Chapter 8

Quality Assurance of Ambient Air Toxic Monitoring

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Table of Contents

Page

1.0 Introduction **1**

2.0 Siting **1**

3.0 PAMS (VOCs) **2**
3.1 Sample Collection 3
3.2 Calibration 3
3.3 Sample Analysis 3
3.4 Quality Control 3
3.4.1 Field 4
3.4.2 Laboratory 4
3.4.3 Data 4
3.5 Quality Assurance 5
3.5.1 Field 5
3.5.2 Laboratory 5
3.5.3 Data 5

4.0 Toxics (VOCs) **5**
4.1 Sample Collection 6
4.2 Sample Analysis 7
4.3 Quality Control 8
4.3.1 Field 8
4.3.2 Laboratory – Toxics Section 10
4.3.3 Laboratory – Ambient Monitoring Section 11
4.3.4 Data 11
4.4 Quality Assurance 12
4.4.1 Field 12
4.3.2 Laboratory 12
4.3.3 Data 12
4.5 Canister Cleaning 13
4.5.1 Quality Control 13

5.0 Carbonyl Monitoring Program **13**
5.1 Sample Collection 13
5.2 Sample Analysis 15
5.3 Quality Control 15
5.3.1 Field 15

5.3.2 Laboratory 16
5.3.3 Data 16
5.4 Quality Assurance 16
5.4.1 Field 16
5.4.2 Laboratory 17
5.4.3 Data 17

TABLES

1 Sampling Unit Inlet Required Minimum Distance from Roadways for Toxics (VOCs) ...2
2 Sampling Unit Inlet Required Minimum Distance from Roadways for PAMS and Carbonyls 2
3 Quality Control Checks 10
4 Data Specifications 12
5 Quality Control Checks 16

FORM

1 (Toxics – Carbonyl Data Check Form) 17

1.0 Introduction

The State of Indiana's air toxic monitoring program's objective is to determine background ambient concentrations of selected hazardous air pollutants listed in the Clean Air Act of 1990. Monitoring provides data for evaluating population exposure and risk assessment. Planning for compliance with standards being developed by the United States Environmental Protection Agency (USEPA) is another use of the data. Additional applications encompass episodic monitoring (i.e., chemical spills and fires), hazardous waste site monitoring, nuisance complaints, and source specific ambient monitoring. All of the newly expected changes that may become effective by 2019 will not be encompassed by this revision. Draft requirements are incorporated in this revision until a final version is approved. Changes incorporated after approval of this draft will be followed, and a revised copy will be sent to US EPA Region V for approval. Requirements stated in this chapter are based on information obtained from "Draft Technical Assistance Document for Sampling and Analysis of Ozone Precursors for the Photochemical Assessment Monitoring Stations (PAMS) Program, Revision 2, 2017" and "Technical Assistance Document for the National Air Toxics Trends Stations Program, Revision 3, October 2016".

Sections 3, 4, and 5 of this chapter focus on the air toxics monitoring, listed below. Although metals can fall under air toxics monitoring, this chapter focuses on the gases. Metals monitoring information can be found in chapter 7 of the Indiana Department of Environmental Management (IDEM), Office of Air Quality (OAQ), Air Monitoring Branch (AMB), Quality Assurance Section's (QAS) Quality Assurance Manual, which serves as the QAPP for metals monitoring.

1. Section 3 – PAMS Ozone Precursors Volatile Organic Compounds (VOCs)
2. Section 4 – Toxics (VOCs)
3. Section 5 – Carbonyls

2.0 Siting

An official Quality Assurance Section site evaluation occurs upon setup and then on a three year cycle. Any other time the site is visited, site operators or Quality Assurance Section staff note any changes or activities which could alter data or have some impact on data collection. Any drastic changes, such as probe displacement, may warrant an official Quality Assurance Section re-evaluation. There are several siting criteria to consider when evaluating a site tree growth, construction or development on or near the site, new pollution sources, and any other activities which impact sample collection or result in a change to measured values. The toxics monitoring must follow these requirements:

A. Sample inlet is 2 to 7 meters in height above ground for PAMS (VOCs) and Carbonyls, and 2 to 15 meters in height above ground for Toxics (VOCs).
B. Sampler must be in an area of unobstructed air flow. The distance between an obstruction and the sampler should not be closer than two times the height of the obstruction above the sampler inlet (2X Rule).
C. Location of the site must not be influenced by nearby sources or activities (i.e., exhaust ducts, chimneys).

