



TOXICS

QUALITY ASSURANCE PROJECT PLAN

VOLUME IV

B-004-OAQ-AMB-QA-24-Q-R3

PREPARED BY:

Indiana Department of Environmental Management (IDEM)
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Revision 3

January 1, 2024

QAPP Revision History

Revision Number	Date	Responsible Party	Description of Change
0	May 1, 2021	QAS Chief	New QAPP format to replace QA Manual, which served as OAQ AMB QAPP, and was last U.S. EPA approved on March 9, 2018
1	May 1, 2022	QAS Chief	<p>Section 5.1 – Information on IDEM history moved to Section 4.1</p> <p>Section 6.1, Table 3 – Updated to list EPA’s current list of optional compounds and the compounds in the AMB ATS new standard</p> <p>Section 6.1 – Under carbonyls, added analytes</p> <p>Section 7.3.2 – Added toxic VOC completeness of 23 to 25 hours for a day, and apply AF in AQS if a sample day is missed</p> <p>Section 7.3.3.2 – Changed duplicate to collocated. Also changed from 10% to every 6th day</p> <p>Section 7.3.4.2 – reworded and added additional information pertaining to bias</p> <p>Section 9, Table 13 - Added TSA questionnaire, audit finding response form, and final report and closeout letter</p> <p>Section 11.2 – Analytical information for Toxics VOC moved to Section 13.2</p> <p>Section 12.1 – Added information for toxic VOC canister setup and pickup</p>

			<p>Section 12.5 – The information presented in this section was moved to section 10</p> <p>Section 12.6 – The information presented in this section was moved to section 16</p> <p>Section 16.1 – A lot of this information was combined with Section 16.0, with some edits</p> <p>Section 16.2 – Some edits made to reflect updates in procedures, which includes: Each canister is cleaned in an oven overnight or over a weekend replaces 20 cleaning cycles; Maximum of 12 canisters cleaned at once replaces 8 canisters cleaned at once</p> <p>Section 20, Table 23 – Removed annual data certification</p> <p>Section 23.2.4.1, Table 25 – Added QAPP issue</p> <p>References – Added references at end of QAPP</p> <p>Revision made do not require signatures</p>
2	May 1, 2023	QAS Chief	<p>All Sections = Updated SOP titles; Added and removed some SOPs</p> <p>List of Acronyms = added ICAL, Initial Calibration; RF, Response Factor</p> <p>Section 4.1 = Added AMS program coordinator</p> <p>Section 4.2 = Added AMS program coordinator</p>

			<p>Section 4.3, Table 2 = Added AMS program coordinator</p> <p>Section 6.2, Table 6 = For Pre-sampling season instrument and support equipment maintenance, changed frequency from March 1 to May 1. For QAS staff, send sample with concentrations of target PAMS VOCs blind to the ATS site operator, changed “Prior to May and toward the end of August” to “Prior to June 1 and soon after August 31”</p> <p>Section 6.2, Table 7 = For ATS Instrument calibration, MDL, and standards, changed “quarterly MDLS” to “MDLs twice a year after maintenance”</p> <p>Section 6.2, Table 8 = For QAS staff, Zero air audit, changed “Prior to May and toward the end of August” to “Prior to June 1 and soon after August 31”</p> <p>Section 7.3.2, Toxics VOC Make-up Sample Policy = added “time” to collect make-up samples as close to the original sampling date as possible; Carbonyls Make-up Sample Policy = added “time” to collect a replacement carbonyl sample, three 8-hour samples during PAMS season, as close to the original sampling date as possible</p> <p>Section 7.3.3.2 = Changed propane standard to propane/benzene standard. Changed “$\pm 10\%$ of 2996 ppbC” to “$\pm 10\%$ of 200 ppbC, or the total of propane and benzene if the total is not 200 ppbC”. Changed</p>
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			<p>“$\pm 10\%$ of 2996 ppbC” to “$\pm 10\%$ of 200 ppbC” for the instrument to pass daily calibration; Changed requirement for determining MDLs.</p> <p>Section 7.3.4.2.2 = Changed “The canister should be analyzed within three days of initial pressurization and total concentration of all 62 analytes must be < 0.200 ppb” to “The canister is analyzed shortly after initial pressurization and total concentration of all 62 analytes must be < 0.200 ppb”</p> <p>Section 11.1 = Reworded inlet information to state the following, “Inlet probe(s) are constructed of borosilicate glass or chromatographic grade stainless steel. Carbonyls and Benzene may also use polytetrafluoroethylene (PTFE) or perfluoroalkoxy (PFA) Teflon®”</p> <p>Section 11.2, Carbonyl, for store and transport changed temperature from “$\leq 4^{\circ}\text{C}$” to “$\leq 4.0^{\circ}\text{C}$”</p> <p>Section 11.2.1, Table 14 = Changed GC Agilent / 7890B temperature range from “$15.0 - 35.0^{\circ}\text{C}$” to “$15.0 - 30.0^{\circ}\text{C}$”</p> <p>Section 12.2, Carbonyls by TO-11A = Changed “Store new cartridges $\leq 4^{\circ}\text{C}$ upon receipt” to “Store new cartridges $\leq 4.0^{\circ}\text{C}$ upon receipt”</p> <p>Section 12.3, Chain of Custody Carbonyls = Changed the temperature for storage of carbonyls from “$\leq 4^{\circ}\text{C}$” to</p>
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			<p>“≤ 4.0°C”; Made some edits to SUMMA Canister Chain-of-Custody Tag</p> <p>Section 14.1.1, Table 15 = Made some edits, including adding Precision Check, added Second Source Calibration Verification</p> <p>Section 14.1.2, Table 16 = Added Collocated Sample</p> <p>Section 14.1.3, Table 17 = Changed Mass Flow Controller calibration/verification required frequency from “Minimally every 30 days during PAMS season” to “monthly”; acceptance criteria from “within ±10% of flow transfer standard” to “≤±10.1% of flow transfer standard”; and Sample retrieval temperature from “≤ 4°C” to “≤ 4.0°C”</p> <p>Section 14.2.1 = Changed “propane” standard to “propane/benzene” standard and “2996” ppbC changed to “200” ppbC. Also changed MDL from “quarterly” to “MDLs are calculated twice a year after maintenance. We will also be checking the MDLs, but not reporting them, twice a year to make sure the MDLs are still valid”</p> <p>Section 20, Table 23 = Changed assessment “Carbonyls PE audit” to “Carbonyls PE zero audit”</p>
3	January 1, 2024	QAS Chief	<p>All Sections = changed QA laboratory to QA standards laboratory; Replaced InfoDUMP with InfoHub; Renamed PAMS VOCs to PAMS Auto-GC VOCs; Updated TAD for Sampling of</p>

			<p>Ozone Precursors for the PAMS Program from Revision 2 of April 2019 to Revision 3 of May 2023; Updated 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 from April 2019 to May 2023; Updated Technical Assistance Document for the National Air Toxics Trends Stations Program, Revision 3, October 2016 to Revision 4, July 2022</p> <p>Section 6.2, Table 6 = Under ATS staff conducting Instrument calibration and MDLS, for significant maintenance, added unless during PAMS season then only calibration</p> <p>Section 7.3, Table 10 = Changed PAMS Auto-GC VOCs Sensitivity (Detection Limit) from ≤ 0.5 ppbC to ≤ 0.6 ppbC</p> <p>Section 9 = Added information for record storage for ATS</p> <p>Section 9, Table 13 = Removed span and one point QC checks; made edit to field logbooks to include only Toxics VOC and carbonyl; added storage information for ATS records</p> <p>Section 14.1.1, Table 15 = Under Initial Calibration (ICAL), some edits made to Description, required frequency, and acceptance criteria. Under Continuing calibration</p>
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			<p>verification, some edits were made to Description and Recommended Corrective Action. Removed Retention time Standard (RTS) and added Secondary Source Calibration Verification (SSCV). Under Precision Check Description, added This is a secondary QC check</p> <p>Section 14.1.1 = Some edits made requiring deletion and addition of information</p> <p>Section 14.1.2, Table 16 = under Collocated Sample Data Status, replaced LJ with LK</p> <p>Section 15.4, Table 20 = Under Auto-GC Maintenance Activity, added hydrogen generator</p> <p>Section 21, Table 24 = Removed QA Reports; added % CV for Reporting vs Collocated by QAS; added Reporting vs. Collocated for TO-15 sample by ATS; added External PT results for PAMS Auto-GC VOC</p> <p>Section 23.2.4.1, Table 25 = For QX, added Fails secondary QC checks for PAMS Auto-GC; For AG, added Fails to stamp at correct time, PAMS Auto-GC; For AN, AV, AX, AZ, and BJ added PAMS Auto-GC; For AS, replaced current information with Used for PAMS Auto-GC when compounds fail CCV; Replaced DA with BL; For TC, added PAMS Auto-GC for SSCV; Replaced IC with MB; Replaced ID with ST; Replaced IE with TC</p>
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			<p>Section 25, References = Added Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air; added Agilaire AirVision</p> <p>QAPP will be routed for signatures and EPA approval</p> <p>Edits made due to EPA findings – IDEM informed via email, no new signatures:</p> <p>Section 3, Table 1 = Updated EPA contact phone number.</p> <p>Section 4.3 = Removed statement However, on occasion, the QAS equipment may be used for a QC check, but never to calibrate a site’s instruments.</p> <p>Section 6.1 = Added AQS ID 180970078 to identify PAMS/NCORE site.</p> <p>Section 11.2 = Added link for method codes for individual parameters.</p> <p>Section 12.2 = Added shipping time frame for carbonyls to get to analytical laboratory.</p> <p>Section 20, Table 23 = Added OAQPS along with their contractor for conducting technical systems audits.</p>
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List of Acronyms

Acronym	Meaning
°C	Degrees Celsius
AC	Assistant Commissioner
ADQ	Audit of Data Quality
AGL	Above Ground Level
AMB	Air Monitoring Branch
AMS	Ambient Monitoring Section
AMTIC	Ambient Monitoring Technology Information Center
ANP	Annual Network Plan
AQS	Air Quality System
ASL	Analytical Support Laboratory
ATS	Air Toxics Section
Auto-GC	Automatic Gas Chromatograph
BFB	Bromofluorobenzene
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
CFR	Code of Federal Regulations
CO	Carbon Monoxide
COC	Chain of Custody
CV	Coefficient of Variation
DART	Data Analysis and Reporting Tool
DAS	Data Acquisition System
DMDS	Data Management Display System
DNPH	2,4-dinitrophenylhydrazine
DQA	Data Quality Assessment
DQI	Data Quality Indicator
DQO	Data Quality Objective
DST	Daylight Savings Time
EMP	Enhanced Monitoring Plan
EPA	Environmental Protection Agency
ERG	Eastern Research Group
ESMB	Extraction Solvent Method Blank
ETM	Elapsed Time Meter
FID	Flame Ionization Detector
GC	Gas Chromatograph

Acronym	Meaning
GCMS	Gas Chromatography Mass Spectrometry
GD	Guidance Documents
HPLC	High Performance Liquid Chromatograph
ICAL	Initial Calibration
IDEM	Indiana Department of Environmental Management
IDOC	Initial Demonstration of Capability
INDOT	Indiana Department of Transportation
IP	Implementation Plan
IPA	Instrument Performance Audit
ISO	International Organization for Standardization
LCS	Laboratory Control Sample
LCSD	Laboratory Control Sample Duplicate
LIMS	Laboratory Information Management System
m	Meter(s)
MB	Method Blank
MDL	Method Detection Limit
MQO	Measurement Quality Objectives
NAAQS	National Ambient Air Quality Standards
NATTS	National Air Toxics Trends Stations
NCore	National Core Network
NIST	National Institute of Standards and Technology
nm	nanometer(s)
NO ₂	Nitrogen Dioxide
O ₃	Ozone
OAQ	Office of Air Quality
OAQPS	Office of Air Quality Planning and Standards
OPS	Office of Program Support
OTR	Ozone Transport Region
PAMS	Photochemical Assessment Monitoring Station
Pb	Lead
PDMS	Polydimethylsiloxane
PE	Performance Evaluation
PFA	Perfluoroalkoxy
PLOT	Porous Layer Open Tubular
PM	Particulate Matter
PM _{1.0}	Particulate matter having an aerodynamic diameter less than or equal to 1.0 µm
PM _{2.5}	Particulate matter having an aerodynamic diameter less than or equal to 2.5 µm
PM ₁₀	Particulate matter having an aerodynamic diameter less than or equal to 10 µm
PM _{10c}	Particulate matter having an aerodynamic diameter between 2.5 µm and 10 µm
ppb	Part(s) per Billion
ppbC	Part(s) per Billion Carbon

Acronym	Meaning
ppbV	Part(s) per Billion by Volume
PQAO	Primary Quality Assurance Organization
PSD	Prevention of Significant Deterioration
PT	Proficiency Test
PTFE	Polytetrafluoroethylene
QA	Quality Assurance
QAIP	Quality Assurance Implementation Plan
QAPP	Quality Assurance Project Plan
QAS	Quality Assurance Section
QAU	Quality Assurance Unit
QC	Quality Control
QMP	Quality Management Plan
QS	Quality System
REQAS	Recycling, Education and Quality Assurance Section
RF	Response Factor
RPD	Relative Percent Difference
RSD	Relative Standard Deviation
RT	Retention Time
RTS	Retention Time Standard
SB	Solvent Blank
SD	Standard Deviation
SIM	Selected Ion Monitoring
SIP	State Implementation Plan
SLAMS	State and Local Air Monitoring Stations
SLT	State, Local, or Tribal (Monitoring Organization)
SO ₂	Sulfur Dioxide
SPM	Special Purpose Monitoring
SOP	Standard Operating Procedure (this includes Technical Standard Operating Procedures)
SSCV	Second Source Calibration Verification
T	Temperature
TAD	Technical Assistance Document
TAD	Technical Assistance Documents
TNMOC	Total Non-methane Organic Carbon
TSA	Technical Systems Audit
TTP	Through-the-probe
UHPLC	Ultra-high Performance Liquid Chromatograph
UV	Ultraviolet
UVC	Ultraviolet Carbon
VOC	Volatile Organic Compound

Section 1: Quality Assurance Project Plan (QAPP) Identification and Approval

Indiana Department of Environmental Management (IDEM) Office Air Quality (OAQ) Air Monitoring Branch (AMB) Quality Assurance Project Plan (QAPP) Toxics Volume IV Revision 3.

This QAPP provides an overview of the minimum quality assurance (QA) and quality control (QC) program requirements for air monitoring networks conducting toxics air sampling in the state of Indiana. Monitoring networks meeting the required criteria allows for consistent, scientifically defensible, and comparable data from each monitoring network.

Toxics sampling consists of:

- Photochemical Assessment Monitoring Station (PAMS) O₃ precursors volatile organic compounds (VOCs)
- Toxics VOCs
- Carbonyls
- Benzene

A QC and QA program encompasses all phases of ambient air sampling and data analysis. These phases include the following activities:

- site selection
- monitoring equipment selection
- calibration, verification, and audit equipment and procedures
- sampling procedures
- lab analysis
- data verification and validation
- chain of custody
- data reporting
- precision and accuracy reporting
- meteorological criteria.

Prior to the implementation of any operational ambient monitoring network, staff designated as QC and QA must have a working knowledge of this QAPP. The QAPP is reviewed annually and approved by EPA Region V within 5 years of the effective date. Reviews are documented in the QAPP revision history table.

The Code of Federal Regulations (CFR) Title 40, Protection of the Environment, contains three basic sections which deal with ambient air monitoring:

- [40 CFR Part 50](#) lists the National Primary and Secondary Ambient Air Quality Standards
- [40 CFR Part 53](#) lists alternate equivalent air monitoring methods and procedures for obtaining equivalency
- [40 CFR Part 58](#) provides detailed descriptions of monitoring methodology; network design and siting; Prevention of Significant Deterioration (PSD) requirements; and QA criteria

Specifically, 40 CFR Part 58 Appendix D Section 5(b) requires state, local, or tribe (SLT) monitoring agencies to collect and report PAMS measurements. Additional documents

containing federal requirements are:

- U.S. Environmental Protection Agency (EPA) Technical Assistance Documents (TAD) for Sampling and Analysis of Ozone Precursors for the PAMS Program
- U.S. EPA PAMS Required Network QAPP
- U.S. EPA TAD for the National Air Toxics Trends Stations (NATTS) Program

Designated QC and QA staff must maintain a working knowledge of all applicable requirements. All monitoring and QA program requirements are kept current and accessible.

Document Approval

Toxics Quality Assurance Project Plan Volume IV
Indiana Department of Environmental Management
Office of Air Quality
Air Monitoring Branch
Indianapolis, IN 46219

B-004-OAQ-AMB-QA-24-Q-R3

This QAPP is hereby recommended for approval and commits the Indiana Department of Environmental Management – Air Monitoring Branch to follow the elements described within

Approval Signatures and Date Signed:

IDEM AMB
Chief

Signature: Steven J. Longenecker Date: 4/11/24

IDEM AMB
AMS 1 Chief

Signature: Paul Amundson Date: 4/9/24

IDEM AMB
AMS 2 Chief

Signature: B. S. Date: 4/12/24

IDEM AMB
ATS Chief

Signature: Stacey Dwyer Date: 4/11/24

IDEM AMB
QAS Chief

Signature: John M. Minton Date: 3/29/24

IDEM OAQ
Assistant Commissioner

Signature: [Signature] Date: 4/16/24

IDEM OPS
QA Staff

Signature: Patricia Collier Date: 4/10/24

U.S. EPA Region 5
R5 Supervisor, Air Monitoring & Analysis Section

Signature: _____ Date: _____

U.S. EPA Region 5
R5 Program Officer

Signature: _____ Date: _____

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Section 3: Distribution / Notification List

All IDEM OAQ staff play an important role in the collection, validation, data analysis, assessment, planning, and reporting of air monitoring data. All staff who are part of this primary quality assurance organization (PQAO) are provided with electronic copies of this QAPP and must adhere to the elements of the QAPP. Courtesy copies of the QAPP are also provided to other PQAOs conducting toxics air monitoring in Indiana. The QAPP is distributed to those identified in Table 1. An approved copy of the QAPP is also available on the [IDEM air quality web page](#) and the IDEM SharePoint™ QA Library. The QAPP is reviewed annually, and documentation is provided in the QAPP revision history table.

