HPLC or UHPLC with UV detection, and the necessary QC procedures. 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 B5-5) 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. Procedures for the setup, calibration, operation, and shutdown of auto-GCs are described in PAMS Required Site SOPs listed in Section B2.1.2. 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.

### **B4.3 True NO<sub>2</sub> by FEM**

True NO<sub>2</sub> analyzers approved as FEMs will be employed for the analysis of true NO<sub>2</sub>. The analyzers continuously sample ambient air routed through an in-line particulate matter (PM) filter, therefore no discrete samples are collected on media which may be retained.

The analyzers are calibrated for NO<sub>2</sub> response by providing the analyzer with a zero concentration gas and an upscale concentration of NO<sub>2</sub> of approximately 80% of the desired measurement range. Immediately following calibration, the analyzer is subjected to a multi-point

verification (MPV) of the calibration, which involves analysis of a zero concentration point and four upscale standard NO<sub>2</sub> concentrations. Following minimally every 14 days thereafter, the analyzer is subject to a zero/span check to verify ongoing instrument calibration. See Table B5-3 for QC acceptance criteria.

## **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, true NO<sub>2</sub> 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 humidified zero air 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.
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 (µg/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.

**Table B5-1 (continued). Carbonyls Field Quality Control Parameters**

QC Parameter	Detail	Required Frequency	Acceptance Criteria	Recommended Corrective Action
Trip Blank	blank cartridge accompanying collected samples to and from the field site	Not required, recommended monthly –Ecology will not be collecting trip blanks	Measured mass per cartridge ( $\mu\text{g}/\text{cartridge}$ ): - 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. 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 <sup>rd</sup> 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 – Ecology will not be collecting duplicate samples	Relative percent difference $\leq 20\%$ for compounds $\geq 0.5 \mu\text{g}/\text{cartridge}$	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 - Ecology will not be collecting collocated samples	Relative percent difference $\leq 20\%$ for compounds $\geq 0.5 \mu\text{g}/\text{cartridge}$	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.



**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. At their discretion, agencies may use other high level concentrations (e.g., 50 or 80 ppbC).	Initially at the beginning of PAMS season, after maintenance (such that response is impacted), following failing continuing calibration checks, and at the conclusion of monitoring each PAMS season.	Linear regression with non-zero y-intercept must show $r^2$ of $\geq 0.99$ . Also $ \text{intercept/slope}  \leq 0.5$ ppbC or $\leq$ MDL, whichever is lower. RSD of determined RFs must be $\leq 10\%$ . 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. 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. PAMS data must not be reported unless calibration meets criteria.
System Blank (SB)	Analysis of humidified zero air to ensure the system is sufficiently clean for continued analysis.	Prior to ICAL, and every $24 \pm 4$ 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 $\leq$ 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 all samples for affected compounds since the last passing SB.

**Table B5-2 (continued). Speciated VOCs Field Quality Control Parameters**

QC Parameter	Description	Required Frequency	Acceptance Criteria	Recommended Corrective Action
Second Source Calibration Verification (SSCV)	Analysis of a known standard prepared from a stock gas including target analytes across the molecular weight range from a supplier different from the stock gas (primary standard) for preparing the ICAL. This check independently verifies the quality of the ICAL for compounds across the molecular weight range.	Immediately following ICAL and minimally weekly thereafter – may serve as the CCV	All target VOCs must recover within $\pm 30\%$ 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 co-eluting peaks. Investigate for system leaks or trap malfunction resulting in low recovery. Unless technical justification is provided to explain nonconformance, minimally qualify as “QX” and potentially invalidate as “AS” samples for affected compounds since the last acceptable SSCV.
Clock Accuracy	Verify clock accuracy against a known accurate time standard	Weekly, recommended to check each site visit	Within $\pm 5$ minutes of the time standard	Reset clock to correct time. Adjust data timestamp accordingly where possible. Ensure adjusted sampling start times are no earlier than 10 minutes before the hour and no later than 30 minutes after the hour. Invalidate sample hours that do not conform.
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 $24 \pm 4$ hours of operation	All target VOCs must recover within $\pm 30\%$ of the expected nominal concentration.	Investigate chromatogram for retention time shifts which may result in peak misidentification. Investigate for instrument contamination resulting in co-eluting 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 all samples for affected compounds since the most recent passing CCV. Invalidation as “AS” may be required at analyst discretion if compound recovery is exceptionally high or low.

**Table B5-2 (continued). Speciated VOCs Field Quality Control Parameters**

QC Parameter	Description	Required Frequency	Acceptance Criteria	Recommended Corrective Action
Retention Time Standard (RTS)	Analysis of a 59-component blend of VOCs in the ~2 to 60 ppbC range to verify established retention time windows	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 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 $\leq 25\%$ on a week-to-week basis.	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.

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 (C<sub>2</sub> to C<sub>10</sub>). 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.

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 True NO<sub>2</sub> Analysis**

True NO<sub>2</sub> analysis QC includes the performance of quality checks on the true NO<sub>2</sub> analyzer sampling instrument to ensure the analyzer calibration is within the defined specifications, the zero setting of the analyzer has not drifted outside the acceptance window, and that the flow controllers, and, if so equipped, the ozone generator, of the dynamic dilution calibrator (DDC) employed to calibrate the analyzer are operating properly and within the prescribed tolerances. True NO<sub>2</sub> QC activities include, as described in Table B5-3 and in the true NO<sub>2</sub> analysis SOP, an MPV, zero/span checks, and zero/span/precision checks for the NO<sub>2</sub> analyzer and flow verification checks and ozone generator calibration verifications for the DDC.