D. Siting must avoid micro meteorological influences due to nearby hills, bodies of water, valley drainage, airflow patterns, etc.
E. Sample inlet is at least 1 meter vertically or horizontally away from any supporting structure, wall, parapet, or other obstruction.
F. Sample inlet is no closer than 2 meters to any high volume sampler.
G. Horizontal collocation requirement is 0 to 4 meters from each other.
H. Vertical collocation requirement is 3 meters or less.
I. Borosilicate glass, stainless steel, or an equivalent are the acceptable probe materials.
J. The residence time is 20 seconds or less.
K. Tarred or asphalt roofs should be avoided as these materials may emit target analytes during warmer sampling periods.

The spacing from roadways for Toxics (VOCs) must meet the minimum distances as stated in Table 1 and for PAMS (VOCs) and Carbonyls in Table 2 below.

Table 1
Sampling Unit Inlet Required Minimum Distance from Roadways for Toxics (VOCs)

Roadway Average Daily Traffic (ADT), Vehicles per Day	**Minimum Distance to inlet (m)**	
≤15,000	15	
20,000	20	
40,000	40	
60,000	60	
80,000	80	
≥100,000	100	

Table 2
Sampling Unit Inlet Required Minimum Distance from Roadways for PAMS (VOCs) and Carbonyls

Roadway Average Daily Traffic (ADT), Vehicles per Day	**Minimum Distance to inlet (m)**
≤1,000	10
10,000	10
15,000	20
20,000	30
40,000	50
70,000	100
≥110,000	250

3.0 PAMS (VOCs)

Ozone precursor monitoring is required as part of the PAMS program. PAMS measurements are required at each NCore site located in a core based statistical areas with a population of

1,000,000 or more, based upon the latest available census figures. 40 CFR 58, Appendix B requires monitoring to start at NCore sites by June 1, 2019. However as an "early adopter", Indiana will start monitoring on June 1, 2018. Indianapolis, Washington Park – (180970078) is Indiana's NCore site. The specific requirements are addressed in 40 CFR Part 58 Appendix D 5. This section deals with hourly averaged speciated VOCs, and other required monitoring for PAMS. According to the plan, 59 PAMS target compounds will be measured.

3.1 Sample Collection

Ozone precursor compounds are monitored remotely using an automated Perkin Elmer Clarus 500 Gas Chromatograph and Turbo Matrix Thermal Desorber. Ambient air is collected for 40 minutes every hour, every day. The thermal desorber draws in 600mL of ambient air. Moisture is removed by a Nafion dryer and the sample is concentrated in a trap by a Peltier electronic cooler. The trapped compounds are thermally desorbed and carried through a heated transfer line, by a transfer gas (Helium), into the Clarus 500 GC. The GC contains two columns with the compounds separated by volatility. The more volatile, heavier, compounds are separated on a PLOT column and the less volatile, lighter, compounds are separated on the BP-1 column. A flame ionization detector monitors the chromatography for each column. Once the first 40 minute sample has been collected and injected into the GC, the trap automatically cools to -30 C and is ready for the new sample.

3.2 Calibration

To calibrate the instrument, five consecutive aliquots of the PAMS calibration standard, provided by USEPA, are run on the system. The average response factors for propene and benzene on the PLOT and BP-1 columns are calculated using an Excel spreadsheet. The response factors are entered into the calibration method, which is saved on the instrument. One of the five aliquots are reanalyzed to ensure the results are within ±20%.

Continuing calibration checks are run on odd days and must be within ±20% of the true value. If not, then the instrument will be recalibrated as described above. The true value is from the certificate of the standard.

3.3 Sample Analysis

Once the sample has been through the desorber and transferred to the GC, the compounds are separated by volatility. The more volatile compounds are separated on a PLOT column and the less volatile compounds are separated on the BP-1 column. A flame ionization detector monitors the chromatography for each column. Staff review and validate the analysis results on a daily basis using the Perkin Elmer TotalChrom software.

3.4 Quality Control

Calibration checks are run on odd days and as needed after maintenance. Compounds in the standard are required to be within ±20% of the true value. Exceptions to the ±20% limit are allowed for compounds with known poor chromatographic behavior, most notably acetylene and styrene.

A set of four seasonal blanks are run at the beginning and the end of the ozone season. Indiana's ozone season is based on the October 26, 2015, National Ambient Air Quality Standard listed in Table D-3 to Appendix D of 40 CFR Part 58. All of the blanks (oven blank, trap blank, system blank, and zero air blank) must contain less than 0.2 part per billion Carbon (ppbC) of any individual target compound and less than 10.0 ppbC of total organic hydrocarbons.

If a leak in the sample system is suspected or if system contamination is suspected at any time during the season, a zero air blank must be run. If the zero air blank meets the above criteria, no further action needs to be taken. If the zero air blank fails, it is necessary to run the full set of four blanks to locate the contamination. System maintenance must be performed to eliminate the contamination. If data has been affected by possible system contamination, the air toxics lab supervisor will be consulted and a memo will be submitted to the QAS and Ambient Monitoring Section Chiefs.