Table 1. Toxics QAPP Volume IV Distribution

Name	Organization	Phone
Air Monitoring Branch chief	IDEM/OAQ/AMB	317-308-3264
Quality Assurance Section (QAS) chief and staff	IDEM/OAQ/AMB/QAS	317-308-3257
Ambient Monitoring Sections (AMS) 1 and 2 chief(s) and staff	IDEM/OAQ/AMB/AMS(s)	AMS#1 317-308-3263 AMS#2 317-308-3260
Air Toxics Section (ATS) chief and staff	IDEM/OAQ/AMB/ATS	317-308-3248
Office of Program Support (OPS) Recycling, Education and Quality Assurance Section (REQAS) chief	IDEM/OPS/REQAS	317-234-6562
Environmental coordinator	Industries conducting air monitoring in Indiana	Contact QAS chief
QA manager	U.S. EPA Region 5	312-353-7203
IDEM quality management staff	IDEM OPS REQAS	Contact OPS REQAS chief

Section 4: Project/Task Organization

To comply with the monitoring requirements to determine if areas of Indiana meet the NAAQS and for special air monitoring studies, IDEM is the PQAO for monitoring sites designated as SLAMS, SPM, NCore/PAMS, and Near-Road. IDEM's Office of Air Quality (OAQ) implements CAA requirements in Indiana. The OAQ consists of five branches: Air Programs

Branch; Permits Branch; Compliance and Enforcement Branch; Billing, Licensing, and Training Branch; and Air Monitoring Branch.

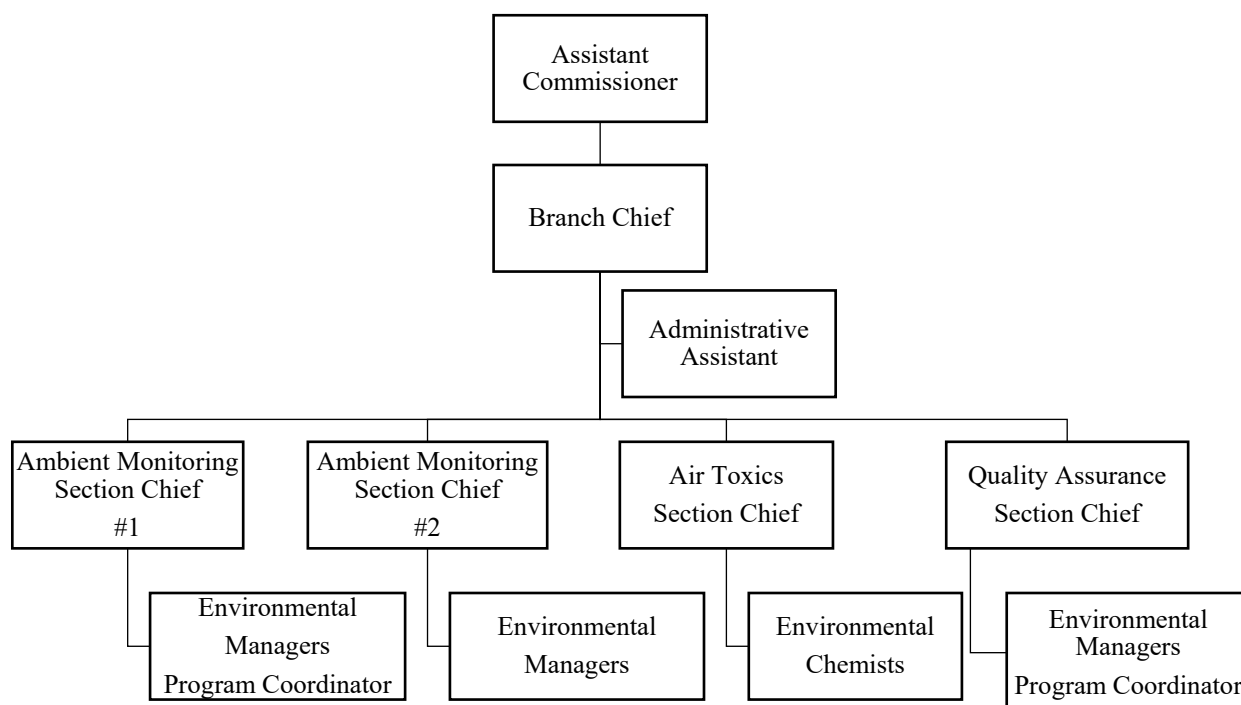
The AMB is divided among four sections (4.2. AMB Organizational Chart) which includes two Ambient Monitoring Sections (AMSs), an Air Toxics Section (ATS) laboratory, and a Quality Assurance Section (QAS).

4.1 Staff Roles and Responsibilities

Key functions and responsibilities in IDEM are:

1. OAQ program management: Assistant commissioner (AC)
2. AMB branch management: AMB chief; AMS 1 and 2 chief(s); ATS chief; QAS chief
3. Initiating equipment and supplies requests: AMS 1 and 2 environmental managers, QAS environmental managers, and ATS environmental chemists with oversight by AMSs 1 and 2 chief(s), QAS chief, and ATS chief
4. Procuring AMB equipment and supplies: Final approval by AMB chief; tracking by AA
5. Air monitoring site selection, maintenance, and operation which includes calibrations, verifications, span, zero, and QC checks: AMS environmental managers and ATS environmental chemists with oversight by AMS (1 and 2) chief(s) and ATS chief. As needed, OAQ Programs Branch assists with site selection and parameters
6. Air monitoring data handling, review, verification, and retrieval requests: AMS environmental managers and program coordinator and ATS environmental chemists with oversight by AMS (1 and 2) chief(s) and ATS chief
7. Air monitoring network review and project grants: AMB chief; AMS (1 and 2) chief(s)
8. QA performance and system audits, site evaluations, and data validation: QAS environmental managers and program coordinator with oversight by QAS chief
9. QA standards laboratory: Designated QAS environmental managers oversees most of the work performed in the QA standards laboratory with some assistance from other QAS environmental managers and oversight by QAS chief
10. Quality management plan (QMP) development and updates, QAPP and standard operating procedure (SOP) approval; SOP agency distribution; review, authorization, and management of QA documentation (part 5 of QMP discusses documents and records): OPS QA staff
11. Programs Branch, Permits Branch, and Compliance and Enforcement Branch: utilize AMB data; see [IDEM Air Quality in Indiana](#) for specific duties of these areas
12. Contractors or subcontractors: provide carbonyl data analysis and program support

4.2 AMB Organizational Chart



4.3 AMB Roles and Responsibilities

The AMB is divided among four sections (See 4.2. AMB Organizational Chart, above) which includes two site monitoring sections (AMSs), an air toxics laboratory (ATS), and a quality assurance section (QAS). Table 2 lists general duties of the positions within the AMB. The AMS #2 has an Environmental Manager designated as the AQS administrator, whose responsibilities include data submittal into AQS. Also, in the AMS #2 is an Environmental Manager designated as the DMDS administrator, whose duties include reviewing and evaluating data outputs as well as setting limits, overseeing programming within DMDS, and coordinating specific work functions of DMDS.

The QAS environmental managers and program coordinator maintain separate equipment from the AMS staff and the ATS staff, thus maintaining the independence of the QA program. QAS staff validate data once AMS staff and the ATS staff verify the data. The QAS maintains QAPP(s) and must make the final decision on data validity.

Table 2. Duties of Air Monitoring Branch Positions

Position	Duties
Air Monitoring Branch chief	Overall program management. Approves all branch expenditures. Supervises section chiefs and AA. Approves the purchase of major equipment. Approves QAPPs, SOPs, and annual data certification.

Position	Duties
Ambient Monitoring Section chiefs	Approves and ensures AMS staff adhere to the QAPPs and SOPs. Oversee and direct all ambient monitoring functions, which includes calibrations; verifications; QC checks; data analysis; site location, setup, and shutdown; site maintenance; and the development or update of the annual network plan (ANP) and 5-year network assessment. Ensures data meets quality standards. Approves annual data certification. Supervises AMS staff.
Air Toxics Section chief	Approves and ensures ATS staff adhere to the QAPPs and SOPs. Oversees and directs all toxic functions, which include laboratory and field GCMS, instrument calibration, and sample analysis. Ensures data meets QC standards. Assists with the update of the ANP and 5-year network assessment. Approves annual data certification. Supervises ATS staff.
Quality Assurance Section chief	Responsible for the creation, maintenance, revisions, and adherence to the QAPPs and SOPs. Oversees and directs all QA functions, which include PE and systems audits, meteorological audits, toxics audits, site evaluations, and operation of the QA standards laboratory. Ensures data meets quality standards, with authority to make the final decision on data validity. Tracks the completion of corrective actions and determines the success of the actions. Approves annual data certification. Supervises QAS staff.
Ambient Monitoring Section environmental managers	Performs the daily operations required for the proper collection, analysis, and verification of air monitoring data. Uploads one-point quality control checks into AQS. One environmental manager designated as the AQS administrator whose responsibilities include data submittal into AQS. One environmental manager designated as the DMDS administrator, whose duties include reviewing and evaluating data outputs as well as setting limits, overseeing programming within DMDS, and coordinating specific work functions of DMDS. Performs site and equipment location setup, maintenance, and shutdown. Performs air monitoring field equipment calibrations, verifications, and QC checks. Reviews, writes, and updates SOPs.

Position	Duties
Ambient Monitoring Section program coordinator	Assists with particulate monitoring chain-of-custody through logging of field-collected filters and delivery of filters to the ATS. Ships and receives filters from regional staff. Reviews, updates, and distributes QAPPs and SOPs.
Air Toxics Section environmental chemists	Performs the daily operations required for the proper collection, analysis, and verification of air monitoring data. Performs site visits to conduct air toxics monitoring equipment maintenance. Reviews, writes, and updates SOPs.
Quality Assurance Section environmental managers	Performs PE and systems audits, meteorological audits, toxics audits, and site evaluations. One environmental manager designated to upload PE audits into AQS. Performs equipment maintenance, calibrations, certifications, and verifications. Validates data. Reviews, writes, and updates QAPPs and SOPs. Tracks the completion of corrective actions and determines the success of the actions.
Quality Assurance Section program coordinator	Assists with meteorological audits and site evaluations. Distributes, tracks, and validates data. Performs audits on the particulate matter (PM) clean rooms. Reviews, writes, updates, and distributes QAPPs and SOPs. Communicates QA work to AMB chief for bi-weekly report, which includes SOP approval and revision updates. Tracks the completion of corrective actions and determines the success of the actions.
Air Monitoring Branch administrative assistant	Produces, enters, and tracks all requisitions in IDEM's purchasing system for purchases of AMB equipment, supplies, and services.

4.4 Contractors Roles and Responsibilities

Contractors who assist in the toxics program include an analytical support laboratory (ASL), ERG, which does the carbonyl analysis and reports the data to AQS, and a PAMS support contractor. Additional information on the ASL and the PAMS support contractor are available in the Technical Assistance Document for Sampling and Analysis of Ozone Precursors for the Photochemical Assessment Monitoring Stations Program and in the Quality Assurance Project Plan for the Photochemical Assessment Monitoring Stations Required Site Network for Speciated Volatile Organic Compounds, Carbonyls, and Meteorological Parameters Including Mixing Layer Height.

4.5 U.S. EPA Regional V Office

Each U.S. EPA region administers the QS for the SLT monitoring agencies in their region and ensures the QS developed by each SLT monitoring agency complies with the national QS

described in this document. IDEM AMB is in Region V. The U.S. EPA regional offices are the major communication link between the monitoring agencies and OAQPS and play an important role in the development and enforcement of effective policies and programs. Specific responsibilities for the regional offices are listed in the EPA PAMS QAPP.

4.6 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 include staff from the OAQPS; U.S. EPA regions; the monitoring agencies (including IDEM AMB); and U.S. EPA's support contractor. The PAMS Required Site workgroup convened in May 2016 to begin a dialogue on the aspects of the PAMS Required Site Network and the steps necessary to ensure a national QS was in place by the June 2021 network implementation date.

The workgroup initially met approximately monthly to discuss various technical and QA issues. The PAMS Required Site workgroup had the following responsibilities:

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

The workgroup continues to meet since 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 workgroup determines the frequency of meetings based on the stakeholder needs.

Section 5: Problem Definition and Background

5.1 IDEM Toxics Monitoring Introduction

In 1970, the Clean Air Act (CAA) was signed into law. This legislation authorized the development of comprehensive federal and state regulations to limit emissions from both stationary (industrial) sources and mobile sources. The NAAQS addressed six pollutants that threatened public health: CO, NO₂, O₃, SO₂, Pb, and PM. The Board of Health was the regulatory agency in Indiana at the time of the CAA being signed into law. Since 1970, changes in the types of pollutants monitored and levels have changed. However, the CAA still provides the regulations and framework for the monitoring of criteria pollutants (CO, NO₂, O₃, SO₂, Pb, PM) by state, local, and tribal organizations through the establishment of an Air Quality Monitoring Program.

In 1986, IDEM was created. Its mission is to implement federal and state regulations to protect human health and the environment while allowing the environmentally sound operations of industrial, agricultural, commercial, and government activities vital to a prosperous economy. The mission of the OAQ is to assure all Hoosiers' ambient air quality meets the National

Ambient Air Quality Standards (NAAQS); provide timely, quality air permits, without unnecessary requirements; and verify compliance with applicable state and federal air pollution laws and regulations. Five branches are part of the OAQ; Programs, Permits, Compliance and Enforcement, Operations, and Air Monitoring. A description and a flowchart of the branches is available in the QMP at [IDEM InfoHub](#).

PAMS monitoring is required as stated in 40 CFR Part 58 Appendix D - Network Design for Photochemical Assessment Monitoring Stations (PAMS) and Enhanced Ozone Monitoring. Additional toxics monitoring is also performed (Toxics VOC, carbonyls) although no requirement is mandated in the CFR. Air toxics monitoring data are collected to:

- Provide data to evaluate and support the development of air quality models
- Track trends in O₃ precursor concentrations to aid ongoing efforts to attain the O₃ NAAQS attainment status
- Detect and analyze pollution trends throughout the state or region
- To determine background ambient concentrations of selected hazardous air pollutants listed in the Clean Air Act of 1990
- Evaluating population exposure and risk assessment
- Episodic monitoring (i.e., chemical spills and fires), hazardous waste site monitoring, nuisance complaints, and source specific ambient monitoring
- Planning for compliance with standards being developed by the United States Environmental Protection Agency (USEPA)

Section 1 identified the stated toxic parameters to be monitored in Indiana. This QAPP is reviewed annually and updated when needed. Any SOPs associated with this QAPP are updated every four years or if the procedures change.

Section 6: Project Description

Air quality is regulated to protect public health and the environment in the state of Indiana and has an on-going requirement to collect air monitoring data. Use of the data determines compliance with the U.S. EPA's NAAQS for the criteria pollutants; CO, NO₂, O₃, SO₂, PM_{2.5}, PM₁₀, and Pb. This QAPP covers toxic parameters which do not have established ambient standards. However, toxic parameters play a major role in providing additional information concerning chemical reactions in the atmosphere, which can alter some of the criteria pollutants. Some of the toxic parameters are monitored because of the great impact on the health and well-being of individuals.

This section provides a summary of the work required and the schedule for implementation, including:

- ambient air measurements, collecting samples, acquiring samples
- performing chemical analysis

- carrying out QA and QC procedures to achieve data quality goals
- meeting the schedules to continue network implementation, operation, and data reporting

6.1 Overview of Monitored Toxics Parameters

Toxic parameters are presented on IDEM's internet air quality monitoring website [IDEM Air Quality in Indiana](#). Monthly and annual summary reports of parameters collected are available from continuous monitors. The DMDS provides on-line access to Indiana's continuous air quality monitoring network. It has been available to the public since July of 2007. DMDS offers access to near real-time data from active sites and historic data from recently discontinued continuous air monitoring sites across Indiana. This allows anyone to track pollutant and meteorological values throughout the day. The DMDS also includes noncontinuous data. The different toxic parameters monitored follow.

PAMS Auto-GC VOC

Ozone is formed by the reaction of certain VOCs with oxides of nitrogen in the presence of solar radiation. Reducing tropospheric O₃ pollution requires reducing or eliminating emission sources of VOCs and oxides of nitrogen.

The primary objective of the PAMS air monitoring program is to provide data to evaluate and support the development of air quality models. Measurement quality objectives (MQOs) were developed with this objective in mind. Use of the data serves other important purposes including tracking trends in O₃ precursor concentrations which aid in ongoing efforts to achieve National Ambient Air Quality Standard (NAAQS) O₃ attainment status. The PAMS program began in 1993 and U.S. EPA revised the program in 2006. The revisions permitted PAMS customization and alignment with the needs of the responsible air quality agencies. On October 1, 2015, the U.S. EPA further revised the PAMS program implementation. The final rule, in its entirety, may be found at the AMTIC website, <https://www.epa.gov/amtic/photochemical-assessment-monitoring-stations-pams>.

U.S. EPA modelers are the primary data users. However, AMB expects the chemical and meteorological measurements to aid with the identification of potential sources of O₃ precursors and 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 dataset is expected to result in a better understanding of O₃ formation and emissions reductions, which are most impactful for a specific area by increasing the likelihood area O₃ concentrations achieve NAAQS O₃ attainment status.

As part of the PAMS program, O₃ precursors require monitoring. PAMS measurements are conducted at the PAMS/NCORE site located in Indianapolis (AQS ID 180970078), since areas with a core-based population of 1,000,000 or more are required to monitor the parameters. Analysis consists of 59 PAMS targeted compounds (see Table 3). The specific monitoring requirements are addressed in 40 CFR Part 58 Appendix D Section 5. All of the other PAMS parameters (NO, O₃, and Meteorological) are covered in the IDEM AMB Gases QAPP and Meteorological QAPP respectively.

Table 3: PAMS Target Compounds

Priority Compounds				Optional Compounds			
1	1,2,3-trimethylbenzene	21	o-xylene	1	1,3 Butadiene ^c	21	Carbon Tetrachloride ^c
2	1,2,4-trimethylbenzene	22	p-ethyltoluene	2	1,3,5-trimethylbenzene	22	cyclohexane
3	1-butene	23	Propane	3	1-pentene	23	cyclopentane
4	2,2,4-trimethylpentane	24	Propylene	4	2,2-dimethylbutane	24	Ethanol ^c
5	acetaldehyde ^a	25	styrene	5	2,3,4-trimethylpentane	25	isopropylbenzene
6	benzene	26	tnmoc	6	2,3-dimethylbutane	26	m-diethylbenzene
7	c-2-butene	27	toluene	7	2,3-dimethylpentane	27	Methylcyclohexane ^c
8	ethane	28	t-2-butene	8	2,4-dimethylpentane	28	methylcyclopentane
9	ethylbenzene			9	2-methylheptane	29	n-decane
10	Ethylene			10	2-methylhexane	30	n-heptane
11	formaldehyde ^a			11	2-methylpentane	31	n-nonane
12	Isobutane			12	3-methylheptane	32	n-octane
13	Isopentane			13	3-methylhexane	33	n-propylbenzene
14	Isoprene			14	3-methylpentane	34	n-undecane
15	m&p-xylenes			15	acetone ^a	35	p-diethylbenzene
16	m-ethyltoluene			16	Acetylene	36	Tetrachloroethylene ^c
17	n-butane			17	Alpha Pinene ^c	37	t-2-pentene
18	n-hexane			18	Benzaldehyde ^a		
19	n-pentane			19	Beta Pinene ^c		
20	o-ethyltoluene			20	c-2-pentene		
Other Compounds				1	n-dodecane ^b	2	1-hexene ^b

^a Carbonyl compounds, measured using Method TO-11a

^b Compounds measured and reported, not required for regulatory purposes

^c Optional Compounds on U.S. EPA Target List that will not be measured, as missing from calibration standard

Toxics VOC

Indiana is using TO-15 and striving to meet TO-15A method to collect toxics VOC data. The method is contained in the U.S. EPA's [Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air](#), which consists of guidance for the sampling and analysis of VOCs in air. Table 4 lists the target compounds.