**Table B5-3. True NO<sub>2</sub> Quality Control Parameters**

QC Parameter	Description	Required Frequency	Acceptance Criteria	Recommended Corrective Action
Calibration	Setting zero and span levels on the true NO <sub>2</sub> analyzer by introducing zero air and an NO <sub>2</sub> standard at 80% of the desired measurement range covering the expected range of ambient measurements (e.g., 160 ppb NO <sub>2</sub> for a measurement range of 0 to 200 ppb NO <sub>2</sub> )	Initially when deployed, minimally every 365 days, following maintenance to the instrument expected to alter the instrument response, following operation interruption of several days (e.g., 48 hours), and following failing span check or zero check	None. Verified by MPV.	Repeat calibration if indicated by MPV. It may be necessary to investigate for system contamination or interferences resulting in suppression or enhancement (check filters, perform leak checks, clean mirrors, etc.)
Multipoint Verification (MPV)	Introduction of a zero and four upscale NO <sub>2</sub> concentration points covering the measurement range. (e.g., 0, 175, 125, 75, and 25 ppb)	Immediately following establishing a new calibration.	Linear regression of the measurements plotted against the theoretical must show r <sup>2</sup> of ≥ 0.995 and have an x-intercept within ± 0.2 ppb NO <sub>2</sub> of the origin. Percent difference of each standard measurement must be within ±10% of the theoretical concentration.	Repeat verification. It may be necessary to investigate for system contamination or interferences resulting in suppression or enhancement of analytes. Recalibration may be necessary.

**Table B5-3 (continued). True NO<sub>2</sub> Quality Control Parameters**

QC Parameter	Description	Required Frequency	Acceptance Criteria	Recommended Corrective Action
Zero/Span Check	Analysis of zero air and span NO <sub>2</sub> standard (~80% of measurement range) to monitor for drift in zero and span levels. Checks are performed on analyzer in as-is condition before modifying instrument settings.	Required every 14 days. More frequent checks are recommended.	Zero drift must be less than $\pm 0.3$ ppb. Span level must be within $\pm 10\%$ of the theoretical concentration.	Repeat zero and span checks to confirm. Investigate system for contamination, leaks, or other causes of drift. Qualify or invalidate data since the last passing QC check. Perform calibration and MPV.
Zero/Span/Precision Check	Verification performed by analyzing a zero and two standard NO <sub>2</sub> concentration levels – span point at approximately 80% of the measurement range and a precision point in the lower 1/3 of the measurement range (e.g., 160 and 50 ppb, respectively for a measurement range of 0 to 200 ppb)	Optional – Recommended minimally every 14 days or more frequently.	Zero drift must be less than $\pm 0.3$ ppb. Span and precision levels must be within $\pm 10\%$ of their theoretical concentration.	Repeat Zero/Span/Precision Verification to confirm. Investigate system for contamination, leaks, or other causes of drift. Qualify or invalidate data since the last passing QC check. Perform calibration and MPV.
Dynamic Dilution Mass Flow Controller (MFC) Check	Verification of diluent gas and standard gas channel MFCs calibration against a NIST-traceably certified flow transfer standard	Quarterly (every 90 days)	Flows covering the 10 to 90% of each MFC (or bracketing range of flows employed) must be within $\pm 2\%$ of the flow transfer standard	Recalibrate (adjust) the slope and intercept of the MFC per the manufacturer instructions and repeat verification. If verification still cannot meet acceptance, MFC may require repair
DDC Ozone Generator Calibration Verification	Verification of ozone generator calibration against a Level 1 or Level 2 ozone standard	Quarterly (every 90 days). Required only when convention of generation of NO <sub>2</sub> standard gas is accomplished by gas phase titration (GPT) of ozone with NO.	Ozone generator performance will be described in QAPP governing ozone monitoring.	Recalibrate (adjust) the ozone generator slope and intercept per the manufacturer instructions and repeat verification. If verification still cannot meet acceptance, ozone generator may require repair.

#### ***B5.1.4 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 B5-4, 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.

Recommended corrective action for all meteorology parameters: 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 “QX” in AQS, as applicable. Potentially invalidate data since last most recent calibration or acceptable calibration check.

**Table B5-4. Quality Control Parameters for Meteorology Measurements**

Meteorology Parameter	Calibration Check Standard	Required Frequency	Acceptance Criteria
Ambient Temperature	Verification in a water bath or dry well against a NIST-traceable thermistor or thermometer at three points bracketing the temperature range of use	Semi-annually	$\leq \pm 0.5^{\circ}\text{C}$ at each of the three temperatures checked
Relative Humidity	Compared to a NIST-traceable psychrometer or standard solutions		$\leq \pm 5\%$ RH of the hourly average from the certified standard over the duration of comparison
Barometric Pressure	Compared to a NIST-traceably certified barometer or pressure transducer over the course of several consecutive hours		$\leq \pm 3$ hPa
Wind Speed	Compared to a NIST-traceable synchronous motor, CTS <sup>a</sup> method, or wind tunnel testing and zero verification.		$\leq \pm 0.2$ m/s or $\pm 5\%$ , whichever is greater Zero verification < 0.3 mph
Wind Direction	Compared to solar noon, GPS, magnetic compass, CTS <sup>a</sup> method, or wind tunnel testing		$\leq \pm 5$ degrees
Solar Radiation	Compared to a NIST-traceable pyranometer		$\leq \pm 5\%$ <sup>b</sup>
UV Radiation	Compared to a NIST-traceable radiometer		$\leq \pm 5\%$ <sup>b</sup>
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	Altitude determination verified against a hard target of known distance <sup>c</sup> or CTS <sup>a</sup> method. Ecology is unable to perform a hard target test at the Seattle-Beacon Hill monitoring site and will follow alternative guidance from the EPA		$\leq \pm 5$ m or $\pm 1\%$ , whichever is greater

<sup>a</sup> CTS = collocated transfer standard. Ecology uses sonic anemometers and does not use mechanical sensors, nor can a mechanical system be mounted next to the sonic anemometer at the PAMS site. A PAMS meteorology training session (Oct. 2020) noted that “if you cannot mount a mechanical system next to the sonic anemometer, you will need to dismount the instrument for testing in a wind tunnel”. The training also noted that “if a mechanical sensor is not available, an independent standardized sonic instrument with appropriate performance is acceptable for performing CTS”.

<sup>b</sup> Comparison should be made during sunny conditions.

<sup>c</sup> The hard target test for ceilometers may not be feasible at some sites due to ranging restrictions. EPA is in process defining a process for calibration verification of ceilometer altitudes as of publication of this QAPP. The ceilometer should minimally include an onboard automated (weekly or more frequently) calibration routine that independently verifies the ranging.