A method detection limit (MDL) study is performed at the beginning and end of every ozone season, to check precision and accuracy of the instrument. The MDL is determined by running seven consecutive aliquots of the PAMS standard at a concentration which is estimated to be three to five times greater than the instrument signal-to-noise ratio. The data from the seven consecutive aliquots of the PAMS standard runs is entered into an Excel spreadsheet to determine the MDL for all 56 target compounds. The spreadsheet calculates the standard deviation for all seven values for each compound and will also calculate the MDL using the appropriate Student's t-value. If relative standard difference (RSD) of any compound exceeds by more than ±20%, then they should be investigated for proper identification and integration. If the peaks are properly identified and integrated, but the MDL for a compound or multiple compounds is still found to be high (>2.0 ppbC), the affected compounds should be reanalyzed at a higher concentration.

3.4.1 Field

The field work associated with PAMS is generally limited to maintenance and repair. Staff visit the site to check the gasses on a weekly basis. This includes Helium, which is the carrier gas, and Hydrogen and Air, which both act as a fuel for the flame ionization detector.

3.4.2 Laboratory

The instruments are located at the Indianapolis – Washington Park site and remotely accessed in the lab. The laboratory functions for PAMS are limited to remote operation and data validation.

3.4.3 Data

Perkin Elmer TotalChrom software performs the calculation of the ozone concentration. For a fixed sample volume, the concentration is proportional to the area of the peak for the compound multiplied by the corresponding response factor:

$$\text{Conc. ppbC} = \text{response factor x area of the peak}$$

Data validation is performed by importing continuous data from the Perkin Elmer AutoGC system into the LEADS software program. The software is designed to flag the data for calibration standard or various null codes to invalidate the data based on system malfunctions. The LEADS software is also designed to format the data into Air Quality System (AQS) files for data submittal to USEPA's AQS database. Examples of other reasons for invalid data include:

Lack of completeness:

- 25% of data invalid – on a quarterly, monthly, hourly basis

Not meeting criteria for a representative sample:

- Response drift >10% from start to finish of analytical run
- Failure of QC/QA checks
- Failure of QA data validation
- Failure of precision and accuracy goals

3.5 Quality Assurance

3.5.1 Field

Annually, a support contractor will prepare a sample mixture with a known concentration of speciated VOCs in a stainless steel canister or aluminum cylinder. The analysis occurs on the site's auto-GC. The concentrations of the target compounds will be unknown to the monitoring site. The measured results will be reported to the support contractor. The contractor will compile the reported concentrations for evaluation against the nominal spiked value and against the overall PAMS required network average (with outliers removed). The limit is ±25% of the target value. Failing this proficiency test requires corrective action.

3.5.2 Laboratory

The instruments are located at the Indianapolis – Washington Park site and remotely accessed in the lab. The laboratory functions for PAMS are limited to remote operation and data validation.

3.5.3 Data

To be determined.

4.0 Toxics (VOCs)

Indiana uses a modification of the TO-15 method to collect toxics VOC data. 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 a stainless steel canisters in the field, using either the Meriter MCS-1-R or the ATEC 2200 Air Toxic Samplers. Samples are analyzed using an Agilent GC/MS to determine the concentration of the compounds found in the sample. Samples are collected for 24 hours on a one-in-six day sampling schedule. Indiana currently operates 10 sites. The locations are Clarksville, IN; Gary Iitri, Whiting Center St., East Chicago Marina, Hammond 141st St., Indianapolis. Washington Park, Indianapolis. I-70 E., Ogden Dunes, Evansville U of E, and

Terre Haute Fort Harrison Road. Listed below are the 62 different VOCs and an aggregate that are being analyzed and reported.
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

4.1 Sample Collection

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 each monitoring site. Each sampler is certified prior to being put into the field. Certification requires a zero air check result of less than 10 ppbC.
- 6L Summa canisters: spherical, stainless steel canisters, which have had their inner surface electro polished to reduce chemical reactivity.

Listed below are the steps for the air canister sampling procedure. Specific details are also listed in the SOP, Toxic Sampler Setup and Pickup LabCommerce – Meriter MCS-1-R, available from the IDEM OAQ AMB.