Table 4: VOC Target Compounds

Propene	Freon-12	Chloromethane	Freon-114
Vinyl Chloride	1,3-Butadiene	Bromomethane	Chloroethane
Ethanol	Acrolein	Acetone	Freon-11
Isopropanol	Vinylidene Chloride	Dichloromethane	Carbon Disulfide
Freon-113	t-1,2-Dichloroethene	1,1-Dichloroethane	Methyl Tert-Butyl Ether
Vinyl acetate	Methyl Ethyl Ketone	c-1,2-Dichloroethene	Hexane
Ethyl Acetate	Chloroform	Tetrahydro-Furan	1,2-Dichloroethane
1,1,1-Trichloroethane	Benzene	Carbon Tetrachloride	Cyclohexane
1,2-Dichloropropane	Bromodichloromethane	Trichloroethene	1,4-dioxane
Heptane	c-1,3-Dichloropropene	Methyl Isobutyl Ketone	t-1,3-Dichloropropene
1,1,2-Trichloroethane	Toluene	Methyl Butyl Ketone	Dibromochloromethane
1,2-Dibromoethane	Tetrachloroethene	Chlorobenzene	Ethylbenzene
m+p-Xylenes	Bromoform	Styrene	1,1,2,2-Tetrachloroethane
o-Xylene	p-Ethyltoluene	1,3,5-Trimethylbenzene	1,2,4-Trimethylbenzene
Benzyl Chloride	m-Dichlorobenzene	p-Dichlorobenzene	o-Dichlorobenzene
1,2,4-Trichlorobenzene	Hexachloro-1,3-butadiene	Total NMOC	

Carbonyls

As one of the PAMS monitoring program components, carbonyls require monitoring. Data are collected using Method TO-11A of the U.S. EPA's Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air. The carbonyls consist of the following analytes:

Formaldehyde; Acetaldehyde; Acetone; Propionaldehyde; Crotonaldehyde; Butyraldehyde; 2-Butanone; Benzaldehyde; Valeraldehyde; Hexaldehyde.

Benzene

Benzene is a known carcinogen. It is in crude oils and released to the environment as a by-product of oil-refining processes. Monitoring benzene can help indicate how much is released in

the atmosphere, whether through an exhaust stack or as an indicator for potential leaks from the coking process. Monitoring information can protect the community and potentially show some correlation between pollution and health effects. Hourly benzene monitoring became operational April of 2020 as part of the enhanced monitoring at the East Chicago Marina monitoring location.

6.2 Project Schedule

AMS staff collect and ATS staff analyze toxic samples to determine toxics' concentrations, except for carbonyl analysis. Carbonyl samples are analyzed by the ASL. Checks on the samplers are performed by the AMS staff, ATS staff, and QAS staff. The QAS staff also perform QA checks on AMS program procedures and ATS laboratory activities. Table 5 lists the various types of toxic data collected. Tables 6, 7, 8, and 9 list the specific checks performed on the samplers. Specific duties to conduct sampling and checks are outlined in the following SOPs:

- Agilent Gas Chromatograph-Mass Spectrometer with Autosampler
- Benzene PE Audit Procedure (pending)
- Canister Cleaning and Certification
- Carbonyl Flow Audit Procedures
- Collection of a Grab Sample for Air Toxics Monitoring
- Determination of Total Non-Methane Organic Compounds (TNMOC)
- Operation of Markes/Agilent System for Online Sampling and Analysis
- PAMS Auto-GC VOC Gas Audit Procedure (pending)
- Preparation of Standards for Toxics Laboratory
- Running a Field Loop
- Toxic Air Canister Sampling Program Audit Procedures
- Toxics and Carbonyl Data Validation

Table 5. Toxics Data Collection Frequency

Parameter	Sampling Duration and Frequency	Value Reported
PAMS Auto-GC VOCs	Continuous collection with hourly 40-minute sample, 30 minutes of the 40 minutes sample must occur during the hour. Sample starts no earlier than 10 minutes before the beginning of the hour and no later than 30 minutes after the beginning of the hour.	Hourly average
Toxic VOC	24-hour sample on a 1-in-6 days schedule, midnight to midnight, collect make-up samples, as needed.	Daily average

Parameter	Sampling Duration and Frequency	Value Reported
Carbonyls (TO-11A)	Once every six days, sample collection runs for 24 hours, midnight to midnight. Except from June 1 through August 31, when a 1-in-3-day schedule with 8-hour sampling runs 4 am to 12 noon, 12 noon to 8 pm, and 8 pm to 4 am. Collect make-up samples as needed. Field blanks are run per U.S. EPA PAMS/NCORE schedule.	24-hour average except during PAMS season then 8-hour average
Benzene	Continuous collection with hourly sample.	Hourly average

NOTE: Report the sample collection time using required local standard time, not adjusted for daylight savings time (DST), at the start of sample collection, or the start of the averaged hour. 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 through 09:59:59. The sample days follow the national [Sampling Schedule Calendar](#) on the AMTIC website.

Table 6. Checks on PAMS VOC

Responsible Entity	Check	Frequency
ATS staff	Pre-sampling season instrument and support equipment maintenance	Annually. Prior to official PAMS season, around May 1
ATS staff	Reference standards acquisition	Annually. Prior to official PAMS season
ATS staff	Instrument calibration and MDLs	Before and after the official PAMS season or after significant maintenance unless during PAMS season then only calibration
QAS staff	Send sample with concentrations of target PAMS VOCs blind to the ATS site operator	Prior to June 1 and soon after August 31

Table 7. Checks on Toxics VOC

Responsible Entity	Check	Frequency
AMS staff	Sampler maintenance which includes cleaning and zero air check in AMS laboratory	6 months
QA staff	Zero air audit	Annually
QA staff	Gas audit	Annually
ATS	Instrument calibration, MDL, and standards	Monthly standards and calibration curves, MDLs twice a year after maintenance, daily QC

Table 8. Checks on Carbonyls

Responsible Entity	Check	Frequency
AMS staff	Flow calibration	Annually
AMS staff	Flow verification	Monthly
QAS staff	Flow audit	Quarterly
QAS staff	Zero air audit	Prior to June 1 and soon after August 31

Table 9. Checks on Benzene

Responsible Entity	Check	Frequency
AMS staff	Analyzer auto calibration	7.5 Hours
QAS staff	PE Audit	Annually

6.3 Site Locations

The locations and toxic parameters measured depend upon the type of monitoring network. Site locations, which include toxics parameters monitored for IDEM AMB, are available in the IDEM OAQ AMB annual network plan (ANP) and through the air quality monitoring website [IDEM: Air Monitoring: Indiana's Ambient Air Monitoring Network](#).

Section 7: Quality Objectives and Criteria for Measurement Data

The primary objective of the toxics site network is to provide data of known quality for use by IDEM staff, U.S. EPA modelers, and scientists.

7.1 Data Quality Objectives

DQOs are qualitative and quantitative statements derived from the DQO Planning Process. The statements clarify the purpose of a study, define the most appropriate type of information to collect, determine the most appropriate conditions under which to collect the information, and specify tolerable levels of potential decision errors. The objectives define the quality of and the acceptable levels of measurement uncertainty and associated uncertainty which can be tolerated when making decisions about the measurements. Stated another way, DQOs statements describe how good the measurements need to be to provide data to control decision risks which meet the project outcomes within known certain confidence levels. Thus, ensuring collected data are of

sufficient quantity and quality to be fit for the stated purpose of objectively assessing the risk in the decisions made.

A formal DQO Planning Process was not undertaken to determine PAMS Required Site Network DQOs of the PAMS Required Site Network. U.S. EPA solicited input on data needs from PAMS monitoring agencies and U.S. EPA modelers, the primary users of the PAMS data. Measurement quality objectives (MQOs), for the various data quality indicators (DQIs), were established based on the expertise of U.S. EPA modelers and data analysts; and the data quality needs for O₃ and O₃ precursor model evaluation and model inputs. Modelers compare their model outputs to observed concentrations. For such comparisons, the measured concentrations are the true value thus minimizing bias. Imprecision was determined to be most important for model skill improvement. Monitoring agencies measuring PAMS parameters and other experts in PAMS measurements reviewed the proposed MQOs, ensuring reasonable and attainable objectives. 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.

7.2 Data Quality Indicators

The DQIs (representativeness, completeness, precision, bias, and sensitivity) are the characteristics describing how good the data must be to meet the DQOs. The DQIs are characterized by prescribing an associated MQO for each DQI which details the specific criteria to be met. These DQIs and associated MQOs are detailed further in 7.3.1 through 7.3.5.

7.3 Measurement Quality Objectives

The MQOs for each DQI are shown in Table 10. U.S. EPA technical staff, QA support contactors, monitoring equipment vendors, and the monitoring agencies provided feedback on the MQOs for various DQIs that would be considered achievable under field conditions. Then the MQOs were discussed with monitoring agencies and other PAMS measurement subject matter experts ensuring that the MQOs were attainable and reasonable. The U.S. EPA reserves the right to revise the prescribed MQOs to determine the suitability and how "achievable" the MQOs have been.

Table 10. PAMS Auto-GC VOCs, Toxics VOCs, Carbonyls, and Benzene DQIs and Associated MQOs

Method or Parameter	DQI				
Chemical Measurements	Temporal Representativeness (Sampling Frequency) ^a	Bias (%)	Precision (%)	Sensitivity (Detection Limit)	Completeness (%)
PAMS Auto-GC VOCs	Continuous, reporting hourly averages	≤ 25 ^b	≤ 25 ^c	≤ 0.6 ppbC	≥ 75
Toxics VOC	Samples for 24 hours every 6 days. Make-up samples will occur as needed	≤ 25 ^d	≤ 25	Determined quarterly by compound	≥ 75

Method or Parameter	DQI				
Chemical Measurements	Temporal Representativeness (Sampling Frequency) ^a	Bias (%)	Precision (%)	Sensitivity (Detection Limit)	Completeness (%)
Carbonyls	Samples for 24 hours, midnight to midnight, every 6 days except during PAMS season, which is June 1 through August 31. Then three sequential 8-hour samples every 3 rd day. Make-up samples will occur as needed	≤ 25 ^d	≤ 15 ^e	≤ 0.25 µg/m ³	≥ 85
Benzene	Continuous, reporting hourly averages	NA	NA	≤ 0.25 µg/m ³	≥ 75

^a Spatial representativeness is addressed in monitor siting as specified in 7.3.1.2.

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

^c Measured as the upper bound of the coefficient of variation (CV) across all single-point QC checks in the PAMS season. For functional form of the calculation, see 40 CFR 58 Appendix A Section 4.1.2, Equation 2.

^d Assessed with twice-annual PT samples.

^e 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>

NOTE: All sample days follow the national [Sampling Schedule Calendar](#) on the AMTIC website.

7.3.1 Representativeness

7.3.1.1 Temporal Representativeness for PAMS Auto-GC

When O₃ production becomes problematic, the concentrations of O₃ and O₃ precursors need to be adequately characterized during PAMS season, defined as June 1 to August 31. The period at a given site may be extended to begin before June 1 and end after August 31. The sampling frequency for PAMS Auto-GC VOCs is continuously daily and the collected data averaged for each hour. 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. Instead, sampling is required on a 1-in-3-day schedule consisting of three sequential 8-hour samples during PAMS season (Table 5 carbonyl duration and frequency). Carbonyl samples are collected per the national [Sampling Schedule Calendar](#) on the AMTIC website.

7.3.1.2 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 represents the sites ambient air in the geographic area. If any issues with meeting the requirements exist, IDEM AMB consults with the U.S. EPA Region 5 office to request a waiver.

The probe must be at least one meter vertically and 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, 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.

Inlet Probe Heights

Inlet probes must be placed at the following heights:

PAMS Auto-GC VOCs	2 to 15 m above ground level (AGL)
Toxics VOCs	2 to 15 m AGL
Carbonyls	2 to 15 m AGL
Benzene	2 to 15 m AGL

Obstructions

The inlet probe must be minimally twice the distance from the potential obstruction as the potential obstruction extends above the inlet probe. For example, if a wall extends two meters above the inlet probe, the inlet probe must be four meters or more from the wall.

Spacing from Trees

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

Spacing from Roadways

Mobile sources represent a significant source of O₃ precursors. Therefore, ensuring the monitoring site inlet probes are sufficiently displaced from roadways to prevent impacts by motor vehicle emissions is important. 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 in Table 11. For toxic sites which are not PAMS, the number of vehicles and minimum distance is in Table 12. The distances are adopted from the U.S. EPA NATTS TAD. The minimum separation distances must also be maintained from other motor vehicle traffic areas such as parking garages and parking lots.

Table 11. Minimum Monitor Separation Distance from Roadways for PAMS

Roadway average daily traffic (ADT), vehicles per day	Minimum distance ^a (meters)
≤ 1,000	10
10,000	10
15,000	20
20,000	30

Roadway average daily traffic (ADT), vehicles per day	Minimum distance ^a (meters)
40,000	50
70,000	100
≥ 110,000	250

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

Table 12. Minimum Monitor Separation Distance from Roadways for non-PAMS

Roadway average daily traffic (ADT), vehicles per day	Minimum distance ^a (meters)
≤ 15,000	15
20,000	20
40,000	40
60,000	60
80,000	80
≥ 100,000	100

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

7.3.2 Completeness

Generation of a dataset sufficient to characterize the daily concentrations of toxic parameters requires a minimum number of valid intended measurements. Completeness is the percentage defined as the number of valid data values compared to the number of values intended to be collected. The MQOs for completeness, specified for each parameter, are detailed in Table 10.

For continuous measurement methods reported as the hourly concentration average, uncollected or invalidated measurement results are lost, and cannot be made up. For hourly benzene measurements, 45 minutes will be considered a valid hour and 18 hours a valid day. Due to limitations with instrument cycling for sample collection and measurement, a valid PAMS Auto-GC VOCs' sampling hour is 40 minutes of valid sampling per hour, and 30 minutes of the 40-minute period must occur during the sampling hour. For continuous PAMS Auto-GC VOC measurements, completeness is based on 2208 hours (the PAMS season).

For toxic VOC samples, a complete day is 23 to 25 hours. For carbonyls samples collected during PAMS season, the total number of potential sampling days are 30- or 31-days, depending on the sampling calendar for the year. Samples collected outside PAMS season can equate to approximately 45 days. For toxics VOC and carbonyls sample collection, when a sample day is missed, a null code "AF" (scheduled but not collected) is reported to AQS for the sample run date. If the sample is invalidated for a particular reason, report an appropriate null code to AQS

for the sample run date. A make-up sample must be collected as soon as practicable according to the make-up sampling policy.

Toxics VOC Make-up Sample Policy

For invalidated or missed toxics VOC sampling events, attempt a make-up sampling event.

Collect make-up samples as close to the original sampling date and time as possible according to and in order of most to least preferential:

1. Before the next scheduled sampling date
2. Within 30 days of the missed collection date
3. Within the calendar year

Carbonyls Make-up Sample Policy

For invalidated or missed carbonyls sampling events, attempt a make-up sampling event. Collect a replacement carbonyl sample or three 8-hour samples during PAMS season, as close to the original sampling date and time as possible but should not exceed two weeks from the originally scheduled collection date. If a sampling occurs during PAMS season, collect within PAMS season barring extenuating circumstances such as equipment failure or if the sampling event is the last of the season. Collect make-up samples accordingly:

1. Before the next scheduled sampling date
2. Within two weeks of the missed collection date, with preference given the rescheduled date, which occurs on a weekday or weekend day to match that of the original schedule

7.3.3 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.

7.3.3.1 Precision for PAMS Auto-GC VOCs

Precision is assessed by analysis of replicate calibration verification standards. For the PAMS VOCs precision check, perform a sequential, back-to-back, analysis of the continuing calibration verification (CCV). 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. The functional form of the calculation is found in 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. Calculate RPD by dividing the absolute value of the difference between the two measurements by the average of the two measurements.

Further evaluate precision on an ongoing basis for groups of CCVs by calculating the relative standard deviation (RSD). Find RSD by dividing the standard deviation (SD) of the measurements by the average of the measurements. For $n > 2$ replicate measurements, RSD must be $\leq 25\%$. When determining RSD for PAMS Auto-GC VOCs, include all measurements in the desired time window (e.g., including the precision CCVs for one month, two months, or the entire PAMS season) unless a valid reason exists for exclusion (such as instrument problem or other documented technical issue).

When reported to AQS, appropriately qualify, or invalidate ambient sample data for target analytes failing precision criteria. IDEM AMB takes required corrective action for precision acceptance criteria failures of priority compounds. For optional compounds failing precision criteria, take corrective action, though not required. The IDEM ATS Auto-GC chemist evaluates precision on an ongoing basis to determine whether precision criteria are in jeopardy and takes corrective action to ensure precision across the monitoring season does not exceed criteria.

7.3.3.2 Precision for Toxics VOC

Field sampling precision consists of collocated sampling performed at the IDEM Indpls - Washington Park air monitoring site. Collocated sampling occurs on the same 6-day sampling schedule as the reporting sampler. Precision between the collocated and replicate analysis samples must be $\leq 25\%$ RPD for target compound concentrations \geq five-fold the laboratory method detection limit (MDL). Qualify both compound results when inputting into AQS, for instances in which collocated samples fail the precision specification. Investigate why the difference did not meet specifications. Additional samples will be performed once the issue has been resolved to show the specifications are within limits.