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 B5-5, which are replicated in the ASL SOP. Laboratory QC samples consist of extraction batch QC (extraction solvent method blanks [ESMB] and DNPH media method blanks [MB] and known standard spikes – LCS/LCSD) and analysis batch QC samples including solvent blanks (SB), SSCV standards, continuing CCV, 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 B5-5. 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 <sub>sp</sub>	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	$r \geq 0.999$ , backcalculated concentration of each standard level within $\pm 20\%$ of nominal, $ \text{intercept/slope}  \leq \text{MDL}_{\text{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. Analysis cannot commence until calibration meets criteria.
Second Source Calibration Verification (SSCV)	Analysis of a known standard prepared from a stock solution sourced from a vendor independent of the primary calibration stock standard; verifies the quality of the ICAL	Immediately following ICAL	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 and reanalyze extracts analyzed since the last passing SSCV. Analysis cannot commence until SSCV following ICAL meets criteria.



**Table B5-5 (continued). Carbonyls Laboratory Quality Control Parameters**

QC Parameter	Detail	Required Frequency	Acceptance Criteria	Recommend Corrective Action
Continuing Calibration Verification (CCV)	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 and reanalyze extracts analyzed since the last passing CCV. If associated samples cannot be reanalyzed, and unless technical justification is provided to explain nonconformance, qualify all samples since most recent acceptable CCV as "QX" in AQS.
Holding Times	Maximum duration from end of sample collection for sample extraction	all field-collected and laboratory QC cartridges	14 days from end of sample collection to extraction	Qualify samples exceeding holding times as "HT" in AQS.
	Maximum duration from sample extraction to analysis		30 days from sample extraction to analysis	
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 $\leq 0.10$ - formaldehyde $\leq 0.15$ - acetone $\leq 0.30$ - other individual compounds $\leq 0.10$	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)	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 $\leq \text{MDL}$	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)	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.

**Table B5-5 (continued). Carbonyls Laboratory Quality Control Parameters**

QC Parameter	Detail	Required Frequency	Acceptance Criteria	Recommend Corrective Action
Laboratory Control Sample Duplicate (LCSD)	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.
Extraction Solvent Method Blank (ESMB)	Aliquot of solvent lot used for extraction contained within a volumetric flask used for extraction	Each extraction batch of 20 or fewer field-collected samples	Target analyte concentrations $\leq$ MDL <sub>sp</sub>	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 $\mu$ g/cartridge	Reanalyze extracts to confirm disparate results. If confirmed, qualify sample results in the analysis batch as "QX" 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 ( $\mu$ 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	As submitted to the laboratory by field site(s)	measured mass per cartridge ( $\mu$ 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.

**Table B5-5 (continued). Carbonyls Laboratory Quality Control Parameters**

QC Parameter	Detail	Required Frequency	Acceptance Criteria	Recommend Corrective Action
Extract Storage	Sample extracts stored refrigerated and protected from light	All extracts	Storage in amber vials at $\leq 4^{\circ}\text{C}$	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	As submitted to the laboratory by field site(s)	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.
Collocated Sample Analysis	Analysis of a separate sample cartridge collected concurrently with a primary 8-hour sample through an independent inlet probe	As submitted to the laboratory by field site(s)	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**

It is expected that field-related equipment and samplers/monitors will be installed by October 2020 for shakedown, testing, and training so as to be ready for full implementation before the June 1, 2021, start of the PAMS Required Site network. Due to the Covid-19 pandemic, the auto-GC was not installed prior to this document's publication date. Once the auto-GC is installed and operational, measurements will conform to this QAPP. All other PAMS parameters will be ready for full implementation by June 1, 2021. Monitoring equipment (e.g., auto-GCs, carbonyls samplers, true NO<sub>2</sub> analyzers, and ceilometers) necessary to outfit the PAMS Required Site will be selected and purchased so as 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 2021 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. Ecology will conduct a shakedown assessment of the PAMS parameters prior to reporting data during the first PAMS Required Site monitoring season and annually thereafter prior to PAMS season (unless the instruments are operated year-round). Ecology 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 3<sup>rd</sup> 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 for most parameters minimally during the 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. The initial shakedown period for the auto-GC will begin upon completion of

installation and testing by the vendor and continue until the instrument is online, calibrated, and stable minimally four weeks prior to reporting data to AQS.

### ***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 will be developed and used to ensure a consistent level of inspection for site operators. An example site visit checklist detailing typical items inspected is included in Appendix E.

### **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**

<b>Instrument</b>	<b>Maintenance Activity</b>	<b>Frequency</b>
Auto-GC	Maintenance activities are prescribed in the associated SOP. They include replacing the Nafion dryer (if so equipped), replacing preconcentrator trap(s), servicing zero air generator, calibrating standard dilution measurement equipment	Performed annually prior to PAMS season
Carbonyls Sampler	Maintenance activities are prescribed in the associated SOP. They include recharging/replacing the ozone denuder, replacing the particulate filter, and performing positive bias challenge	Performed annually prior to PAMS season
True NO <sub>2</sub> Analyzer	Maintenance activities are prescribed in the associated SOP. These include replacement of particulate filter, servicing zero air generator, calibrating standard dilution equipment	Performed annually prior to PAMS season
Precipitation Gauge	Weighing gauges: Routine visual check. Clean gauge by soaking and wiping with a clean cloth and soapy water. Change chart, chart pen, wind clock or change batteries	Each site visit
	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 quarterly
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 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 as needed
Ceilometer	Maintenance activities are prescribed in the associated SOP. 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 the ASL QAPP and associated SOP. Such includes servicing pumps, replacing guard columns, replacing solvent frits, injector needles, etc.	As prescribed in the ASL QAPP (or equivalent) and SOP

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 and document in the onsite logbook basic checks during each site visit which include visually examining the instruments at the site and verifying communication with the data acquisition system (DAS). An example site visit checklist is included in Appendix E. The intent of this checklist is to serve as a comprehensive list of items for operators to verify when onsite such that the risk of data loss is minimized and to demonstrate that equipment is operating normally. 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. Calibration is established by analysis of minimally three concentration levels of a representative compound for each respective FID, typically propane or butane for the light hydrocarbon ( $C_2$  to  $C_6$  or porous layer open tubular - PLOT column) channel and benzene for the heavy hydrocarbon ( $C_6$  to  $C_{12}$  or polydimethylsiloxane – PDMS column) channel. The stock calibration gas (primary standard) will be NIST-traceably certified for propane (or butane) and benzene. The calibration is then to be immediately verified by analysis of a NIST-traceably certified SSCV containing compounds representing the molecular weight range ( $C_2$  to  $C_{10}$ ). This SSCV is to be analyzed minimally weekly thereafter and must be within  $\pm 30\%$  of the nominal concentration for the target compounds.

#### ***B7.1.3 Calibration and Calibration Verification for True NO<sub>2</sub> Analyzers***

True NO<sub>2</sub> analyzer instruments require calibration initially when placed into service by introduction of a zero and an upscale span point (approximately 80% of the intended measurement range). The calibration will be verified immediately thereafter by conducting the MPV described in Section B.5.1.3. The MPV will show the analyzer calibration response has been effectively established through linear regression of the theoretical concentrations and instrument readings with a correlation coefficient of  $r^2 \geq 0.995$  and an x-intercept within  $\pm 0.2$  ppb of the origin. Additionally, the percent difference of each standard measurement in the MPV will be within  $\pm 10\%$  of the theoretical concentration. Once the MPV meets acceptance criteria, the instrument calibration and zero must be verified minimally every 14 days. For the zero, the zero drift must be less than  $\pm 0.3$  ppb and the span level (a concentration approximately 80% of the intended measurement range) must be within  $\pm 10\%$  of the theoretical concentration. More

frequent verifications are encouraged, and operators are also encouraged to conduct zero/span/precision checks which include verification of a zero concentration and two standard concentration levels – a span point of approximately 80% of the measurement range, and a precision point in the lower 1/3 of the measurement range. Instruments which do not meet the listed calibration verification acceptance criteria listed in Table B5-3 will be recalibrated by adjusting the instrument response to match that of the zero and reference standard or may be replaced with a known operable, calibrated instrument. Data collected since the most recent acceptable MPV or zero/span check or zero/span/precision check will be qualified or invalidated, as appropriate, when reported to AQS.

#### ***B7.1.4 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 B5.1.4. Instruments which do not meet the listed calibration verification acceptance criteria listed in Table B5-4 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. Certification standards for calibration equipment are detailed in Section 14 of the Washington State Ambient Air Monitoring Quality Assurance Plan.

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 <sup>a</sup> Frequency Requirement	Calibration Verification <sup>b</sup> Check Frequency
Flow Transfer Standard	≤ 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	Tolerance within manufacturer specifications	Delivery of known liquid volumes – preparation of carbonyls calibration standards	Initially and every six months thereafter or when calibration checks demonstrate an out of tolerance condition	Each day of use by weighing delivered volumes of deionized water bracketing those dispensed; Must cover the range of use
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 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 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>	Annual at temperature range of use – Correction factors applied to match certified standard	Annual calibration is sufficient
Balance	Tolerance within manufacturer specifications	Laboratory – Weighing standards, calibration of pipettes	Annually or when calibration checks demonstrate an out of tolerance condition	Each day of use with certified calibration check weights bracketing the balance load; Must cover the range of use

**Table B7-1 (continued). Calibration Requirements for Critical Support Instruments**

Critical Support Equipment	Specifications and Acceptable Uncertainty	Area of Use	Calibration <sup>a</sup> Frequency Requirement	Calibration Verification <sup>b</sup> Check Frequency
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	Within ± 0.5 psi or manufacturer-specified tolerance, whichever is smaller	Field and Laboratory – Measure canister pressure/vacuum for standards preparation	Annual	Annual calibration is sufficient; Must cover the range of use
Mass Flow Controller – Gas Calibrator	Within ±2% of certified flow transfer standard	Precise metering of standard and diluent gases for calibration of monitoring instruments	Annual or when calibration checks demonstrate flows are out of tolerance	Minimally quarterly (before and at the end of PAMS season), monthly recommended

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

<sup>b</sup> 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. Air monitoring staff receiving supplies and consumables must:

- Perform a rudimentary inspection of the package(s) as received
- Note any obvious problems with the shipment such as a crushed box or wet cardboard
- Open the package and inspect the contents
- Compare contents against the packing slip to determine that the order is complete
- Plug in and turn on the instrument or equipment (if applicable) to ensure it powers up correctly

If problems with the order are discovered:

- Note problems/issues on the packing list

- Notify agency Shipping & Receiving of missing or damaged items and immediately call the vendor

If the order is complete and in good condition:

- Sign and date the packing list and send it to the Air Quality Program Purchasing Coordinator so that payment can be made in a timely manner
- Place Ecology tag on the item (if purchased with Ecology funds)
- Place ordered supplies in stock equipment/supplies in the appropriate predetermined area
- Enter equipment receiving an Ecology tag into the Site Information Management System Equipment Inventory

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

When available, standard NO<sub>2</sub> gases for calibrating NO<sub>2</sub> analyzers will be procured from a reputable supplier and certified concentrations must be traceable to a reference material, such as those prepared by the NIST or the Van Swinden Laboratorium (VSL). Such NO<sub>2</sub> standard gases will be accompanied by a COA indicating the levels of impurities, which will be less than 1 ppm of residual NO. When employing GPT to calibrate NO<sub>2</sub> analyzers, NO standard gases will be Standard Reference Material (SRM) or Certified Reference Material (CRM) quality and compliant with Protocol 2 of the EPA's Protocol Gas Verification Program (PGVP).<sup>11</sup> Ozone generators employed to produce standard NO<sub>2</sub> gas by GPT with excess NO will be standardized against a Level 1 or Level 2 ozone standard<sup>12</sup> as prescribed in the criteria gas monitoring QAPP.

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.

COAs 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. 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 COA 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 for VOCs analysis 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 ASL 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.

**Table B8-1. DNPH Cartridge Lot Blank Acceptance Criteria**

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

## 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. Ecology's data management system is described in the Washington State Ambient Air Monitoring Quality Assurance Plan.