7.3.3.3 Precision for Carbonyls

The network MQO for carbonyls is based on an evaluation of the entire PAMS season's data. In all cases a CV of $\leq 15\%$ must be met. The overall precision is assessed as the coefficient of variation (CV) of the RPDs across (1) duplicate field-collected cartridges, (2) duplicate laboratory control sample precision, and (3) replicate laboratory analysis. 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>

The AMB will assess field sampling precision for carbonyls at the PAMS Indpls. – Washington Park air monitoring site. Assessments entail collection of duplicate samples, a pair of samples collected through a common inlet probe, concurrently with the primary sampling events. The duplicate cartridges are collected minimally at a rate of 10%, equivalent to three per month. Precision of duplicate samples is assessed as the RPD of the concentrations measured for the duplicate pair and must be $\leq 20\%$ for samples for which both cartridges measure ≥ 0.5 $\mu\text{g}/\text{cartridge}$. Duplicate samples where one or both cartridges measure < 0.5 $\mu\text{g}/\text{cartridge}$ are not required to meet this acceptance criterion. Duplicate 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 are taken for precision failures for optional carbonyl compounds.

The ASL will assess laboratory extraction and the analysis procedures' precision by preparation and analysis of duplicate laboratory control samples (LCS). LCS consists of a pair of blank DNPH cartridges spiked with target compounds at the laboratory and extracted and analyzed with collected field samples. Process includes accessing LCS and LCS duplicate (LCSD) precision, using RPD, which must be $\leq 20\%$; preparing, extracting, and analyzing an LCS/LCSD pair at a minimum of twice quarterly; and qualify ambient sample results associated with LCS/LCSD results not meeting the precision acceptance criterion, when entering in AQS. Unmet

criterion for priority compounds prompts the ASL to perform corrective actions to correct the discrepancy. Corrective actions should be taken for LCS/LCSD precision failures for optional carbonyl compounds, but they are not required.

Laboratory analysis precision is assessed by replicate analysis of an extract from a field-collected cartridge, which is not a trip or field blank. The replicate analysis precision is assessed as RPD and must be $\leq 10\%$ for samples which measure $\geq 0.5 \mu\text{g}/\text{cartridge}$. Perform a replicate analysis 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 prompt the ASL to take corrective action, which should include a reanalysis of the sample extract to confirm the failure. If the analytical precision failure cannot be corrected, qualify associated ambient sample results when entering in AQS, for affected compounds. Corrective actions should also be taken for replicate analysis failures for optional carbonyl compounds but are not required.

Note: The 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.

7.3.3.4 Precision for Benzene

Precision for benzene is not available since the sampler does an automated calibration every 7.5 hours.

7.3.4 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 whether instruments remain calibrated over time, and by minimizing sources of background contamination.

7.3.4.1 Bias for PAMS Auto-GC VOCs

All instruments must be suitably calibrated before PAMS season. Thereafter, the instruments must demonstrate calibration periodically, to remain valid, by comparison with a known traceable certified reference standard or transfer standard.

Evaluate bias of continuous chemical analysis parameters by challenging the instruments with a known standard daily, typically during nighttime hours when ambient concentrations of the target analytes are lower, and the measurements are less critical in predicting O_3 levels for the following day. Analyze a known standard to demonstrate the instrument calibration remains within tolerance and is typically immediately followed by a blank or “zero” check to demonstrate that the instrument signal returns to background levels in the absence of target analyte. Bias for speciated VOCs is evaluated across the entire PAMS season as the upper bound of the mean absolute value of the percent differences across all CCVs. The functional form of the bias calculation is given in 40 CFR 58 Appendix A Section 4.1.3, Equations 3, 4, and 5. The overall bias MQOs for the continuous parameters for the entire PAMS season are in Table 10. The nightly continuing calibration checks and zero background checks for the auto-GC are described in 14.1.1.

7.3.4.2 Bias for Toxic VOCs

Poor or infrequent instrument or instrument inlet maintenance causes bias in reported concentrations for Toxics VOCs. In addition, Table 10 indicates the ATS laboratory is provided with semi-annual PT samples, which have concentrations unknown to the ATS. Results of these blind tests assist in determining bias across the AMB toxics VOC network. Actions needed to improve bias can be determined from: failure to meet the indicated bias limit for the blind tests, and the condition of the data collected from earlier checks. Inlet maintenance as well as instrument maintenance, as described in 15.4 and in the supporting instrument SOPs, can help improve bias.

7.3.4.2.1 Canister Bias

All canisters are evaluated for bias whether they are newly purchased or older in-service canisters. Assessment for bias of any in service canister is performed identically. Canisters which exhibit a bias exceeding the criteria in section 7.3.4.2.2 are segregated and reconditioned before reuse or removed from service. Consult the manufacturer for methods to clean or recondition cans which fail these bias criteria.

7.3.4.2.2 Canister Integrity and Zero Air Check

Once cleaning is complete, canisters are pressurized with 25 PSI of dry zero-grade air (or UHP-N₂). Canisters are tested shortly after cleaning to avoid analytes having time to “grow” in the canister. Leak tightness for each canister is assessed by real world testing. Once the canister leaves the laboratory setting, it is carried to a site for sampling to occur. The ambient operator will check the canister’s pressure prior to setting up the sample for collection. If the vacuum is not within limits, the canister is returned to the laboratory and is re-evaluated. The canister’s pressure is then tested in the laboratory to ensure the field pressure is accurate. If it is accurate, the canister’s pressure is dropped to 0.3 ± 0.1 PSI and removed from service for 7-10 days without a cap and retested. If the canister pressure increases more than 0.1 PSI from its last pressure, its canister valve is changed. If the canister valve has been changed within the last 6 months, the canister is removed from service permanently.

The canister is analyzed shortly after initial pressurization and total concentration of all 62 analytes must be < 0.200 ppb. The maximum holding time for each canister is 60 days from the time the canister is analyzed for cleanliness to being used for sampling. All samples collected after the 60-day period will be classified as invalid.

Laboratories have reported growth of oxygenated compounds (e.g., ketones, alcohols, aldehydes) in canisters. Of particular concern in the canister zero air checks is acrolein, which evidence suggests may “grow” in canisters that are stored for extended periods. The mechanism for acrolein growth is not well understood; however, such is widely regarded as problematic in performing ambient concentration analysis. Suggested pathways of acrolein growth are decomposition of particulate residue; slow time-release of acrolein from interstitial spaces within the canister; breakdown of cutting oil residues in valves, or decomposition of other volatile constituents within the canister. Concentrations of target compounds above twice the laboratory MDL should be closely scrutinized as they indicate the presence of canister background concentrations which may cause issues with future sample collection measurements.

7.3.4.3 Bias for Carbonyls

Poor or infrequent instrument or instrument inlet maintenance causes bias in reported concentrations. Preventive maintenance is described in 15.4 and in the supporting SOPs. Assess and minimize bias resulting from field activities by a combination of pre-deployment bias checks; flow calibration and calibration verification for sample collection instruments; and by periodic collection of field blanks.

Following annual maintenance and prior to field deployment at the beginning of each PAMS season, perform a positive bias verification and flow calibration on the carbonyls sampling unit. The positive bias verification is briefly described in 14.1.3, detailed in [TAD for Sampling and Analysis of Ozone Precursors for the PAMS Program - Revision 3](#), and in the carbonyls field sample collection SOP. The AMB carbonyls field sample collection SOP describes the positive bias verification procedure and must demonstrate the sampling unit contribution for each target carbonyl is $< 0.2 \mu\text{g}/\text{cartridge}$. This is evidenced by measurement of target compounds on a challenge cartridge collected with humidified zero air being $\leq 0.2 \mu\text{g}/\text{cartridge}$ greater than the co-collected reference cartridge for each individual target carbonyl compound. The sampling unit must meet this specification before field deployment or once at the site.

The AMS parameter specialist verifies sampling unit flow rates before field deployment and monthly, thereafter, against a National Institute of Standards and Technology (NIST)-traceable certified/verified reference flow transfer standard. Indicated flow rates must be $\leq \pm 10.1\%$ of the flow transfer standard. If the flow is $\geq \pm 10.1\%$, ambient sample data obtained since the most recent passing flow check will be qualified or invalidated.

Laboratory bias is controlled by establishing a multi-point calibration curve with subsequent analysis of a CCV standard every 12 hours of analysis. This CCV must demonstrate the instrument calibration remains within $\pm 15\%$ of the original response. If this criterion is exceeded, corrective action will be performed to demonstrate appropriate calibration response and the extracts since the last passing CCV will be reanalyzed. If reanalysis cannot be performed, ambient sample data for affected target analytes will be qualified when reported to AQS. The CCV is followed by a solvent method blank, when analyzing additional samples, to demonstrate the instrument has returned to a stable baseline and no carryover or significant interferences exist in the instrument system. Bias of carbonyls will be assessed twice annually just prior to PAMS season and towards the end of PAMS season through analysis of PT samples.

Bias for Benzene

Bias for benzene is not available since the sampler does an automated calibration every 7.5 hours.

7.3.5 Sensitivity

Sensitivity must be established for the PAMS Auto-GC VOCs, Toxics VOCs, and carbonyls by experimentally determining the method detection limit (MDL). The Benzene MDL is determined from the instrument manufacturer. The ATS chemists who operate the Auto-GC establish the MDL 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 3 of the PAMS TAD in Sections 4.3 and 5.6 for PAMS Auto-GC VOCs and carbonyls, respectively; the procedure is described briefly below.

MDLs are determined according to the Method Update Rule revision of the MDL procedure described in 40 CFR Part 136 Appendix B by analyzing a series of low concentration standard sample replicates and a series of blanks. The spiked samples and blanks are prepared and analyzed over the course of three or more different dates and an average and standard deviation are calculated from the resulting spike data and blank data. The calculated spike standard deviation is multiplied by an appropriate Student's T statistic according to the number of spiked samples to calculate an MDL for the spikes, MDL_{sp} . The blank standard deviation is multiplied by an appropriate Student's T statistic according to the number of blanks and added to the average blank value to calculate an MDL for the blanks, MDL_b . The higher of the MDL_{sp} and MDL_b is reported for the site MDL for the target analyte. Determined MDLs will be determined annually prior to PAMS season and may not exceed those listed in Table 10. 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.

Section 8: Training

8.1 General Training Information

AMB staff conducting ambient measurements resulting in data generation (field operators, laboratory instrument analysts), data verification and validation, and audits/assessments must possess the skills and education or experience to perform activities for which they are responsible. Formal staff training is scheduled for new staff, and to periodically update staff's skills and program operations. Required training consists of QAPP and SOP review, air monitoring instrument manuals and corresponding SOPs, and hands-on training on air monitoring instruments which are related to the required work for specific staff (e.g., GC analysis for ATS staff, Toxics VOC canister setup and pickup for AMS staff, carbonyl zero audits for QAS staff). Formal staff training is coordinated with the section chiefs, senior level staff, or parameter specialists in the AMB AMS, QAS, and ATS on an as needed basis for staff engaged in the following: operating, calibrating, verifying, validating, and auditing analyzers or samplers; laboratory procedures; field duties; safety; and any other items related to work performed by staff in the AMB. The training for staff is tracked and documented by the individual section chiefs, except for any in-house training pertaining to computer safety, which is documented by the Indiana State Personnel Department but able to be tracked by individual section chiefs. Standard literature references are readily available to all staff to access, whether through the internet or saved on a staff's home drive and include the Federal Register, manufacturer's instrument manuals, and QA GDs related to the program objectives. U.S. EPA vendors (e.g., AirKnowledge) also provide courses and other training.

Section 9 Documentation and Records

IDEM's goal is collection of data which is accurate and representative of the actual conditions. To meet this goal, documentation and record keeping must be performed at an elevated level of accuracy and consistency. The AMB establishes and maintains document control procedures for the timely preparation, review, revision, approval, issuance, use, retirement, and archival of documents and records. The AMB shared drive is only available to AMB staff which provides security from any tampering issues. Documents on the extranet can only be seen by IDEM staff. Documents on the extranet and internet can only be changed by the IDEM computer staff. Documentation in DMDS is secure and cannot be changed once entered. Data in DMDS can be

changed only by AMSs' chiefs and staff, the DMDS administrator, and the ATS's chief and staff.

The QA standards laboratory cabinet contains calibration, certification, and verification files, which are in a secure location with limited access. The ATS GC stores calibration records. ATS calibration standards information are stored in a file cabinet located in the ATS laboratory. PT results for the ATS are available through the Battelle portal. Table 13 summarizes the documentation involved, location of the documents, retention time (RT), and the main custodian. All records are either kept at the minimum requirements as addressed in the IDEM QMP or kept indefinitely.

Examples of documentation and records generated and maintained include:

1. Monitoring agency Toxics QAPP
2. SOPs
3. Sample collection records in electronic and written format
4. Logbooks and data sheets in electronic and written format
5. Training records
6. Instrumental and equipment calibration information
7. Quality assurance records (e.g., 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 is maintained in a manner from which activities can be reconstructed, whether hand recorded in ink on paper, through electronic entry, or captured through a computer system. The AMB SOPs describe how to execute routine procedures, include but are not limited to instrument operation; maintenance; sample collection and analysis for each of the toxic measurement methods; data verification, validation, and reporting; corrective action; training; and data management.

Each SOP includes information on equipment and instruments required; calibration; QC activities and acceptance criteria; calculations; and typical corrective actions for routine nonconformances. Where activities involve a potential physical hazard, safety precautions are addressed.

Table 13. Documentation and Records

Document	Location	Retention Time	Custodian
ANP; 5-Year network plan; QAPP	IDEM internet and InfoHub; AMB shared drive	The latest can be found on IDEM internet and InfoHub. AMB shared drive maintains previous versions indefinitely	ANP and 5-Year network plan – AMSs (1 and 2) chief(s); QAPP – QAS chief

Document	Location	Retention Time	Custodian
SOPs; QMP	SharePoint IDEM QA Library; AMB shared drive	The latest can be found on SharePoint IDEM QA Library. Archived versions in SharePoint Archived QA Documents. AMB shared drive maintains previous SOPs indefinitely	QAS program coordinator, OPS QA
Logs	Electronic log available through DMDS	Kept indefinitely	AMS environmental manager DMDS administrator
Audit forms	AMB shared drive	Kept indefinitely	QAS environmental manager
Data; sample collection and chain of custody forms; calibration, zero, site sampler inspection and maintenance	DMDS; ATS GC; ATS cabinet located in ATS laboratory	All items maintained indefinitely.	AMS environmental manager; DMDS administrator; ATS environmental chemist
Field logbooks for Toxics VOC and carbonyl	Kept with sampler	Stays at the site unless the book runs out of space or sampler is pulled. Then kept at AMS lab indefinitely.	AMS parameter specialist
QAS data memos; QAS data checks; QAS exceedance reports; QAS site evaluations; QAS AQS data summary and verification reports	AMB shared drive; VFC; site evaluation record also on DMDS	Kept indefinitely.	QAS chief, QAS program coordinator

Document	Location	Retention Time	Custodian
Calibrations, certifications, and verifications performed by the QA standards laboratory; QA standards laboratory instrument inspection and maintenance	DMDS; AMB shared drive	Information is kept for at least 3 years unless item is still in circulation. Then information is kept indefinitely.	QA standards laboratory manager
Staff training	AMB shared drive	Kept indefinitely.	Chiefs of AMB, AMS, ATS, or QAS
TSA questionnaire, audit finding response form, and final report and closeout letter	AMB shared drive	Kept indefinitely	QAS Chief and QAS Program Manager

The AMB staff maintain a system, such as a controlled electronic document in an access-controlled network folder, internal website, or similar, listing the most current version of quality system documentation containing the information given in Table 13. Superseded versions of controlled QS documents will be inaccessible ensuring only the current procedures are performed. All previous versions of QS documents are archived and maintained ensuring measurement data are traceable to the policies and procedures in place at the time of data generation, transformation, or reduction, and reporting.

As the toxics network matures, the national QS documents will require revision to accommodate lessons learned and best practices. Revisions are handled in a manner which ensures only current approved procedures are available. If a revision to the document cannot be completed and approved in a timely manner, a quality bulletin or similar memorandum distributed to the toxics site stakeholders ensures AMB and U.S. EPA Region 5 staff are aware of the changes and expected effective date. When revisions to the toxics site guidance and QS documents are announced, the AMB staff revise AMB QS documents accordingly, where applicable.

9.1 Chain-of-Custody Records

A chain of custody (COC) form must accompany samples collected for analysis, packaged, and transported to another location (e.g., toxic canisters, carbonyls samples). The COC documents how such media are handled and tracks the integrity of the collection media through the various stages of transportation and receipt. COC procedures are described in SOPs specific to the media type. The approved COC form is a controlled document within IDEM or laboratory document control system. Completed COC forms, or a copy, are retained by the laboratory as part of the

official analytical record. COC procedures and requirements for carbonyl cartridges and toxic canisters are detailed in 12.3.

9.2 QA and QC Records

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

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

Record the outcomes of these QA and QC-related activities on hard copy forms, in electronic spreadsheets, electronic pdfs, in data management software systems, or by another appropriate means governing the activity, as indicated in Table 13. Documentation methods (electronic or hard copy) include spreadsheets, worksheets, and data management systems.

9.3 Records Archival and Retention

Retain records, described in Table 13, for a minimum of three years as per the statute of limitations codified in 2 CFR 200.333 and further clarified in Section 5.0 of the U.S. EPA QA Handbook, Volume II. The statute states to maintain records for a minimum of three years from the date the grantee submits the final expenditure report, unless otherwise noted or for records involving a legal action. In some instances, the AMB prescribes more stringent records retention schedules, as indicated in Table 13, and meet the minimum requirements in 2 CFR 200.333.

The toxics QAPP and supporting SOPs are archived for a minimum of 10 years following the superseded date. Electronic data (e.g., databases, raw and processed electronic instrument data, electronic logbooks, etc.) is backed up a minimum of monthly to a physically separate storage device, separate hard drive, server, or similar. Archived electronic data is stored a manner which protects from inadvertent alteration (e.g., password protected, access limited). Once archived, the

data is reviewed or tested at a minimum of annually ensuring complete records are maintained, and data have not been corrupted.

9.4 Sample Retention

Toxic measurement methods include continuous GC, 24-hour canister sampling, and benzene. Carbonyls involve the collection of samples onto discrete media. Therefore, sample retention applies to the canisters and carbonyls samples.

Canisters, whether clean or exposed, have the following limits:

- Analyze samples within 30 days of sample collection
- Use canister within 60 days of cleaning and evacuation

Once carbonyls samples are extracted (≤ 14 days of sample date) by the ASL, the spent cartridge is no longer useful and can be discarded. To afford reanalysis in the event problems occur with the analysis, sample extracts are maintained in refrigerated storage until the analysis data are validated and approved or exceed the 30-day extract holding time. However, in the event expired extracts are analyzed, the reported data from such expired extracts require a QA qualifier (QX) when reported to AQS. Sample extracts are not archived and are properly disposed according to hazardous waste procedures established by the ASL.