## 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
- PEs

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

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

Staff conducting assessments (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 (informal TSA and IPA)	Evaluation of PAMS Required Site readiness	Monitoring agency QAU	Recommended prior to each PAMS season as resources allow
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, as resources allow and after TSA training and checklists are provided
		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
	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 ASL QAU	Annually during active PAMS monitoring and before 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 ASL 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
Performance Evaluation (PE)	Analysis of known standard concentrations of target analyte NO <sub>2</sub> gas provided to the analyzer	Monitoring agency QAU and EPA Regional staff or EPA support contractor through EPA NPAP	Monitoring agency PE to be conducted annually. EPA NPAP audit minimally every 6 years

### ***CI.1.1 Instrument Performance Audit***

IPAs are an independent check of instrument performance by an individual not involved in routine operation and with reference standards independent from those used to calibrate the instrument or to perform routine calibration checks. IPAs involve comparing the output of an instrument to an independent reference standard and quantifying the difference between the measurement generated by the instrument undergoing assessment and the reference standard. The 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.

#### ***CI.1.1.1 Carbonyls Instrument Performance Audit***

Flow rate bias in ambient air sampling for carbonyls has an inverse relationship with the resulting concentration bias. That is, flow rates that are biased low result in overestimation of air concentrations whereas flow rates that are biased high result in underestimation of air concentrations. Minimally once annually (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.

#### ***CI.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 B5-4. Audit procedures for meteorological

instruments are described in Ecology's Meteorological Monitoring Standard Operating Procedure.

### ***CI.1.2 Technical Systems Audit***

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

To increase the uniformity of TSAs, EPA has developed checklists for the PAMS Required Site program for both monitoring agency and ASL 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). After EPA provides training and checklists, Ecology 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.

Laboratory QA staff will conduct 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 ASL QAU will distribute the TSA report to the monitoring agencies operating sites supported by the laboratory. The laboratory will notify supporting monitoring sites 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. The monitoring agency will subsequently notify the EPA Region of the outcomes of the annual ASL TSA, including any corrective actions taken by the monitoring agency.

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.

#### ***CI.1.2.1 Shakedown Audits***

After EPA provides TSA training and checklists, Ecology will conduct a shakedown audit of the PAMS monitoring program to evaluate readiness for the upcoming PAMS season when resources allow. This shakedown audit will consist of an informal 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 as a result 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.

### ***CI.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

Monitoring agency and ASL 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.

### ***CI.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 PAMS Required Network Sites and/or ASLs 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 support laboratory (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. Sites or ASLs

will analyze the PT sample(s) on the auto-GC (VOCs) or via their 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, each PAMS ASL 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. Sites or ASLs that do not meet the bias acceptance criterion 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.

### ***C1.1.5 Performance Evaluation***

A PE is a test of the measurement system performed by providing a series of known standard concentrations of NO<sub>2</sub> gas to the monitoring station analyzer TTP and evaluating the bias of the measurements at each provided concentration. PEs are required annually as prescribed in 40 CFR Part 58 Section 3.1.2. Measured concentrations must be within  $\pm 15\%$  or  $\pm 1.5$  ppb, whichever is greater, of the theoretical challenge concentration.

In addition to the annually required PE conducted by the monitoring agency or cognizant PQA, the EPA will conduct an audit of the NO<sub>2</sub> measurement system TTP minimally every six years, as prescribed in 40 CFR Part 58 Section 3.1.3.

### **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. Corrective action processes are described in parameter-specific SOPs as well as the Washington State Ambient Air Monitoring Quality Assurance Plan.

If monitoring agency sites or ASLs 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 annually. 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, PEs, 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 associated ASLs 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;<sup>13</sup> 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,<sup>14</sup> which for PAMS is to assist in the development and refinement of predictive models for the formation of ground-level O<sub>3</sub>.

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 ASL. The ASL will minimally verify the carbonyls data reported to ensure the data are correct and comply with the established laboratory QAPP and SOP(s). As the ASL for the PAMS Required Site carbonyls data, Eastern Research Group (ERG) validates analytical data, conducts inter- and intra-laboratory testing, assesses and reports data quality, and verifies all laboratory QA activities. ERG's data verifications and validation methods are described briefly in Ecology's Air Toxics Monitoring Quality Assurance Project Plan, and in detail in ERG's Support for the EPA National Monitoring Programs Quality Assurance Project Plan. Ecology's data validation process for hourly VOC data is described in the Auto-GC SOP, currently under development.

Personnel performing data verification and validation activities will:

- Be familiar with the types of data each instrument system produces and the typical measurement ranges produced by each for various parameters (e.g., typical solar radiation levels, benzene concentrations, and true NO<sub>2</sub> concentrations).

- 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 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 ASL 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 NO<sub>2</sub> 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 QC check 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 the instrument's present performance.

**Table D1-1. Routine Review Activities and Associated Frequency**

<b>Verification Activity</b>	<b>Frequency</b>
Measurements did not exceed the alarm limits set in the DAS	Daily <sup>a</sup>
The rate of change observed for the analyte is consistent with ambient data trends (specific to high frequency measurements – e.g. minute data)	Daily <sup>a</sup>
Measurement data that exceed the instrument calibration range	Daily <sup>a</sup>
Measurement data are complete (sample collection and COC forms are not missing information, expected electronic files are recorded, and logbook entries are complete)	Daily <sup>a</sup>
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 <sup>a</sup> , as applicable
Chromatography is acceptable (stable baseline, adequate peak separation, etc.), integration parameters provide proper peak integration, and that analyte identification is appropriate based on the established RT windows	Daily <sup>a</sup>
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

<sup>a</sup> Daily on normal business days when staff are on duty.

### ***D1.2.2 Technical (Peer) Review***

Once the data have undergone routine review by the instrument operator, the data are 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

**Table D1-1 (continued). Routine Review Activities and Associated Frequency**

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 and manual integration changes are justified and appropriate
- Carbonyls sample holding times were met and the ASL 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 by the use of 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 comprise the initial first step to 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**

<b>Parameter</b>	<b>Appropriate Duration (Size) of Dataset</b>
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
True NO <sub>2</sub>	Two to four weeks’ worth – ensure that QC checks bracket the duration undergoing 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 (Carbonyls and Speciated VOCs)***

Instrument sensitivity for carbonyls and speciated VOCs 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**

Ecology will utilize the Data Analysis and Reporting Tool (DART) software developed by Sonoma Technology, Inc. and other tools to validate auto-GC data; validation specifics are detailed in the Auto-GC SOP, currently under development. Data validation procedures for other PAMS parameters are described in the following SOPs published by Ecology:

- Air Monitoring Documentation, Data Review, and Validation Procedure
- Meteorological Monitoring Procedure
- Ozone Monitoring Standard Operating Procedure
- Gaseous Pollutant Monitoring Standard Operating Procedure

### **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 end 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 such as true NO<sub>2</sub>), 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. Data verification procedures are also detailed in Ecology's parameter-specific SOPs and Ecology's Air Monitoring Documentation, Data Review, and Validation Procedure.

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 each critical element was satisfied. Such checklists will be included in the SOP(s) prescribing data verification and validation as specified in this QAPP.

### **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.

### ***D2.2.1 Data Visualization Methods***

Graphical techniques permit comparison of concentrations of each PAMS parameter to the expected concentrations/measurements and relative concentrations/measurements 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. Processes utilized by Ecology for data visualization are detailed in the Auto-GC SOP, currently under development.

### ***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, Performance Evaluation, and Proficiency Test Results:** Deviations from acceptance or advisory limits during IPAs, PEs, or PTs indicate bias is present in the measurement system. The validator will review IPA, PE, 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:** ASL results reports may include sample narratives or include QC sample results that provide context for the sample measurements. Data provided by the ASL will be verified with respect to the laboratory processes and method QC acceptance criteria; the ASL will flag data when operational or QC criteria nonconformances occur and notify the site monitoring agency. This will typically involve data flags or comments on electronic data deliverables. It is the responsibility of the site monitoring agency 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 degrees 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 B5-5 for carbonyls, Table B5-2 for speciated VOCs, and Table B5-3 for true NO<sub>2</sub>. In situations when no qualifier or combination of qualifiers exists to adequately describe the valid compromised data, the data should be estimated by adding the QA qualifier LJ to the data. When invalidating compromised data and no NULL qualifier exists to describe the rationale for invalidation, the data should be invalidated with the NULL qualifier AM.

**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
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
DN	DNPH peak less than NATTS TAD requirement, reported value should be considered an estimate	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	

**Table D2-1 (continued). AQS Qualifiers and Null Codes for PAMS**

Qualifier Code	Qualifier Description	Qualifier Type	Comment
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 for ozone & NO <sub>2</sub>
BA	Maintenance/Routine Repairs	NULL	
BB	Unable to Reach Site	NULL	
BE	Building/Site Repair	NULL	
BF	Precision/zero/span	NULL	
BH	Interference/co-elution/misidentification	NULL	applies to auto-GC parameters only
BI	Lost or damaged in transit	NULL	applies to carbonyls only

**Table D2-1 (continued). AQS Qualifiers and Null Codes for PAMS**

Qualifier Code	Qualifier Description	Qualifier Type	Comment
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	
EC	Exceeds Critical Criteria	NULL	use a more descriptive NULL qualifier when possible
MC	Module End Cap Missing	NULL	applies to carbonyls only
QV	Quality Control Multi-point Verification	NULL	
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 be 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% or more 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.

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## **APPENDICES**



## **APPENDIX A**

### **SLT MONITORING AGENCY QAPP APPROVAL**

## Approval of PAMS Required Site SLT Monitoring Agency QAPP

Washington State Department of Ecology 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 in the National QAPP):

A3	Distribution List	B3	Sample Handling and Custody Requirements
A5.1	PAMS Required Site(s)	B5.1	Quality Control for Field Activities (QA Sample Collection)
A6.2	Personnel and Organization	B6.1	Instrument Acquisition
A6.3	Schedule for PAMS Required Site Activities	B6.4	Instrument Maintenance
A7.3.1	Waiver for Speciated VOCs by Auto-GC	B7.2	Calibration Support Equipment
A8	Special Training Requirements/Certification	B8	Inspection/Acceptance Requirements for Supplies and Consumables
A9	Documentation and Records	B10	Data Management
A9.1	Recording of Data	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	Data Review, Verification, and Validation Requirements
B2	Sampling and Measurement Methods	D1.1	Data Verification and Validation Responsibilities
B2.1	Chemical Parameters – Inlet Composition	D2	Data Verification and Validation Methods

By signing below, the signatories indicate that the SLT Monitoring Agency 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.

### State/Local/Tribal Agency

Print Name: \_\_\_\_\_  
Date: \_\_\_\_\_

Signature: \_\_\_\_\_  
Director

Print Name: \_\_\_\_\_  
Date: \_\_\_\_\_

Signature: \_\_\_\_\_  
Quality Assurance Officer

Print Name: \_\_\_\_\_  
Date: \_\_\_\_\_

Signature: \_\_\_\_\_  
Technical Services Section Manager

Print Name: \_\_\_\_\_  
Date: \_\_\_\_\_

Signature: \_\_\_\_\_  
Air Monitoring Coordinator

Print Name: \_\_\_\_\_  
Date: \_\_\_\_\_

Signature: \_\_\_\_\_  
Quality Assurance Coordinator

### EPA Regional Office Acknowledgement or Approval

Print Name: \_\_\_\_\_  
Date: \_\_\_\_\_

Signature: \_\_\_\_\_  
PAMS Regional Coordinator

Print Name: \_\_\_\_\_  
Date: \_\_\_\_\_

Signature: \_\_\_\_\_  
Quality Assurance Manager

## **APPENDIX B**

### **EXAMPLE QUALITY BULLETIN**

Example Quality Bulletin

Subject:

Number: \_\_\_\_\_  
Date: \_\_\_\_\_  
Page \_\_\_ of \_\_\_  
Supersedes No.: \_\_\_\_\_  
Dated: \_\_\_\_\_

Background

\_\_\_\_\_  
QA Lead


Replace and Discard Original	Y/N _____
Add Material to Document	_____
Retain this bulletin until further notice	_____
Discard this bulletin after noting contents	_____

This bulletin will be invalid after: Date: \_\_\_\_\_

This bulletin will be incorporated into quality Procedure No. \_\_\_\_\_ by Date: \_\_\_\_\_