Section 10: Network Description (or Sampling Process Design)

Toxics sampling is primarily conducted in population centers per U.S. EPA requirements. Additional sites are also operated to establish rural background concentrations, provide statewide as well as regional coverage, and for areas of specific interest, such as sources and near road. Consistent with 40 CFR Part 58.10, the AMB annually reviews the appropriateness of the current monitoring network design and determines any necessary changes that should take place by the first of the next year (to allow for complete annual datasets). The Annual Network Plan (ANP) provides information on monitoring sites and any proposed changes. The ANP is available for public review and comments prior to submittal to EPA Region 5 by July 1 for review and approval. The current IDEM ANP can be found at <https://www.in.gov/idem/airquality/>.

Network design and sampler siting is established based on 40 CFR Part 58, Appendices D and E, and is mentioned in Sections 6 and 7 of this QAPP. Site evaluations are performed biennially to verify the monitoring site continues to meet the requirements in 40 CFR Part 58. Site evaluation documentation is found on the AMB shared drive.

Toxic sampling is primarily conducted in population centers per U.S. EPA requirements, for health concerns, or to provide an air quality database for use in O₃ prediction model evaluation and refinement. A secondary objective is to characterize O₃ precursor concentrations and temporal patterns and associated meteorological conditions to assist the AMB in evaluating, tracking the progress of, and if necessary, refining control strategies to achieve O₃ NAAQS attainment. The IDEM ANP provides information on sites and can be found at <https://www.in.gov/idem/airquality/>

When photographs or digital images are taken for documenting and supporting a field investigation, save a record of each exposure or image as a file on an AMB shared computer drive. Record the following information:

- Include in the record's filename, the site name and a description of the imagery shown.

Include in the file the year the photos were taken. For example, file name “Indpls-WP-CAMS42-1A-North” stored under the path G:\QA\Site Information\Site Evaluations\Indpls – Washington Park - 180970078\2024\Photos

- The name of the staff taking the photograph or digital image and corresponding paperwork, such as a site evaluation form. If no paperwork is used, a log entry on DMDS is adequate.

Section 11: Sampling Method Requirements

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. The procedures are provided in the following AMB SOPs:

- Agilent Gas Chromatograph- Mass Spectrometer with Autosampler
- Benzene PE audit (pending)
- Canister Cleaning and Certification
- Carbonyl Flow Audit Procedures
- Determination of Total Non-Methane Organic Compounds (TNMOC) U.S. EPA Method TO-12
- Gaseous Data Validation Using DMDS
- Operation of Markes-Agilent System for Online Sampling and Analysis
- PAMS Auto-GC VOC gas audit (pending)
- Preparation of Standards for Toxics Laboratory
- Toxic Air Canister Sampling Program Audit Procedures
- Toxics and Carbonyl Data Validation

11.1 Sampling Equipment

A list of manufacturers and models for the measurement parameters is available in the IDEM AMB annual network plan. This section describes ambient air sample field collection methods, automated analyzers, and methods used for conducting measurements of chemical parameters in the field.

Collect ambient air samples through one or more inlet probes. The materials comprising, the siting of, and the configuration of the inlet probe comply with 40 CFR Part 58 Appendix E and Section 7.3.1.2 which ensures the sampled atmosphere is representative of the ambient air in the geographic area intended to be represented by the site. Inlet probe(s) are constructed of borosilicate glass or chromatographic grade stainless steel. Carbonyls and Benzene may also use polytetrafluoroethylene (PTFE) or perfluoroalkoxy (PFA) Teflon®. Additional guidance for inlet probe siting is included in Section 3.3.1.2 of Revision 3 of the U.S EPA PAMS TAD.

An air monitoring instrument inlet is either connected to an inlet probe dedicated to the instrument or to an inlet manifold which connects multiple instruments. Consider the length of

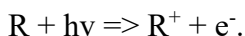
the sampling inlet pathway (including the manifold, if so equipped) and flow rate to ensure sample residence time is kept to 20 seconds or less. Also, consider pathway length to minimize intrusion of PM and condensed water into the sampling inlet. One method for controlling the latter is by inverting the terminus of the inlet and installing a rain shield (such as an inverted borosilicate glass 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 3 of the U.S. EPA PAMS TAD, Sections 4.2.2.1 and 5.7.2 for PAMS VOCs and carbonyls, respectively. The inlet composition and configuration for these measurements is described within AMB SOPs.

11.2 Sampling Methodology

Below is a summary of the method of how each toxic parameter is analyzed. Specific concepts and procedures are provided in the instrument's operating manual. Method codes for the individual parameters are available at <https://www.epa.gov/aqs/aqs-code-list>.

- **PAMS Auto-GC VOC** – PAMS Auto-GC VOCs measurement uses a Markes-Agilent system, model 7890B gas chromatograph, a Markes Unity thermal desorber, a Markes Kori water management system, and a Markes CIA Advantage Autosampler. The Markes-Agilent system collects and preconcentrates VOCs from the sampled atmosphere and subsequently separates the VOCs for detection via a pair of flame ionization detectors (FIDs). Additional details on auto-GC sampling methods, including technical guidance regarding moisture management, are provided in Section 4.2.3 of Revision 3 of the U.S. EPA PAMS TAD.
- **Toxics VOC** – Toxics VOC data are collected using a modified TO-15 method. TO-15 is part of [USEPA's Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air](#), and consists of guidance for the sampling and analysis of VOCs in air. Ambient air samples are collected in stainless steel canisters in the field, using either the Meriter MCS-1-R or the ATEC 2200 Air Toxic Samplers. Samples are separated and analyzed using an Agilent GC/MS system to determine the concentration of the compounds found in the collected sample.
- **Carbonyl** – Sampling methods for the collection and analysis of carbonyl compounds by TO-11A are described in detail in the national U.S. EPA PAMS SOPs. For this method, a vacuum pump pulls ambient air through an O₃ denuder to remove O₃. The sampled air scrubbed of O₃ passes through a silica gel sorbent cartridge impregnated with DNPH. Carbonyls in the air stream react with DNPH to form hydrazone derivatives. The hydrazones are maintained within the sorbent bed until extraction by the analyzing laboratory. Eluted extracts are analyzed by HPLC (or ultra-high performance liquid chromatograph [UHPLC]) with a UV detector at a wavelength of 360 nm.
- **Benzene** – This instrument uses a port valve with a single absorbent trap, and a 30-meter metallic 0.28 mm ID column to capture and separate VOCs by retention times. The separated VOCs pass through an ionization chamber. Photoionization is initiated by the absorption of short wavelength ultraviolet light by a gas molecule (R). This can lead to

ionization as follows:



If the ionization potential of R is less than or equal to the energy of the photon, $h\nu$, then the species are ionized. The detector consists of a sealed interchangeable ultraviolet lamp that emits a selected energy line.

11.2.1 Shelter Types and Temperature Requirements

Toxic analyzers or samplers, calibrators, and zero air systems are located inside an IDEM shelter, e.g., a CAS or Ekto, or a room located inside a building. Probes and manifolds, which these gases pass through, consist of the material listed in section 11.1.

The toxics analyzers or samplers are required to operate under specific temperatures. Table 14 lists the temperature range required for each type for data collected to be valid. The standard deviation limit is to provide temperature stability information and is not necessarily an indication of a temperature infraction resulting in invalid data.

Table 14. Indoor Temperature Requirements

Item	Make/Model	Temperature Range
GC	Agilent / 7890B	15.0 – 30.0°C; < 2.1°C SD over 24 hours
Thermal desorber	Markes / Unity-xr	15.0 – 30.0°C; < 2.1°C SD over 24 hours
Toxics VOC	Meriter / MCS-1-R	4.0 – 41.0°C; < 2.1°C SD over 24 hours
Carbonyls	Atec / 8000-2-4 DNPH Cartridge	0.0 – 60.0°C; < 2.1°C SD over 24 hours 10.0 – 100.0°C; < 2.1°C SD over 24 hours
Benzene	Chromatotec / GC 866	18.0 – 24.0°C; < 2.1°C SD over 24 hours

11.3 Failed Sample Events

In the event of a malfunctioning analyzer or sampler that was not collecting data according to specific requirements, the AMB will provide information into the DMDS, giving detailed information why the data are invalid or if a QA qualifier needs to be added. If the QAS finds an issue, then a memo will be sent to the AMS or ATS, who will then confirm the results. A detailed log is also entered in DMDS by the QAS for the specific site.

Section 12: 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 Auto-GC VOC and benzene measurements are continuous while sample handling occurs for toxic VOC canisters by TO-15 and for carbonyls by TO-11A. Therefore, custody requirements only apply to toxic VOC canisters and 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 assisting in identification and resolution of

instances where sample identity or integrity is called into question. A sample is in custody if in one's actual physical possession or stored in a secured area restricted to authorized personnel.

12.1 Toxic VOCs TO-15

The following equipment is utilized for obtaining a representative 24-hour air sample for analysis:

- Meriter or ATEC Sampler: an automatic, programmable canister sampler installed at designated monitoring sites. Each sampler is certified prior to being put into the field. Certification requires a zero-air check result of less than 10 ppbC total carbon
- 6-L canisters: spherical, stainless-steel canisters, which have had their inner surface electro polished to reduce chemical reactivity

Assigned AMS staff will install the canister at least one day prior to the scheduled sample day. The Meriter flow is checked to ensure proper flow range. The canister pressure is checked, which must be -28 to -30 psi. The ETM is set to zero. After the sample day, assigned AMS staff will collect the canister. The ETM must be 23 to 25 hours and the canister pressure approximately 5 psi. Specific details are also listed in the IDEM AMB SOPs, LabCommerce Meriter Maintenance, and Running Field Loop

In some instances, such as a citizen's complaint or a special study, a grab sample is collected. Grab samples of ambient or indoor air are collected in air sampling canisters using a sample probe. The sample probe is made using 1/4" stainless steel tubing attached to a flow metering valve with a seven-micron particulate filter, which is capped with a 1/4" plug. The sample flows through the particle filter and is regulated by the flow metering valve before entering the canister. Specific details are listed in the IDEM AMB SOP, Collection of a Canister Grab Sample for Air Toxics Monitoring.

12.2 Carbonyls by TO-11A

The New Waters cartridges, used by the AMB, are typically shipped at ambient temperature. Each cartridge is typically individually sealed in a foil pouch. To maintain cartridge integrity and limit potential contamination, do not open the sealed foil cartridge storage pouch until the cartridge is ready for use in the field or laboratory. Also follow these procedures:

- Store new cartridges $\leq 4.0^{\circ}\text{C}$ upon receipt.
- Only handle cartridges with gloved hands. Chemicals from hand sanitizers, lotions, etc., can contaminate sample cartridges.
- Do not use markers containing volatile solvents (e.g., permanent markers such as Sharpie®, which emit solvents such as acetone) for marking on foil storage pouches. Ball-point pens or printed stick-on labels are preferred.
- Label cartridges in such a manner as to uniquely identify the cartridge (i.e., to permit the identification of the site, sampling date, time, and whether it is a scheduled sample, field QC sample, or a field blank. QA samples include cartridges for zero air audits)
- Store cartridges in carbonyls free areas. Do not use climate-controlled storage units for storage of solvents or carbonyl-containing solutions or standards.

Carbonyl sampling during PAMS season involves collecting three consecutive 8-hour samples on a 1-in-3-day schedule as described in Section 7 and one 24-hour sample during other times of

the year. Preferably, retrieve samples as soon as possible after collection ends. However, cartridges must be retrieved within 72 hours of completion of either the last of the three sequential samples or one 24-hour sample.

Upon retrieval, seal each field-collected cartridge in its individual foil pouch, and immediately place in refrigerated storage (e.g., refrigerator onsite or cooler with ice packs). Appropriately document collection details on the sample collection form (whether hard copy or electronic) and record sample storage information on the COC form or similar form or database (e.g., a laboratory information management system [LIMS]). Samples are shipped the next business day after pickup, except not to be received by the analytical laboratory on Fridays (follow ERG laboratory request). Ensure samples arrive at the laboratory under refrigeration, by hand-carrying or shipping, samples by overnight courier or shipper. Experience has shown that extended shipping times will result in samples arriving at the laboratory at elevated temperatures (> 4.0°C), which can impact data with either a QA qualifier or a null data qualifier.

12.3 Chain of Custody

Chain of Custody Toxics VOC Canisters

For chain of custody, each canister has a tag attached. This tag must be filled out appropriately. Failure to provide this information can result in the sample being invalidated. An example of a 6L canister chain-of-custody tag is shown below.

Canister Chain-of-Custody Tag

IDEM /Air Toxics Monitoring			
Site:		Sample Date:	
Canister#:		Field Setup (initials):	
Vacuum (Start):		Flow (Start):	
Elapsed Time (min):		Flow (End):	
Field Pickup (initials):		Pressure (End):	
LAB Staff (Date rec'd):		LAB Staff (initials):	
Canister (Final PSI):		Dilution Factor:	
Canister Cert.(date):		Canister Cert (Initials):	
Canister Cert (Instr.):		Canister Cert (Conc):	

Sample Date should be within 60days of the Canister Cert date.

Comment:

Chain of Custody Carbonyls

The ASL prescribes COC procedures. Regardless of the new cartridge media's origin, each cartridge, whether an ambient sample or field QC sample (such as a duplicate or field blank), the COC form lists (documents) transfers of the sample cartridges from their origin, through

collection, and transport to and receipt by the analyzing laboratory. Minimally, record the following required information on the COC form:

- Origin of cartridges (e.g., analyzing laboratory, field office)
- Cartridge transfers between individuals – dates, times, and signatures of individuals relinquishing and receiving cartridges
 - Relinquishing cartridges to the site staff (either by handoff or shipment by courier)
 - Receiving cartridges by the site staff
 - Relinquishing sampled cartridges by site operator following retrieval, for handoff to the analyzing laboratory or for shipment by courier)

Note: Shipping couriers are not expected to sign COC forms. The staff relinquishing the samples to the shipper/courier will indicate relinquishment to the shipper or courier on the COC form. Custody is presumed to be with the courier until received at the laboratory.

- Receiving field-collected cartridges by the analyzing 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 staff, including during shipment
 - Storage of field-collected cartridges at the monitoring site, if applicable (e.g., stored at $\leq 4.0^{\circ}\text{C}$ in onsite refrigerator)
 - Shipping conditions (e.g., on ice packs) and associated information for tracking or evaluating the shipping conditions, including certified thermometers placed in a shipping cooler
 - Upon receipt, the laboratory documenting the thermometer used for measuring temperature as received and location for storage within the laboratory (e.g., uniquely identified refrigerator)

Note: The convention for recording custody information for the samples can include recording transfers and storage on the field collection data sheet. However, and possibly more conveniently, include a separate COC form for each shipment encompassing 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 staff responsible for assuring sample custody, will ensure that sample custody documentation is complete. Contact site operators, as appropriate, to complete all missing information. Maintain COC documentation in accordance with Section 9.

12.4 Storage of Data

After reducing and quality assuring, store data for a minimum of three years, according to the IDEM OAQ guidelines. The guidelines can be found in the [Indiana Archives and Records Administration, Retention Schedules](#).

Section 13: Analytical Methods

The analytical methods to be employed include methods for the determination of PAMS Auto-GC VOCs, Toxic VOCs, and carbonyls.

13.1 PAMS Auto-GC VOCs

The auto-GC system collects and preconcentrates VOCs from the ambient atmosphere and subsequently separates the VOCs for detection by FID. PAMS Auto-GC VOCs analysis by the GC is considered a continuous method. Therefore, no discrete samples are collected on media or are available for retention.

Additional details on auto-GC sampling methods, including technical guidance regarding moisture management, are provided in Section 4.2.3 of Revision 3 of the U.S. EPA PAMS TAD.

13.2 Toxic VOCs by TO-15

Samples collected for toxics VOC analysis are extracted and analyzed per [U.S. EPA Compendium Method TO-15](#) and described in IDEM SOPs.

The analytical strategy for EPA Method TO-15 involves using a high-resolution GC coupled to a low- or high-resolution MS, which may consist of a linear quadrupole, ion trap, or time-of-flight (TOF) system. Target VOCs are identified by a combination of the retention times (RTs) and the associated mass spectra by comparing observed fragmentation patterns to reference spectral patterns and relative ion abundances established during calibration. For any given VOC, the intensity of the observed quantitation ion in the unknown sample is compared with the system response to the same ion for known amounts of the compound. The presence of one or more secondary ions in a known relative abundance to the chosen quantitation ion increases certainty of the identification.

Mass spectrometric detection is considered a more definitive identification technique than nonspecific detectors such as flame ionization detectors, electron capture detectors, photoionization detectors, or a multidetector arrangement of these. The use of both gas chromatographic RTs and the mass fragmentation patterns reduces the likelihood of compound misidentification. If the technique is supported by a comprehensive mass spectral database and a

knowledgeable operator, then the correct identification and quantification of VOCs is further enhanced.

13.3 Carbonyls by TO-11A

Samples collected for carbonyls analysis are extracted and analyzed per U.S. EPA Compendium Method TO-11A, which must meet the performance specifications listed in Table 19. The national SOPs describe the method for collection and analysis of carbonyls for the PAMS Required Site Network. The national SOPs describe the solvent extraction procedures for derivatized carbonyl-hydrazones collected on the DNPH cartridge samples; analysis of the extracts by HPLC or ultrahigh performance liquid chromatograph (UHPLC), with ultraviolet (UV) detection; and the necessary QC procedures. Analysis of extracted ambient air and QC samples must occur within 14 days of collection. Extracted samples are analyzed by HPLC or UHPLC with UV at 360 nanometers (nm) within 30 days of extraction. The resulting carbonyl concentrations in the ambient air sample (or QC samples) are calculated from the measured concentrations in the sample extracts and the volume of air sampled onto the cartridge. Alternative detectors (e.g., time-of-flight (TOF)) and alternative wavelengths (e.g., 365 nm) may be employed, if method performance criteria (listed in Table 19) are met.

Section 14: Quality Control Requirements

QC is the overall system of technical activities which measures the performance of an ongoing process against established standards verifying performance meets the stated requirements established by the data user or stakeholder. QC activities ensure that the quality objectives and criteria for measurement data, as discussed in Section 7, are maintained so that the program DQO can ultimately be met. Perform QC checks and procedures at a frequency sufficient to ensure data of adequate quality are obtained while minimizing loss of data when non-conformances occur.

14.1 Quality Control for Field Activities

QC, for field activities, relates to PAMS Auto-GC VOC analysis, Toxic VOC canister sample collection, carbonyls sample collection, and benzene.

14.1.1 Quality Control for PAMS Auto-GC VOCs Collection and Analysis

QC processes for PAMS Auto-GC VOC collection and analysis, as described in Table 15 and replicated in the PAMS Auto-GC 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; and independently verify the calibration for compounds.

Table 15. PAMS VOCs Field Quality Control Parameters

QC Parameter	Description	Required Frequency	Acceptance Criteria	Recommended Corrective Action
Initial calibration (ICAL)	Multi-point calibration for each of the 56 compounds on the Auto-GC system. A separate calibration standard bought from Restek is used for this application. Minimum of three concentrations covering approximately 0.25 to .75 ppbC for ethane and 1.50 to 36.75 ppbC for dodecane.	At the beginning and end of PAMS season. After maintenance impacting the CCV response. Following failing continuing calibration checks.	The final calibration curve must be within 20% of the Response Factor percentage of relative standard deviation. Measurements exceeding the calibration range will be qualified as "EH".	<ul style="list-style-type: none"> • Prepare new calibration. • If necessary, 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. <p>NOTE: PAMS data must not be reported unless calibration meets criteria.</p>

QC Parameter	Description	Required Frequency	Acceptance Criteria	Recommended Corrective Action
System blank	Analysis of humidified zero air to ensure the system is sufficiently clean for continued analysis.	Prior to ICAL, and every 24 ± 4 hours of operation following or preceding the CCV. The preference is to follow the CCV to ensure absence of carryover before analyzing ambient samples.	All target VOCs must be ≤ 0.5 ppbC	<ul style="list-style-type: none"> Analyze another blank, if possible, to investigate potential carryover from a high concentration sample. Investigate system for contamination. <p>NOTE: Unless technical justification is provided to explain nonconformance, qualify all samples for affected compounds, since the last passing SB, as "LB" in AQS.</p>
Clock accuracy	Verify clock accuracy against a known accurate time standard.	Weekly, recommended check during each site visit.	Within ± 5 minutes of the time standard.	<p>Reset clock to correct time. Adjust data timestamp accordingly where possible.</p> <p>Ensure adjusted sampling start times are no earlier than 10 minutes before the hour and no later than 30 minutes after the hour.</p> <p>Invalidate sample hours which do not conform.</p>

QA Parameter	Description	Required Frequency	Acceptance Criteria	Recommended Corrective Action
Continuing calibration verification (CCV)	Analysis of a Restek standard containing all the PAMS-compounds which are used for ICAL are also used for the CCV check. All compounds must remain within tolerance to be considered valid. Concentration of CCV should be approximately 1.0-8.0 ppbC for all target analytes. CCV is also used as retention time standard.	Every 24 ± 4 hours of operation.	All target VOCs must recover within ±30% of the expected nominal concentration.	<ul style="list-style-type: none"> Investigate chromatogram for peak misidentification. Investigate for instrument contamination resulting in co-eluting peaks. Investigate for system leaks or trap malfunction resulting in low recovery. <p>NOTE: Since this test is required daily or a primary test, all compounds that fail to meet the requirements for this 24-hour period will be identified as “AS” in AQS for all affected hourly samples.</p>

QC Parameter	Description	Required Frequency	Acceptance Criteria	Recommended Corrective Action
Secondary Source Calibration Verification (SSCV)	Analysis of the EPA supplied 59-component blend which has VOCs in the ~18 to 62 ppbC range. It is then diluted to ~1 to 3 ppbC range. This is a secondary QC check.	Weekly.	All target VOCs must recover within $\pm 30\%$ of the nominal concentration.	Investigate system for reproducibility using a secondary source. Investigate contamination, leaks, or suppression, as indicated by trends in compound behavior. NOTE: Qualify ambient sample data for affected compounds since the last passing SSCV check as “QX” in AQS.
Precision Check	Perform a sequential, back-to-back, analysis of the continuing calibration verification (CCV). This is a secondary QC check.	Weekly	All target VOCs must recover within $\pm 25\%$ of the CCV concentration	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.

On an ongoing basis, an acceptable instrument’s performance needs to be confirmed. System performance QC checks involve verifying the bias criteria are met for representative compounds across the molecular weight range and ensuring instrument contamination and carryover are sufficiently low. PAMS VOCs in ambient air are typically measured at concentrations of less than 2 ppbC. This translates to the initial calibration should consist of a five-level calibration. The lowest level should be at least double the minimum detection limit for each compound. The third level will be equivalent to the CCV, and the highest level will be 5 times higher than the CCV or 25 times higher than the lowest level. Levels 2 and 4 have concentrations that fall in between their adjacent levels. The initial calibration consists of establishing calibration curves for each of the 56 compounds in ppbC which complicates things because the lowest level for ethane will be ~0.27ppbC while it is ~1.47ppbC for dodecane. Using a 56-compound calibration

negates the need for a separate retention time standard and improves credibility for each compound. While FID response is established as 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). When trap materials have aged, nonlinear performance may be more pronounced. For this reason, include a suite of compounds representing the molecular weight range, compounds containing two to ten carbon atoms, C2 to C10, in the daily CCV. With the carbon-response calibration method, several analytes are known to be problematic (recovered at less than 70% of the theoretical concentration). Acetylene, alpha-pinene, and beta-pinene exhibit degradation in standard cylinders 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 AMB will document the low recovery of these compounds and will qualify the associated ambient concentration data when reporting to AQS.

14.1.2 Quality Control for Toxic VOC Canister Sample Collection

Table 16 provides a summary of the QC checks and how the QC check affects the data.

Table 16. Toxic VOC Quality Control Checks

QC Check	Data Status
Sampler Flow Rate $\geq 10.1\%$ from transfer standard	Data are suspect back to last passing flow check. Further review of any checks and the data may result in a QA qualifier, a null data qualifier, or void the flow check
Canister cleaned more than 60 days prior to sample date	Data are invalid
Sample Time	If not 23 to 25 hours, data are invalid
Date	If the date is incorrect but the time is accurate to within 60 minutes, the sample can be reported to AQS with the corrected date. The data are valid, and an information flag is added
Time	If the time is off between 5 minutes and 60 minutes, then adjust the time and the data are valid but has a QA qualifier. If the time is incorrect by more than 60 minutes, the sample is invalid

QC Check	Data Status
Collocated Sample	If precision is >25.0% RPD for target compounds at which the concentration is 5x's the MDL, then qualify results for affected VOC as LK, or a QA qualifier that best represents the comparison
Missing information on canister tag, which includes site, flows, and sample time	Data are invalid unless information can be retrieved from the site logbook or computer log entry
All other information	Data are valid but further review may require a QA qualifier

14.1.3 Quality Control for Carbonyls Sample Collection

Carbonyls sample collection QC includes performing quality checks on the sampling instrument which ensures the instrument is not imparting a positive bias (i.e., contaminating collected samples); flow control is accurate; and the clock is accurate. Carbonyl field QC samples, described in Table 17 and in the carbonyls sample collection SOP, include field blanks, which characterize the level of contamination attributable to sample handling and transportation, and duplicate samples, which characterize the precision between samples collected from the same air mass.

For flow controller calibration verification and clock accuracy, immediately take corrective action when non-conformances are observed. When clock setting deviations are noted, reset the clock, and apply the offset to the sample start and stop times. For example, if the carbonyls sampler clock shows 11:06 a.m. when the actual time is 10:59 a.m., the operator resets the clock and subtracts seven minutes from the sample start and stop times recorded in the sample collection records.

Prior to deploying the sampling instrument for sample collection, perform a positive bias challenge described in 7.3.4.3 and detailed in the PAMS TAD (Revision 3) to ensure compliance with acceptance criteria. If instrument contamination is suspected during operation, a positive bias challenge is recommended. Contamination is indicated by poor precision for duplicate samples or unusually elevated concentrations. The need for follow up corrective action for field blank or duplicate sampling criteria failures are not apparent until analysis results are available. Perform root cause analysis as soon as possible for field QC sample non-conformances and evaluate the efficacy of corrective actions by collection of follow-up field QC samples.

Table 17. 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 zero air to investigate contamination contributed by the sampler	Prior to the beginning of every PAMS season following instrument maintenance (O ₃ denuder recharge or 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 verification	Verify sampling flow of each channel at the sampling flow setting	Monthly	<±10.1% 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 “W” and “LL” (reported concentration biased low for flow verification results biased high) as appropriate in AQS.

QC Parameter	Detail	Required Frequency	Acceptance Criteria	Recommended Corrective Action
Clock accuracy	Verify clock accuracy against a known accurate time standard	Each sampling event	Within ± 5 minutes of the time standard	Reset clock to correct time. Apply offset to sample start and stop times.
Field blank	Blank cartridge installed in a sampling channel for five to ten minutes	One per month except during PAMS season then twice monthly (approximately every 14 days)	Measured mass per cartridge ($\mu\text{g}/\text{cartridge}$): - Acetaldehyde ≤ 0.40 - Formaldehyde ≤ 0.30 - Acetone ≤ 0.75 - Sum of other compounds ≤ 7.0	Investigate sources of contamination in handling and transport. Qualify associated field collected samples as “FB” in AQS. Associated samples are those in the shipment with the field blank and since the most recent acceptable field blank.
Sample retrieval	Samples are retrieved, capped, protected from light, and stored at $\leq 4.0^{\circ}\text{C}$	Each sampling event	Within 72 hours after end of 3 rd sequential sample, whose sampling is nominally completed at 4:00 a.m.	Qualify associated data as “HT” in AQS.

QC Parameter	Detail	Required Frequency	Acceptance Criteria	Recommended Corrective Action
Duplicate sample collection	Collection of a separate cartridge through a common inlet probe concurrently with a primary 8-hour sample	One per month except during PAMS season then three 8-hour per month	$RPD \leq 20\%$ for compounds ≥ 0.5 $\mu\text{g}/\text{cartridge}$	Qualify both samples as estimated “QX” in AQS.
Sample Time	Collection of 24-hour and 8-hour samples	Each sampling event	Must be 23 to 25 hours for 24-hour sample. Each 8-hour sample must be ± 20 minutes.	Data are invalid. Apply appropriate null data qualifier

14.1.4 Benzene

Table 18 provides a summary of the QC checks and how the QC check affects the data.

Table 18. Benzene Quality Control Checks

QC Parameter	Detail	Required Frequency	Acceptance Criteria	Recommended Corrective Action
Sample Time	Collection 1-hour samples	Each hour	Must be 75% of the hour sample	Data are invalid. Apply appropriate null data qualifier
Nitrogen Carrier gas head pressure	Nitrogen gas injects the sample into the column at a defined rate to meet the benzene retention time window	Continuous	The head pressure must be $0.812 \text{ bars} \pm 0.01$	Data are invalid. Apply appropriate null data qualifier. Instrument maintenance is required to adjust head pressure to within limits

QC Parameter	Detail	Required Frequency	Acceptance Criteria	Recommended Corrective Action
Automatic Calibration	Single-point calibration of the BTEX instrument's PID sensor with a known benzene standard at approximately 80-90% of the range.	Every 7.5 hours	Must be activated in the instrument Vistachrom software with a positive cylinder pressure	Data are invalid. Apply appropriate null data qualifier
Automatic Lamp Cleaning	Zero air is activated for a few seconds at the end of each sequence to prevent accumulation of VOC on the lamp	Every 15 minutes	Zero air generator must be operating a positive pressure	Data are invalid. Apply appropriate null data qualifier

14.2 Quality Control for Laboratory Activities

14.2.1 Toxic VOC Laboratory QC

The TNMOC Thermo GC/FID system is calibrated with a propane/benzene standard. The standard is run three times for instrument calibration. The runs are averaged and must be within $\pm 10\%$ of 200 ppbC.

The propane/benzene standard must also be within $\pm 10\%$ of 200 ppbC for the instrument to pass the daily calibration. If the instrument fails to meet the requirement after two tries, then it must be recalibrated as described above.

The GC/MS system is calibrated with a TO-15 NIST traceable standard mixture that has been diluted on an Entech 4700 Precision State Dilution System. The diluted standard is good for 30 days. A calibration curve, which consists of seven levels ranging from 0.1 to 10 part per billion volume (ppbV), is generated when:

- a new SCAN/SIM method has been developed,
- a daily calibration fails, or
- a new diluted standard is attached.

The diluted standard is analyzed on the GC/MS system by varying the trapping volume to establish seven levels of standards. After reviewing the integrated peaks for each level, the calibration curve is generated. Only two outliers may be removed to improve linearity of the curve, provided five levels remain in a row that constitute the calibration curve. A 2.5 ppbV

calibration is reprocessed as a quality control check to verify the curve. At least 60 of the 62 compounds must be within $\pm 30\%$ of 2.5 ppbV.

There are three QC measurements performed on the GC/MS with each batch of canisters. The QC measurements must pass prior to analyzing any ambient air samples:

- Bromofluorobenzene (BFB) criteria verified (all parameters must pass.)
- TO-15 calibration (90% of compounds must be within $\pm 30\%$ of 2.5ppb, which means no more than 6 compounds can be outside 1.75-3.25ppb range.)
- Blank (90% of compounds must be less than 3x's the MDL, which means no more than 6 compounds can be >0.05 ppb.)

The QC performance check is good for 24 hours. The 24 hours begins with the injection of the BFB. The mass calibration and resolution of the GC/MS system are verified by the instrument performance check solution of BFB. If the BFB fails to pass, then it may be necessary to clean the ion source.

A TO-15 calibration standard (2.5 ppbV) is run with each batch of sample canisters to verify the system's calibration. If several of the compounds fall outside the range of $\pm 30\%$ of 2.5 ppb, the system will be recalibrated with seven levels of the standard and the samples will be reanalyzed.

A laboratory method blank checks the GC/MS system for possible lab contamination. The blank is a canister that has been pressurized with ultra-pure zero air. If the blank fails, the source of contamination must be investigated, appropriate corrective measures taken, and documented.

MDLs are determined twice a year after maintenance. The ATS will verify the MDLs, but not report them, twice a year to make sure the MDLs are still valid. The MDL is defined by making seven replicate measurements of the compound of interest at a concentration near (within a factor of five) the expected detection limit; computing the standard deviation for the seven replicate concentrations; and multiplying this value by 3.14 (i.e., the Student's t value for 99 percent confidence for seven values). The MDL checks the precision and accuracy of the GC/MS system.

14.2.2 Carbonyl Laboratory QC

Laboratory QC procedures cover laboratory extraction and analysis of carbonyls cartridges identified in Table 19, which are replicated in the ASL SOP. Laboratory QC samples consist of:

- Extraction batch QC samples include extraction solvent method blanks (ESMB); DNPH media method blanks (MB); and known standard spikes LCS or LCSD)
- Analysis batch QC samples include 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 19. Carbonyls Laboratory Quality Control Parameters

QC Parameter	Detail	Required Frequency	Acceptance Criteria	Recommended 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 $\leq \text{MDL}_{\text{sp}}$	Analyze several SBs and pump mobile phase to flush system. If contamination or interference persists, further investigate the source of contamination.
Initial calibration (ICAL)	Analysis of five or more different calibration standard solutions covering the concentration range of interest	Prior to PAMS season, after failed continuing calibration verification, and after changing instrument components or maintenance which impacts calibration response	$r \geq 0.999$, back calculated concentration of each standard level within $\pm 20\%$ of nominal, $ \text{intercept/slope} \leq \text{MDL}_{\text{sp}}$	Review chromatography for co-eluting peaks or improper integration. If a 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.

QC Parameter	Detail	Required Frequency	Acceptance Criteria	Recommended Corrective Action
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	<p>Review preparation records, calculations, procedures, and chromatography to investigate discrepancy with ICAL.</p> <p>If root cause is not found, prepare new SSCV or ICAL and reanalyze extracts analyzed since the last passing SSCV. Analysis cannot commence until SSCV following ICAL meets criteria.</p>
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	<p>Review chromatography for co-eluting peaks or improper integration.</p> <p>If a problem is not found, establish new ICAL and reanalyze extracts analyzed since the last passing CCV.</p> <p>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.</p>

QC Parameter	Detail	Required Frequency	Acceptance Criteria	Recommended Corrective Action
Laboratory control sample (LCS)	Spike a blank cartridge with a known amount of target analytes and extract.	Minimally twice quarterly, recommended each extraction batch of 20 or fewer field-collected samples	Formaldehyde recovery within 80 to 120% All other target analytes recovery within 70 to 130%	Review preparation records, chromatography, and procedures for sources of contamination or suppression. Unless technical justification is provided to explain nonconformance, qualify sample results in the extraction batch as “QX” in AQS.
Laboratory control sample duplicate (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. Recommend 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 $\leq \text{MDL}_{\text{sp}}$	Review preparation records, chromatography, and procedures for sources of contamination. Qualify sample results in the extraction batch as “LB” in AQS.

QC Parameter	Detail	Required Frequency	Acceptance Criteria	Recommended Corrective Action
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)	$RPD \leq 20\%$ of the associated primary cartridge for compounds ≥ 0.5 $\mu\text{g}/\text{cartridge}$	Unless technical justification is provided to explain nonconformance, qualify both samples as “QX” in AQS.

Section 15: Instrument/Equipment Testing, Inspection, and Maintenance Requirements

Maintain instrumentation used to conduct toxics measurements or to calibrate toxics equipment in accordance with the manufacturer's guidelines regarding routine maintenance of the specific instrument or equipment. Inspection and maintenance procedures are followed, as described in the approved instrument SOPs. Routine instrument maintenance activities and prescribed frequencies are in Table 20.

15.1 Instrument Implementation

All the equipment to perform PAMS Auto-GC VOCs, Toxics VOCs, Carbonyls, and Benzene have been purchased and are operating. While training on instrument use is on-going, IDEM AMB will plan for site operators and auditors to attend formal training sessions whenever



available.

15.2 Annual Instrument Shakedown

IDEM AMB operates the instruments year-round. Staff will follow the maintenance schedule prescribed for each instrument. For each measurement, suitability will be evidenced by the QC procedures and checks required for PAMS Required Site measurements. If, IDEM AMB should opt to shutdown PAMS monitoring at the conclusion of PAMS season, instruments will go through shakedown minimally four weeks prior to the start of PAMS season ensuring instruments are online, calibrated, and stable in sufficient time to demonstrate proper operation as evidenced by acceptable PT results.

15.3 Equipment Inspections

In general, conduct the following routine inspections:

- Inspect monitoring shelters, sample inlets, and equipment facilities (e.g., pump or compressor housings) monthly to ensure conditions do not adversely affect instrument operation or data integrity.
- Review data collection and data quality each business day to determine trends or signs of problems. Data trends indicating 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.

- Inspect equipment during site visits to ensure instruments are in appropriate working order.
- Develop and use site visit checklists to ensure a consistent level of inspection for site operators.

15.4 Instrument Maintenance

Preventive maintenance minimizes instrument downtime and associated data loss. Conduct routine preventive maintenance in accordance with the manufacturer’s operation manuals, applicable maintenance bulletins, or issued updates and according to procedures and frequencies described in the approved instrument SOPs. Additional information on instrument maintenance is found in Revision 3 of the PAMS TAD and Revision 4 of the NAATS TAD. Perform instrument and support equipment maintenance activities per the frequency detailed in Table 20. Note: The information in Table 20 is generic and IDEM AMB provides specific information in SOPs.