## **APPENDIX C**

### **EXAMPLE CHAIN-OF-CUSTODY FORM**



ERG Lab ID # \_\_\_\_\_

501 Keystone Park Drive, Suite 700, Morrisville, NC 27560

### PAMS CARBONYL COMPOUNDS CHAIN OF CUSTODY

<b>Lab Pre-Samp.</b>	<b>Site Code:</b> _____ <b>Cartridge Lot #:</b> _____ <b>Duplicate Event (Y/N):</b> _____ <b>Collection Date:</b> _____ <b>Field Blank Event (Y/N):</b> _____ <b>Relinquished by:</b> _____ <b>Date:</b> _____
<b>Field Setup</b>	<b>Received by:</b> _____ <b>Date:</b> _____ <b>Set-Up Date:</b> _____ <b>Operator:</b> _____ <b>Sys. #:</b> _____ <b>City/State:</b> _____ <b>AQS Code:</b> _____
<b>Field Recovery</b>	<b>Recovery Date:</b> _____ <b>Sample Duration (8 or 24 hr):</b> _____ <b>Operator:</b> _____ <b>Status:</b> <b>VALID</b> <b>VOID</b> (Circle one) <b>Cartridges Capped (Y/N):</b> _____ <b>Relinquished by:</b> _____ <b>Date:</b> _____
<b>Lab Recovery</b>	<b>Received by:</b> _____ <b>Date:</b> _____ <b>Status:</b> <b>VALID</b> <b>VOID</b> (Circle one) <b>Uncorrected Temperature:</b> _____ <b>If void, why:</b> _____ <b>Corrected Temperature:</b> _____ <b>IR Gun:</b> <b>1</b> <b>2</b> (Circle one) <i>Samples stored in Refrigerator # 11</i>

<b>PAMS</b>	Sample Date	Sample Time	Sample Duration	Sample Volume	Cartridge Pouch #	Sample ID	Lab ID
	M/D/Y	0400 to 1200	8 hr	ex. 800L	ex. 21G0201	Site - Ch. 1	
	M/D/Y	1200 to 2000	8 hr	ex. 800L	ex. 21G0202	Site - Ch. 2	
	M/D/Y	2000 to 0400	8 hr	ex. 800L	ex. 21G0203	Site - Ch. 3	
	Field Blank and duplicate samples will also be listed here						

Comments: **ERG completes items highlighted in yellow**  
**Site completes items highlighted in blue**

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## **APPENDIX D**

### **EXAMPLE STAFF PROFICIENCY TRAINING FORM**



EXAMPLE PAMS REQUIRED SITE TRAINING FORM

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	Version and Effective Date	Date Read/Initials
Monitoring Agency PAMS Required Site QAPP						
Determination of Speciated VOCs by Auto-GC						
Collection of Carbonyls Samples						
Measurement of True NO <sub>2</sub>						
Measurement of Mixing Layer Height by Ceilometer						
Measurement of Wind Speed and Wind Direction						
Measurement of Solar Radiation and UV Radiation						
Measurement of Precipitation						
Measurement of Temperature, Relative Humidity, and Barometric Pressure						
Data Verification and Validation						
Other SOPs as defined by the monitoring agency						

**EXAMPLE INITIAL DEMONSTRATION OF CAPABILITY**

Staff will read the current version of the SOP governing the procedure(s) and complete an initial demonstration of capability (IDOC) which will include either:

- a. Observing a trained individual perform the procedure(s), performing the procedure with assistance from a trained individual, and performing the procedure(s) independently under the observation of a trained individual, or
- b. Performance of the procedure(s) independently under the observation of a QA staff member or supervisor

<b>Procedure</b>	<b>Date Trainee Observed Trainer Perform Procedure(s)</b>	<b>Date Trainee Performed Procedure(s) with Trainer</b>	<b>Date Trainee Performed Procedure(s) Independently Under Observation</b>	<b>Approval by Director to Perform Procedure Independently</b>
Determination of Speciated VOCs by Auto-GC				
Collection of Carbonyls Samples				
Measurement of True NO <sub>2</sub>				
Measurement of Mixing Layer Height by Ceilometer				
Measurement of Wind Speed and Wind Direction				
Measurement of Solar Radiation and UV Radiation				
Measurement of Precipitation				
Measurement of Temperature, Relative Humidity, and Barometric Pressure				
Other Procedures as necessary				

**EXAMPLE CONTINUING DEMONSTRATION OF CAPABILITY**

Once the IDOC is completed, staff 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.

<b>Procedure</b>	<b>Date Trainee Performed Procedure(s) Independently Under Observation</b>	<b>Approval by Director to Perform Procedure Independently</b>
Determination of Speciated VOCs by Auto-GC		
Collection of Carbonyls Samples		
Measurement of True NO <sub>2</sub>		
Measurement of Mixing Layer Height by Ceilometer		
Measurement of Wind Speed and Wind Direction		
Measurement of Solar Radiation and UV Radiation		
Measurement of Precipitation		
Measurement of Temperature, Relative Humidity, and Barometric Pressure		
Other Procedures as necessary		

**ADDITIONAL AND SUPPLEMENTAL TRAINING**

The staff member has received the following additional or supplemental training: (provide documentation examples, such as attendance forms, certificates of course completion, etc.)

<b>Training Title</b>	<b>Type of Training<sup>1</sup></b>	<b>Initials/Date</b>

<sup>1</sup> ATS = Attended training sessions, ATW = Attended training webinars, RTV = Reviewed training videos, RTC = Received training certifications – refer to attached certificates

## **APPENDIX E**

### **EXAMPLE SITE VISIT CHECKLIST**

Site operators should complete this checklist with each visit to the PAMS Required Site during PAMS season. The form below is an example of items checked during site visits and any deviations or issues will be documented in the site logbook.