The ATS Laboratory has a service contract with Agilent to perform annual preventive maintenance visits and service on GC/MS and Auto-GC Markes Agilent equipment, as needed. IDEM AMB maintains an appropriate supply of critical spare parts and ensures tools are available prior to conducting routine maintenance. Components known to fail or require frequent replacement are readily available to address unforeseen events. A list of these supplies will be detailed in the specific equipment SOPs.

Table 20. Routine Instrument Maintenance Activities

Instrument	Maintenance Activity	Frequency
GC/MS	The associated SOP prescribes maintenance activities and includes cleaning the source, calibrating the standard dilution equipment, and replacing traps, column, and ferrules.	Annual PM visit
Auto-GC	The associated SOP prescribes maintenance activities and include replacing preconcentrator traps, servicing hydrogen and zero air generators, and calibrating standard dilution measurement equipment.	Performed annually prior to PAMS season
Carbonyls Sampler	The associated SOP prescribes maintenance activities and include recharging or replacing the O ₃ denuder, replacing the particulate filter, and performing positive bias challenge.	Performed annually prior to PAMS season

Instrument	Maintenance Activity	Frequency
HPLC for carbonyls analysis	The ASL QAPP and associated SOP prescribes maintenance activities and include servicing pumps, replacing guard columns, replacing solvent frits, and injector needles.	As prescribed in the ASL QAPP, or equivalent, and SOP
Benzene	The Air Toxic GC 886 user's manual prescribes maintenance activities. Activities include maintaining head pressure; auto zero air lamp cleaning (15 min) and auto-calibration of base sensitivity (7.5 hours); manual lamp cleaning (quarterly); and replacing the particulate filter (annually).	As prescribed in the user's manual

Prior to each PAMS season, and annually for all other programs, complete maintenance on the instruments and support equipment necessary for measurements. Replace worn items as needed, verify proper operation, and calibrate instruments so instruments are certified for collecting and reporting data.

The AMS and ATS staff perform basic checks during each site visit which include visually examining the instruments at the site and in the laboratory and verifying communication with the data acquisition system (DAS). A standard checklist is used to capture different or additional aspects of monitoring when operators are on site or in the laboratory.

Section 16: Instrument 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. Calibrate instruments and devices prior to use and according to the schedule or frequency described within this section. The procedures for items used in the PAMS and Toxic VOC program are duplicated in their respective TAD and national SOPs. Calibration checks, which may involve verification of calibration at one or more different levels, ensure the calibration remains valid, but does not involve adjustment of the instrument. Calibration verification failures require adjustment of the calibration, or re-calibration, of the instrument or monitor.

Document instrument calibration in logbooks or an electronic log. Document the instrument's unique identifier; date of calibration; identification of standards used for calibration including certification date; calibration outcome, such as slope, intercept, or other metric indicating acceptable calibration; and any needed corrective actions in the appropriate logbook or electronic log. Do not use standards past their expiration date. The AMS parameter specialist, QAS staff, and ATS chemist maintain documentation for any equipment used in the PAMS VOC, toxics VOC, carbonyls, or benzene programs to perform calibrations, verifications, and audits. Keep a certification/verification file for each item and store in the QA standards laboratory and on the AMB shared drive.

16.1 Calibration and Calibration Verification for PAMS VOCs by Auto-GC

Calibrate PAMS auto-GC for measuring VOCs, 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. Establish calibration by analysis of five concentration

levels. Since the five levels are converted to ppbC, the concentration levels for each compound will be different while the levels for ppbV stay the same. The ppbV concentration levels for each of the 56 compounds are from a Restek standard. The daily verification or continuous calibration verification (CCV) of the calibration will be by analysis of the same NIST-traceable standard used to do the initial calibration while the EPA supplied NIST-traceable standard, which is used by other states as a Retention Time standard (RTS) and contains all 56 compounds in various concentrations representing the molecular weight range (C2 to C12), is used as a secondary source verification standard, followed by a blank. Analysis results of the CCV must be within $\pm 30\%$ of the nominal concentration for the target compounds for valid results. If the target compound for the CCV is outside of the nominal range, then the data for only that target compound would be classified as invalid.

Instrument calibration instructions are specified in the following SOPs:

- Operation of Markes-Agilent System for Online Sampling and Analysis

16.2 Calibration and Calibration Verification for Toxic VOCs

The GC/MS system is calibrated with a TO-15 NIST traceable standard mixture that has been diluted on an Entech 4700 Precision Static Dilution System. The diluted standard is good for 30 days. A calibration curve, which consists of seven levels ranging from 0.1 to 10 part per billion volume (ppbV), is generated;

- When a new SCAN/SIM method has been developed,
- a daily calibration fails, or
- a new diluted standard is attached.

The diluted standard is analyzed on the GC/MS system by varying the trapping volume to establish seven levels of standards. After reviewing the integrated peaks for each level, the calibration curve is generated. Only two outliers may be removed to improve linearity of the curve, provided five levels remain in a row that constitute the calibration curve. A 2.5 ppbV calibration is reprocessed as a quality control check to verify the curve. At least 60 of the 62 compounds must be within $\pm 30\%$ of 2.5 ppbV

A TO-15 calibration standard (2.5 ppbV) is run with each batch of sample canisters to verify the system's calibration. If several of the compounds fall outside the range of $\pm 30\%$ of 2.5 ppb, the system will be recalibrated with seven levels of the standard and the samples will be reanalyzed.

A laboratory method blank checks the GC/MS system for possible lab contamination. The blank is a canister that has been pressurized with ultra-pure zero air. If the blank fails, the source of contamination must be investigated, appropriate corrective measures taken, and documented.

Canister cleaning and certification are critical to ensure the highest possible quality of data from canister sampling and analysis. Each canister is cleaned in an oven overnight or over a weekend at 80 °C and evacuated to 100 mTorr or lower. The procedure for cleaning is further described in the SOP, Canister Cleaning and Certification.

A maximum of twelve canisters can be cleaned at one time. After the cleaning procedure is complete, all canisters must be tested on one of the Agilent GC/MS. The total concentration of

all compounds must be less than 0.20 ppb. If any canister fails, then it will be re-cleaned and tested again.

ATS staff will re-clean any canister that has exceeded 60 days which are waiting for field deployment.

Instrument calibration instructions are specified in the following SOP:

- Agilent Gas Chromatograph-Mass Spectrometer with Autosampler

16.3 Carbonyls Instrument Calibration

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

16.3.1 Carbonyls Field Sampling Instrument Calibration and Calibration Verification

Calibrate carbonyls sampling unit flow controllers initially prior to the beginning of PAMS season and verify the flow calibration minimally monthly. Flow calibration verification must be $\leq \pm 10.1\%$ of the flow indicated at standard conditions of 760 mmHg and 25°C against a NIST-traceable certified flow transfer standard.

16.3.2 Carbonyls Laboratory Instrument Calibration and Calibration Verification

The ASL calibrates the HPLC or UHPLC initially; following maintenance or repair which would reasonably impact the instrument response; and following failure of CCV or SSCV, 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. Calibrate instruments, which are not operated continually (e.g., those shut down for several months at a time), when returned to online status. Verify calibration 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 must within $\pm 15\%$ of the nominal concentration or corrective action must be taken.

16.4 Benzene Calibration

Calibration for the benzene occurs every 7.5 hours. The procedures for this calibration will be provided in a pending SOP. The manufacturer can provide general details on how to calibrate the Chromatotec GC866.

16.5 Calibration Support Equipment

Calibration support equipment, for measurement instruments, includes, but is not limited to flow transfer standards, reference thermometers, reference barometers, volumetric labware, and mass flow controllers. Perform calibration and calibration verifications by comparison to known standards traceable to NIST standards. Evidence of traceability to a NIST standard is on a calibration certificate provided by either the metrology lab, standards provider, or certification provider attesting to the accuracy or uncertainty associated with the standard. Standard certification providers may be the manufacturer, in-house laboratory, third-party laboratory, or other suitable certifier. Metrology certification providers typically operate under an International Organization for Standardization (ISO) quality standard or other similar performance standard which requires certifications to a certified NIST standard. IDEM AMB specifies the certification

provider, primary standards of comparison, and approved method or SOP for each appropriate support instrument.

Support equipment requiring calibration and the associated calibration frequency and acceptance criteria are listed below in Table 21.

Table 21. Calibration Requirements for Critical Support Instruments

Critical Support Equipment	Specifications and Acceptable Uncertainty	Area of Use	Calibration ^a Frequency Requirement	Calibration Verification ^b Check Frequency
Flow transfer standard	<±2.1% of NIST-traceable standard across the 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 is not required
Mechanical pipette	Tolerance within manufacturer specifications	Delivery of known liquid volumes for 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 is not required
Volumetric syringe	Tolerance within manufacturer specifications	Delivery of known liquid or gas volumes	Received with a certification of calibration or initially calibrated gravimetrically at 10% and 100% of full volume	Calibration check is not required

Critical Support Equipment	Specifications and Acceptable Uncertainty	Area of Use	Calibration ^a Frequency Requirement	Calibration Verification ^b Check Frequency
Thermometer (not for reporting meteorological ambient temperature data)	0.1°C resolution; <±0.51°C accuracy of a NIST-traceable certified standard thermometer	Laboratory and site storage unit monitoring for carbonyls sample and extract storage. Temperature monitoring of monitoring shelter. Note: this is not a thermometer for reporting meteorological data	Annual at temperature range of use – Correction factors applied to match certified standard	Annual calibration
Barometer	<±2.26 mmHg	To determine flow rates	Annually	Annually
Balance	Tolerance within manufacturer specifications	Laboratory for 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
Certified weights	Tolerances within those assigned to the class of weights	Laboratory for calibration verification of balances	Annually or as required by the manufacturer	Annual calibration

Critical Support Equipment	Specifications and Acceptable Uncertainty	Area of Use	Calibration ^a Frequency Requirement	Calibration Verification ^b Check Frequency
Pressure gauges or transducers	Within ± 0.5 psi or manufacturer-specified tolerance, whichever is smaller	Field and Laboratory to measure canister pressure or vacuum for standards preparation	Annually	Annual calibration. Must cover the range of use
Mass flow controller – gas calibrator	$<\pm 2.1\%$ of certified flow transfer standard	Precise metering of standard and diluent gases for calibration of monitoring instruments	Annually or when calibration checks demonstrate flows are out of tolerance	Minimally quarterly. Before and at the end of PAMS season. Monthly recommended

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

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

Section 17: Inspection and Acceptance Requirements for 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, etc. Where possible, purchase supplies and consumables 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, which are available in Section 11. Inspect and confirm materials meet the specifications detailed in the respective SOP before using or placing them into service. Confirm performance of the supply or consumable items by verifying proper instrument function or operation evidenced by meeting applicable QC criteria. IDEM AMB specifies processes and procedures for inspection and acceptance of supplies and consumables in SOPs listed in this QAPP.

17.1 Acceptance of Standard Materials

On an annual basis, IDEM AMB inspects NIST-traceable transfer standard equipment that is subject to wear and tear during use (e.g., temperature, pressure, and flow rate check devices). Return such equipment annually to the vendor or an appropriate accredited metrology laboratory, as specified in 16.5, for cleaning, servicing, and recertification against NIST standards. Consult Table 21 for equipment requiring annual certification or the IDEM AMB QAPP on Calibration,

Certification, and Verification Methods of Transfer Standards, Volume V, B-005-OAQ-AMB-QA-24-Q-R3.

Stock gaseous standards for calibration of the PAMS, Toxics, and Benzene analyzers are sourced from reputable certified gas vendors. Similarly, derivatized carbonyls calibration stock materials are sourced from reputable chemical suppliers. Standard gases and carbonyls stock materials must, preferably, be NIST-certified or traceable to a NIST certified standard and accompanied by a certificate of analysis stating the purity (for neat materials or pure gases), or certified concentration with associated uncertainty for each component as well as the expiration dates.

Note: U.S. EPA employs a national contract laboratory to independently verify the concentration of propane and benzene standard and in the EPA retention time standard (RTS) cylinders against a NIST-certified standard. The verification laboratory provides a certificate of analysis for the verification of each individual 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, the 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 U.S. EPA regional representative.

Certificates of analysis will be maintained by the IDEM AMB and be available for inspection during TSAs.

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

17.2 Acceptance of Sampling Media - Carbonyls

The ASL is expected to perform lot blank analysis for each lot of media for use at supported sites. Prior to use in the field for sample collection, test each lot of DNPH cartridges to ensure the background contamination is acceptably low. Minimally, extract and analyze three cartridges per lot or 1% of the received lot, whichever is greater, 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 must meet the criteria in Table 22.

If the criteria in the table are not met, do not use the lot cartridges, and return to the vendor.

Table 22. 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

Section 18: Non-direct Measurements

IDEM will use non-direct measurement data to support data validation activities, as described in Section 10 of Revision 3 of the PAMS TAD on data verification and validation. Such data may include historical PAMS data or reported concentrations from other monitoring sites. Data acquired from non-direct measurements may also include site operator observations.

Section 19: Data Management

IDEM AMB ensures data are recorded, verified, validated, reported, managed, and archived in a manner which permits reconstruction of activities throughout the data lifecycle. SOPs documenting the processes are stored on shared, secured AMB computer drives or in other secured network drives. AMB's goal is to maintain at least 75% valid data with exception of carbonyls being 85%. The valid data determination process and the parameter QC and QA are mentioned in Section 7. Data must be collected, validated, audited, and reported to the U.S. EPA's AQS database quarterly. Quarterly data are reported to the AQS within 90 days after completion of the quarter. Data consists of sample values, flow verifications, and flow audits. Continuous data are planned to be available on the IDEM website as it is being collected, except for PAMS Auto-GC VOC. Therefore, that data has not undergone QC or QA processes. Data from the PAMS Auto-GC VOC located at the PAMS site will be available in the DMDS once it is collected and had QC performed, so usually within a day.

Canisters for the Toxics VOC program and the cartridges for the carbonyl program are collected either once or twice per week. The data consists of 24-hour samples except during PAMS season, which is June 1 through August 31, at which time carbonyl samples are sampled for eight hours. Other sections of this QAPP provide specific collection and data analysis requirements.

ATS performs all analyses for the Toxics VOC program. A U.S. EPA contract laboratory analyzes carbonyl cartridges, and performs its own internal QC and QA checks, and provides

validated data to the AMB monthly, typically 45 days after the end of the month in which it was analyzed.

Carbonyl flow data generated by the AMS during verifications and the QAS during audits is entered into an excel file. The file is uploaded to a shared computer drive. These results are then uploaded into AQS quarterly.

Section 20: Assessments and Response Actions

One of the major objectives of this QAPP is to specify the policies and establish procedures necessary to ensure toxics data are of sufficient quality and quantity to meet the required site network DQOs. Site operators and laboratory staff are responsible for preventing nonconformances, where possible, and minimizing nonconformances' impact to data quality and fitness for the purpose, once identified. Every effort is made to anticipate and resolve potential nonconformances before the quality of the toxics data is compromised. Report nonconformances impacting data quality to the appropriate AMB section chief who will work with the site operators or laboratory staff to take corrective action. Adherence to the quality policies described in this QAPP is also ascertained by way of various ongoing assessments listed in Table 23.

The AMB utilizes several assessment procedures to identify and correct issues. The corrective action process may include formal or informal communication and response.

Table 23. Assessments and Response Actions

Assessment	Conducted By	Frequency	Requirement
PAMS Auto-GC VOC CCV and blank	ATS staff	Daily	QAPP
PAMS Auto-GC PT	ATS staff	Twice Annually	TAD for Sampling and Analysis of Ozone Precursors for the PAMS Program – Revision 3 – May 2023
PAMS Auto-GC PE audit	ATS & QAS staff	2 times per year (one before and one after PAMS season)	QAPP
Toxics VOC standards and blank	ATS staff	Daily	QAPP
Toxics VOC sampler verification	AMS staff	6 months	QAPP
Toxics VOC PE audit	QAS staff	Annual	QAPP
Toxics VOC PT	ATS staff	2 times per year	NATTS
Carbonyls verification	AMS staff	Monthly	QAPP
Carbonyls semi-annual flow rate audit	QAS staff	Quarterly	QAPP
Carbonyls PE zero audit	QAS staff	2 times per year (one before and one after PAMS season)	QAPP

Assessment	Conducted By	Frequency	Requirement
Benzene calibration	AMS staff	Daily	QAPP
Benzene PE audit	QAS staff	Annually	QAPP
Data verification	AMS and ATS staff	Monthly	Screening of data, chart trace, QC checks
Data validation	QAS staff	Monthly	Screening of data, chart trace, QC and QA checks
QAPP	QAS staff	Annually	Determine if changes are needed which accurately describes the project
ANP	AMB staff	Annually	40 CFR § 58.10
Site Evaluation	QAS staff	2 years per site	QAPP
5-Year network assessment	AMB staff	5 years	40 CFR § 58.10
Technical systems audit	U.S. EPA OAQPS along with their contractor and/or Region 5 staff	Once every 3 years	40 CFR 58 Appendix A § 2.5

In the event an assessment identifies an area of concern, there are specific corrective actions which occur depending on what the finding shows. Below is listed the assessment and corrective action time frame for follow-up.

PAMS Auto-GC VOC CCV and blank – Daily, the ATS staff reviews the CCV and system blank chromatogram data. Investigate for instrument contamination. A QA qualifier is added if technical explanation of non-conformance is not available. Data may be invalidated back to the previous passing CCV and blank.

PAMS Auto-GC VOC PT - The U.S. EPA contractor prepares PAMS Auto-GC VOCs samples for shipment to the field site on a biannual basis. Samples are spiked with target analytes at concentrations blind to the sites. Sites analyze the PT samples on the auto-GC and report the resulting concentrations to the PT provider. The provider compiles the reported concentrations for evaluation against the nominal value and against the overall required network mean, after removing statistical outliers. Auto-GC results must be within $\pm 25\%$ of the assigned target value for each evaluated target compound. Sites 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.

PE audits - The QAS is set up as an independent section within the AMB and as such performs internal PE audits using equipment (e.g., gas calibrators, zero air generators, and compressed gas cylinders) which are independent of calibration and verification equipment used by the AMS and ATS. QAS staff members notify the AMS and ATS parameter specialist of any issues either from site or once back in the office with written notification (memorandum or e-mail) following

soon after. Once the issue is resolved, the AMS or ATS parameter specialist must document the issue resolution.