Site ID: \_\_\_\_\_ Date of Visit and Operator Initials: \_\_\_\_\_

	<b>Check</b>	<b>OK? (Y/N)</b>	<b>Comments</b>
GENERAL	Vandalism		
	Operational Hazards (broken decking, stinging insects, snakes, icicles, etc)		
	Nearby recent construction		
	Landscaping activities (mowing, tree trimming, etc)		
	Weather damage		
	Shelter environmental conditions within specification		
MANIFOLD INLET	Inlet probe clear (no insect nests, debris, etc)		
	Bypass fan operating		
	Manifold flow within spec		
	Connections to manifold secure		
	Manifold cleaned within prescribed frequency		
SITE LOG	Visitors or events since last visit?		
	Log updated with this visit?		
DATA ACQUISITION SYSTEM	Verify no DAS error messages/alarms		
	Ensure DAS communication with instruments		
	DAS clock is accurate to $\pm 1$ minute		

	Check	OK? (Y/N)	Comments
TRUE NO <sub>2</sub>	Instrument display is on		
	No error messages/alarms		
	Instrument reading is reasonable for scheduled monitoring (ambient, span, zero)		
	Calibration cylinders > 400 psi		
	Zero air generator cycling properly		
	Calibrator does not show errors/alarms		
	Instrument clock is accurate $\pm$ 1 minute		
CARBONYLS	Instrument status correct for sampling program		
	If sampling day, instrument is sampling and flow is correct (1LPM)		
	If non-sampling day, program displays correct date for next sample		
	Sample cartridges are installed correctly		
	Sampling unit does not show error messages/alarms		
AUTO GC	No error messages/alarms		
	Correct sequence line is active (should be ambient sample during daytime)		
	Correct part of the measurement cycle is active (sample collection, sample desorption, GC analysis, GC cooling, etc)		
	Hydrogen generator has sufficient water and does not show error messages/alarms		
	Carrier gas, RTS, H <sub>2</sub> cylinders have sufficient pressure		
	Instrument clock is accurate $\pm$ 1 minute		
	Zero air generator(s) operating properly		
	Compressor operating properly		

	<b>Check</b>	<b>OK? (Y/N)</b>	<b>Comments</b>
METEOROLOGY	Complete weekly meteorology sensor visual checklist		
	Temperature is reasonable with ambient conditions and recorded in DAS		
	Wind speed and direction operation are reasonable for conditions		
	Shrouds for thermometer and hygrometer are clear of debris		
	Solar and UV data in DAS are reasonable to conditions (sunny, cloudy, etc)		
	Precipitation gauge is operational and has registered precipitation events in DAS		
	Ceilometer lens is clean		
	Meteorology measurements reasonable compared to nearby NWS sites		

Additional comments:



## **APPENDIX F**

### **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 entirely<sup>i</sup>, or to make PAMS measurements at alternative locations such as existing PAMS sites or existing National Air Toxics Trends Station (NATTS) sites<sup>ii</sup>. 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 days<sup>iii</sup>. In addition, a monitoring organization may request that it utilize data from a nearby meteorological station rather than establish its own<sup>iv</sup>. 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, 2019, 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 O<sub>3</sub> 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 O<sub>3</sub> 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 O<sub>3</sub> sites; additional NO<sub>x</sub> or NO<sub>y</sub> 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

<sup>i</sup> 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.

<sup>ii</sup> 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.

<sup>iii</sup> 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.

<sup>iv</sup> 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) program<sup>2</sup> will be used.

**Nitrogen Oxides** – Will monitor for NO and NO<sub>y</sub> (total oxides of nitrogen) in addition to true NO<sub>2</sub>. The true NO<sub>2</sub> is required to be measured with a direct reading NO<sub>2</sub> analyzer, cavity attenuated phase shift (CAPS) spectroscopy or photolytic-converter NO<sub>x</sub> analyzer. We have elected to use (*insert type and manufacturer*) for the true NO<sub>2</sub> measurement. NO and NO<sub>y</sub> will be measured using a (*insert manufacturer*).

**Table 1 PAMS Target Speciated VOCs List**

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

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

<sup>a</sup> Important SOAP (Secondary Organic Aerosols Precursor) Compounds

<sup>b</sup> HAP (Hazardous Air Pollutant) Compounds

<sup>2</sup> See NATTS Technical Assistance Document for TO-11A method.

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

## **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 rule<sup>1</sup> 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.

<sup>1</sup>80 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**  
**(Example)**



## Attachment 3 Waiver to collect solar radiation measurements at an alternate site



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY  
REGION 10  
1200 Sixth Avenue, Suite 155  
Seattle, WA 98101-3123

AIR & RADIATION  
DIVISION

November 3, 2020

Ms. Jill Schulte  
Ambient Air Monitoring Coordinator  
Department of Ecology  
State of Washington  
P.O. Box 47600  
Olympia, Washington 98504-7600

Dear Ms. Schulte:

This letter is in response to your October 7, 2020, correspondence requesting a waiver to collect solar radiation measurements for the Seattle Photochemical Assessment Monitoring Station (PAMS) at an alternative location. In this correspondence you explained that the Seattle-Beacon Hill station (AQS ID: 53-033-0080), where the remainder of the PAMS sampling will be located, is unacceptable for solar radiation measurements. This is due to the shadow cast on the monitoring site for part of the day by a nearby driving range net. Your proposed solution is to locate the radiometer and pyranometer instruments at the Seattle-Duwamish monitoring station (AQS ID: 53-033-0057) instead. You explained that this alternative siting is appropriate because of the proximity of the stations (1.55 miles) and the lack of obstructions at the Seattle-Duwamish station.

My staff completed the review of the information you provided and consulted the EPA's Office of Air Quality Planning and Standards regarding this request. We agree that siting the PAMS solar radiation instrumentation at the Seattle-Duwamish station is an acceptable solution. Per 40 CFR Part 58, Appendix D, Section 5(c) the EPA can grant a waiver to allow the collection of required PAMS measurements at an alternative location if the alternative location will provide representative and useful data. In this instance, we conclude that those standards will be met at the alternative location.

Region 10 approves the alternative siting of the PAMS solar radiation measurements at the Seattle-Duwamish station (AQS ID: 53-033-0057), instead of the Seattle-Beacon Hill station (AQS ID: 53-033-0080). Please reference and attach this waiver in future Annual Network Plan reports, and address whether this alternative location continues to be appropriate in future five-year network assessments. We also request that you continue to keep my staff informed of any other developments with the PAMS monitoring. If you have any questions regarding this waiver, please contact me at (206) 553-0985 or Sarah Waldo at (206) 553-1504.

Sincerely,

DEBRA SUZUKI

Debra Suzuki, Manager  
Air Planning, State/Tribal Coordination Branch

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United States  
Environmental Protection  
Agency

Office of Air Quality Planning and Standards  
Air Quality Assessment Division  
Research Triangle Park, NC

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