Toxics VOC standards and blank – The ATS must verify that QC criteria pass (the BFB criteria pass, 90% of the compounds in the TO-15 standard are $\pm 30\%$ of 2.5 ppbv, and blanks have no more than six compounds > 0.5 ppbv) prior to conducting sample analysis.

Toxics VOC verification- AMS staff perform cleaning of the Meritor sampler every six months. Once cleaned, AMS staff collect a zero air sample and ATS staff analyze to verify less than 10ppb TNMOC.

Toxics VOC PT - The U.S. EPA contractor prepares Toxic VOCs samples for shipment to the laboratory on a biannual basis. Samples are spiked with target analytes at concentrations blind to the sites. Sites analyze the PT samples on the GC/MS and report the resulting concentrations to the PT provider. The provider compiles the reported concentrations for evaluation against the nominal value and against the overall required network mean, after removing statistical outliers. GC/MS results must be within $\pm 20\%$ of the assigned target value for each evaluated target compound. Sites 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.

Carbonyl flow verification- AMS staff perform a monthly flow check. If 10.1% or greater, samples back to last passing flow check may require a QA qualifier or null data code pending further review.

Benzene Calibration- AMS staff review daily calibration results. If calibration does not pass, data will require a QA qualifier or a null data code pending further review.

Data Verification Process – The AMS and ATS parameter specialist performs a verification of the ambient data within one to three weeks after the end of a month. Documentation of the process can be found in the DMDS validator notes.

Data Validation Process – A QAS staff member performs a validation review of the data within 15 working days after the QA Program Coordinator is informed that a data package is available for review. Data validation is documented on the Validation Check form, and the completed validation records are stored on the AMB shared drive.

QAPP – QAS section chief ensures QAPP is being followed and makes necessary changes, with approval by AMB chief, AMS (1 and 2) chiefs, and ATS chief. An annual check is documented or when a change needs to be made in the QAPP revision history.

ANP – The Annual Network Plan is due to the U.S. EPA Region 5 Administrator by July 1st. The AMB tries to have a complete ANP available for public comment by mid-May to allow for the 30-day public comment period to be completed by mid-June. Corrective actions taken immediately (prior to the start of the new year) by AMB based on U.S. EPA feedback.

Site Evaluation – The QAS performs site evaluations on a 2-year cycle from the previous site evaluation. The AMS addresses issues based on QAS findings (usually within one workday if data are impacted or some time frames may be extended based on the nature of the issue and if the site is on private property). QAS chief ensures corrective action is taken to resolve the issues.

5 Year Network Assessment – The 5-year Network Assessment is due at U.S. EPA by July 1st for years ending in zero or five. Corrective actions by AMB based on U.S. EPA feedback within the time frame allotted for the response.

Technical Systems Audit – Technical System Audits are scheduled by the U.S. EPA Region 5 on a 3-year frequency. The QAS works with AMS(s) and ATS to address any audit findings. All findings should be resolved within one year of the TSA report. Additional TSAs are expected to be conducted for the PAMS program. More details of this are outlined in the PAMS QAPP.

Section 21: Reports to Management

Reports that are generated and utilized in the toxics program are listed below in Table 24. Report any anomalies to the AMS and ATS section chiefs, and the AMB chief. The reports will identify the point(s) the data failed to meet DQOs and at what point in time, after corrective action, the data again meets DQOs. Flag and comment on the corresponding data and include all supporting documentation in the report.

Table 24. Reports to Management

Report	Frequency	Responsible Party
AMP Reports	Quarterly	QAS
% CV for Reporting vs. Collocated at Indianapolis Washington Park site	Quarterly and Annual	QAS
Reporting vs. Collocated TO-15 which exceed 25% difference and were above 5xMDL at Indianapolis Washington Park site	As needed per sample	ATS
External PT results for PAMS Auto-GC VOC	Annually	EPA or contractor
Invalid Data Memos	As needed	AMB
Annual Network Plan	Annually	AMB
5-year Network Plan	5 years	AMB

Section 22: Data Validation and Usability

Many of the criteria used to review and validate data have been detailed in the previous sections of this QAPP. The AMB utilizes this established QAPP, SOPs, and U.S. EPA TADs to determine data validity. Once data has gone through all the processes, then it is deemed usable for its intended objective.

Section 23: Validation and Verification Methods

Data verification is the process of evaluating the completeness, correctness, and conformance of a specific data set against the method, or procedural or contractual requirements, as specified in both the SOPs and [40 CFR Part 58](#). Data validation is a process which extends the evaluation of data beyond method, or procedural or contractual compliance (i.e., data verification) to ensure

that reported values meet the quality goals of the environmental data operations and that the data can be used for its intended purpose.

The AMB brackets all toxics data using the results of the monthly verifications, calibrations, or PE audits to ensure the instruments were in proper operating condition between the checks. When an instrument fails a check, data are suspect back to the last passing check until the originating failure is remedied. For some continuous samplers DMDS software automatically flags the data as LIM starting when the error occurs and ending the time & date when the issue causing failure is remedied. The AMS or ATS parameter specialist reviews the data, determines the cause for the failure, and verifies the extent of the data invalidation period. During the validation process, the QAS reviews the invalid data period to ensure it is proper, accurate, and documented.

23.1 Data Verification Methods

Instrument operators and technical reviewers will ensure data are complete, correct, and comply with this QAPP and supporting SOPs. The end results of data verification are to ensure all data reviewed are traceable; generated with instruments calibrated with certified standards according to an approved standard process, for which calibration and other QC checks were performed at the proper frequency and meet criteria; and all calculations and transformations are correct. Data verification activities are tailored to verify data are error-free and flagged (qualified) or invalidated when data integrity is compromised.

Routine reviews and technical reviews will include examining data manually and using automated tools to verify the data. Examples of manual methods include direct examination of chromatography data for GC/MS and auto-GCs, 1-minute data for continuous monitoring methods, 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; DMDS summary reports and alarm reports; data completeness reports; and similar reports which provide an aggregation of data to provide efficient confirmation 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 3 of the PAMS TAD. AMB SOPs listed in Section 11 provide details on the data verification procedure and tools.

The AMB has checklists to ensure that critical data verification elements are reviewed, and the review documented during routine reviews and technical reviews. Checklists will indicate whether the critical element was satisfied. Such checklists are included in the specified data verification and validation SOPs listed in Section 11.

23.2 Data Validation Methods

This section describes general tools for conducting data validation for PAMS Auto-GC VOCs, Toxic, carbonyls, and benzene. These tools are useful in identifying anomalous data and increasing confidence in datasets. However, the AMB staff will use a combination of such tools

to validate data, and do not rely on one specific tool to confirm or nullify data validity. The AMB tools are described in SOPs listed in Section 11 or similar controlled documents.

23.2.1 Data Visualization Methods

Graphical techniques permit comparison of concentrations of each of the parameters to the expected concentrations and relative concentrations of other datasets to inspect for values which stand out. The 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 DMDS 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 3 of the PAMS TAD and Revision 4 of the NAATS TAD. The IDEM AMB incorporates these tools and methods, as appropriate, in the data validation procedures, and specifies the checks and comparisons applicable to the given parameter types. The processes are described in appropriate SOPs listed in Section 11.

23.2.2 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 DMDS software packages include automated screening checks and statistical tools which aid in identifying data which 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.

23.2.3 Examination of Supporting Data

Comprehensive data validation requires the data validator to examine materials and records which support the reported parameter measurements but are not directly reported data. The supporting data sources are integral in identifying data which may be compromised and require qualification or invalidation. As part of data validation activities, validators review these supporting data sources and verify compromised data are appropriately flagged or invalidated.

Technical Systems Audit Reports: TSAs may uncover non-conformances which can affect the validity of data. For example, if a site maintenance staff is found to have stored a gasoline container near the inlet probe, the associated data impacted, during the period, would likely be

invalidated. Review TSA reports and related CAPs during data validation to ensure findings impacting measurement data quality have been addressed through corrective action and data validators assessed 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 into the instrumentation instead of 3.19 ppbC to generate calibration standards for benzene. Such a situation could probably be corrected, and the data reprocessed with an updated calibration curve for the parameters on the higher molecular weight hydrocarbon channel (PDMS column) of the auto-GC.

Instrument Performance Audit and Proficiency Test Results: Deviations from acceptance or advisory limits during IPAs or PTs indicate bias is present in the measurement system. The validator reviews IPA and PT reports for unacceptable results; verifies 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, 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 the sampling unit when reporting to AQS.

Laboratory Analysis Result Reports: ASL results reports may include sample narratives or include QC sample results which provide context for the sample measurements. Verify data provided by the ASL with respect to the laboratory processes and method QC acceptance criteria. The ASL flags data when operational or QC criteria non-conformances occur and notifies the site monitoring agency. This will typically involve data flags or comments on electronic data deliverables. The site monitoring agency is responsible for ensuring 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 or collocated sample results to ensure acceptance criteria are met. Poor agreement between duplicate or collocated, and primary sample pairs is indicative of a problem with the measurement system, data transformation, or data reduction process and will be investigated. Minimally, qualify results for sample pairs when precision acceptance criteria are exceeded, unless a technically justifiable rationale is determined and documented (e.g., 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, invalidate the data from the primary samples 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 including electronic logs, if available; maintenance logs; and on sample collection or COC forms to assess unusual events or instrument problems which 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 IDEM AMB uses its best judgment about the impact of site conditions on the acceptability of the data and may consult with the U.S. 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, qualification of, or invalidation of data, as appropriate.

23.2.4 Treatment of Deviations from Requirements

Deviations from procedural or QC criteria call for the AMS staff or ATS staff to correct the data, where possible; take corrective action to limit the impact or recurrence of such deviations; appropriately flag or invalidate affected data, when reported to AQS; and notify U.S. EPA Region 5 staff when a significant amount of data (e.g., 10% of the quarterly values or the potential inability to meet the completeness MQO) are affected.

23.2.4.1 Identifying Compromised Data in AQS

If data affected by deviations cannot be appropriately corrected, the IDEM AMB identifies compromised data within AQS by addition of a qualifier or combination of qualifiers. Qualifiers associated with data are listed in Table 25. Note: the U.S. 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 are either flagged or invalidated in AQS as described below and in Section 14.

Flagging Data in AQS: Only flag compromised monitoring data in AQS 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 or informational (INFORM) qualifiers.

Invalidating Data in AQS: Data of uncertain origin, data with unacceptable levels of uncertainty, or data known not to 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 are coded with a Null qualifier to ensure the data are 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, qualify, and estimate data with descriptive QA and INFORM flags when compromised but remain valid. In general, such qualification is preferable to invalidation as a

measurement value remains 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).

Table 25. AQS Qualifiers and Null Codes

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	
6	QAPP Issue		QA	
7	Below Lowest Calibration Level		QA	
DI	Sample was diluted for analysis		QA	applies to carbonyls only
EH	Estimated; Exceeds Upper Range		QA	
FB	Field Blank Value Above Acceptable Limit		QA	
HT	Sample pick-up hold time exceeded		QA	applies to carbonyls only
LB	Lab blank value above acceptable limit		QA	applies to PAMS Auto-GC and carbonyls only
LJ	Identification Of Analyte Is Acceptable; Reported Value Is An Estimate		QA	most common qualifier when an estimate is needed

Qualifier Code	Qualifier Description		Qualifier Type	Comment
LK	Analyte Identified; Reported Value May Be Biased High		QA	
LL	Analyte Identified; Reported Value May Be Biased Low		QA	
MD	Value less than MDL		QA	
ND	No Value Detected		QA	
NS	Influenced by nearby source		QA	rare – in most situations such data should be invalidated
QX	Does not meet QC criteria		QA	Fails secondary QC checks for PAMS Auto-GC
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	
W	Flow Rate Average out of Spec		QA	
AC	Construction/Repairs in Area		NULL	
AD	Shelter Storm Damage		NULL	
AE	Shelter Temperature Outside Limits		NULL	
AF	Scheduled but not Collected		NULL	

Qualifier Code	Qualifier Description		Qualifier Type	Comment
AG	Sample Time out of Limits		NULL	Fails to stamp at correct time, PAMS Auto-GC.
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	PAMS Auto-GC
AP	Vandalism		NULL	
AQ	Collection Error		NULL	
AR	Lab Error		NULL	
AS	Poor Quality Assurance Results		NULL	Used for PAMS Auto-GC when compounds fail CCV
AT	Calibration		NULL	
AU	Monitoring Waived		NULL	
AV	Power Failure		NULL	PAMS Auto-GC
AW	Wildlife Damage		NULL	
AX	Precision Check		NULL	PAMS Auto-GC
AY	QC Control Points (zero/span)		NULL	
AZ	QC Audit		NULL	used for analysis of the VOCs PT sample & TTP for O ₃ & NO ₂ ; PAMS Auto-GC

Qualifier Code	Qualifier Description	Qualifier Type	Comment
BA	Maintenance/Routine Repairs	NULL	
BB	Unable to Reach Site	NULL	
BE	Building/Site Repair	NULL	
BH	Interference/co-elution/misidentification	NULL	applies to auto-GC parameters only
BI	Lost or damaged in transit	NULL	applies to carbonyls only
BJ	Operator Error	NULL	PAMS Auto-GC
BK	Site computer/data logger down	NULL	
BL	Benzene/Propane standard for QA Audit	NULL	PAMS Auto-GC
DL	Detection Limit Analyses	NULL	
MC	Module End Cap Missing	NULL	applies to carbonyls only
SC	Sampler Contamination	NULL	
TC	Component Check & Retention Time Standard	NULL	PAMS Auto-GC for SSCV
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.
MB	Method blank	NULL	PAMS Auto-GC blanks that follow tests
ST	Calibration verification standard	NULL	PAMS Auto-GC for CCV
TC	Secondary source verification calibrate/Component check/Retention time standard	NULL	PAMS Auto-GC for SSCV
IH	Fireworks	INFORM	rare
II	High Pollen Count	INFORM	rare
IJ	High Winds	INFORM	rare, may apply to wind speed and direction data

Qualifier Code	Qualifier Description	Qualifier Type	Comment
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

23.2.4.2 Corrective Action Process

Follow the IDEM AMB corrective action process in cases of systematic problems or problems affecting a significant amount of data. The process is described in Section 20.

23.2.4.3 Notification of U.S. EPA or Other Stakeholders

For serious or systematic problems impacting data, notify staff within the monitoring agency responsible for determining the impact of the data and determining the validation status of the data. Also notify stakeholders and users of the data which might be impacted by the validation status shall also be notified. IDEM AMB contacts the U.S. EPA Region 5 who may themselves notify or may instruct IDEM AMB to notify the U.S. EPA 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 impacted data represented 10% of the season's data or jeopardized the ability to meet the completeness MQO. Notify stakeholders when corrective actions are completed and return to conformance has been demonstrated. QAS will include significant problems in their annual QA reports to management.

Section 24 Reconciliation with Data Quality Objectives

The DQOs and intended uses for the toxics data are discussed in Section 7 of this QAPP. The DQO for the PAMS Required Site network is to provide a database of O₃ precursors and associated meteorology data which modelers can use to evaluate O₃ prediction models. Toxics VOC and benzene help evaluate criteria gases as related to the U.S. EPA NAAQS and to measure air pollutant concentrations which may be of concern for public health concerns and public welfare considerations. The MQOs listed in Section 7 were established to provide the expected data quality needed by modelers. Following the first year of PAMS Required Site measurement data collection, U.S. EPA modelers are expected to 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, the U.S. EPA will perform a DQA to assess and characterize the overall network data quality. The U.S. EPA will prepare a report aggregating the PAMS QA and QC data for the year which may be combined with U.S. 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. The AMB will perform a DQA for its PAMS site to evaluate the site's attainment of the specified MQOs. This will include a description of the DQA and the outcomes in the annual QA report described in 23.2.4.3.

Section 7 of this QAPP also lists the measurement quality objectives, established to provide the expected data quality required by users.

The QAPP establishes procedures to control measurement uncertainty to an appropriate level to achieve the objectives for which monitoring data are collected. If guidelines and any SOPs governing the measurement process are followed and all measurement quality objectives listed in this QAPP are met, the DQOs can be achieved. However, a chance exists in which exceptional field events may negatively affect the performance of the monitoring station. Therefore, reconciling the monitoring data with the DQOs is important to evaluate whether the data set is adequate for its intended use. This involves reviewing routine data, such as the monthly verification and validation reviews described in Section 23 of this QAPP, and the results of monthly verification checks.

On a quarterly basis, AMB staff evaluate the monitoring network performance by reviewing the data quality statistics (precision, bias, and completeness) of the QA and QC data set and comparing the results to the monitoring project goals. Precision for carbonyl and VOC sampling are determined by calculating the coefficient of variation of the RPDs between primary and collocated sample collections. Bias is monitored through twice per year performance testing using an EPA approved contractor and the results of the PT samples are provided by the EPA approved contractor summarizing the PT results and providing a synopsis of any data quality issues experienced that may impact the final PT results. Data assessment statistics are taken from the AQS AMP450NC Report, Quick-look Report, and the AQS AMP430 Report, Data Completeness. The AMP450NC Report provides summary statistics on the toxic pollutant data collected. The AMP430 Report provides a status of the quantity of toxic pollutants collected.

Unacceptable performance for any of the DQO goals does not automatically indicate that the data set cannot be used for its intended purpose, i.e., the support of the decision process for a NAAQS. However, the impact on the confidence with which the data set can be used for its intended purpose in the decision process will have to be reviewed and communicated. This is done in the quarterly reports generated by the QAS environmental manager and QAS chief.

24.1 EPA Corrective Actions for PAMS

The U.S. EPA may review PAMS QA and QC data and collected measurements and may adjust the stated MQOs to meet the intended use. The U.S. 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.

Section 25 References

- (1) [Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air](#)
- (2) [EPA QA/R-5 \(March 2001\), Requirements for Quality Assurance Project Plans, U.S. Environmental Protection Agency, Washington, DC.](#)
- (3) [EPA-454/B-18-006 \(August 2018\), Guide to Writing Quality Assurance Project Plans for Ambient Air Monitoring Networks, U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Air Quality Assessment Division, Research Triangle Park, NC](#)
- (4) [EPA-454/R-23-003 \(May 2023\), 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 – Revision 1](#)
- (5) [EPA-454/R-23-002 \(May 2023\), Technical Assistance Document for Sampling and Analysis of Ozone Precursors for the Photochemical Assessment Monitoring Stations Program – Revision 3](#)
- (6) [Technical Assistance Document for the National Air Toxics Trends Stations Program, Revision 4, July 2022](#)
- (7) [40 CFR Part 50](#)
- (8) [40 CFR Part 53](#)
- (9) [40 CFR Part 58](#)
- (10) [QAPP: Calibration, Certification, and Verification Methods of Transfer Standards, Volume V \(2022\)](#)
- (11) [Agilaire AirVision](#) Manual, July 2022