1. Obtain a 6L SUMMA canister certified to be free of contamination within the last 90 days and has been evacuated to -28 to -30 inches of mercury. The sample canister must collect the sample, within 90 days of being cleaned and evacuated.
2. Verify that the timer, pumps, and solenoid valve are operating properly.
3. Verify that the flow controller is correctly calibrated and set to 7.8 cc/min., for a 24-hour sample time.
4. Verify that the date is correct.
5. Verify the timer is within 5 minutes of the local standard time; and is correctly set for the desired sample period.
6. Verify the solenoid valve is closed.
7. Activate the Meriter sampler and make sure any water is purged.
8. Connect the certified SUMMA canister to the solenoid valve.
9. Open the canister valve and record its initial pressure reading on the absolute gauge.
10. Set the clock(s) for the desired sample period.
11. After the sample period, record the final pressure reading in psig and close the canister valve.

12. Fill out the canister's identification tag, as necessary. Return canister to the laboratory. The canister must be analyzed within 30 days from the time the sample was collected.
13. Complete records of the sampling should be entered into a bound notebook or an electronic log located at the site, including meteorological conditions or unusual events that may affect sample composition.

In some instances 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. Listed below are the steps for performing a grab sample. Specific details are listed in the SOP, Collection of a Canister Grab Sample for Air Toxics Monitoring, available from the IDEM OAQ AMB.

1. Obtain a 6L SUMMA canister, with a plug, certified to be free of contamination within the last 90 days. The canister must be evacuated to -28 to -30 inches of mercury.
2. Remove canister plug and attach the sample probe to the canister inlet. Tighten the nut to finger-tight, then turn an additional 1/4 turn with a wrench.
3. Verify that the flow metering valve on the sample probe is in the off position.
4. Open the canister valve. If you hear air entering the canister at this time, close the canister valve. Recheck the flow metering valve and the canister's inlet connection to ensure that both are closed or turned off.
5. Open the flow metering valve and set the flow directly between 0 and 1 on the meter scale. This corresponds to a sample flow of 150 ml/minute.
6. Monitor the flow metering valve so that it's always between 0 and 1. The flow rate will continue to drop until the canister has reached atmospheric pressure. At this point, flow can no longer be adjusted.
7. Close the canister valve and the flow metering valve.
8. Remove the probe from the canister.
9. To ensure that the canister has reached atmospheric pressure, open the canister valve briefly to fill any residual vacuum.
10. Close the canister valve and replace the plug on the canister.
11. Fill out all relevant information on the sample tag for proper recordkeeping. Include all ambient weather conditions in the comments section.
12. Submit the sample to the laboratory for analysis.

4.2 Sample Analysis

The Air Toxics Monitoring Laboratory uses USEPA Method TO-12 for the determination of total non-methane organic carbon (TNMOC) and USEPA Method TO-15 for the determination of toxic organic compounds in ambient air samples collected by the Indiana Air Toxics Monitoring Network, and in complaint air samples collected throughout the state of Indiana. These air samples are collected in 6 liter stainless steel Summa canisters, which are cleaned, certified, and evacuated prior to use. This cleaning and certification is performed in accordance with our standard operating procedure Canister Cleaning and Certification. The samples are collected in accordance with either of two standard operating procedures: Collection of Canister

Grab Sample for Toxics Monitoring or Toxic Sampler Setup and Pickup Lab Commerce – Meriter MCS-1-R.

Samples are analyzed for TNMOC concentration on a Thermo Scientific Trace GC 1310 with a flame ionization detector. TNMOC analysis is performed to determine the optimal sample size (dilution factor) for analysis on the GC/MS. Chromeleon 7 software is used for data analysis. The procedure for total non-methane organic carbon analysis is described in the Determination of Total Non-Methane Organic Compounds (TNMOC) Using Thermo Fisher Trace 1300 GC/FID System U. S. EPA Method TO-12 SOP.

The Agilent 7890B GC/ 5977B MS analyzes ambient air samples for 62 hazardous air pollutants using USEPA Method TO-15 Determination Of Volatile Organic Compounds (VOCs) In Air Collected In Specially-Prepared Canisters And Analyzed By Gas Chromatography/Mass Spectrometry (GC/MS). The GC/MS is interfaced with an Entech 7200 preconentrator and 7016 D autosampler. Both systems are programmed to operate harmoniously. The Entech 7200 is designed to concentrate the VOCs which are at trace levels in ambient air. The Entech 7016D is a 16 position canister sampler interfaced with the GC/MS. The Summa canisters are attached to the autosampler from lowest to highest TNOMC concentration. The lowest concentration would go in position 3 and the highest in position 16. The autosampler pulls 500mL of each sample into the GC/MS for analysis.

The procedure for Toxics VOC determination is described in the Agilent 7890B-5977B Gas Chromatograph-Mass Spectrometer with Autosampler SOP.

4.3 Quality Control

4.3.1 Field

When site operators are at the site, they will perform the following checks:

1. Sampler flow rate is 7.8 cc/min.
2. Purge any moisture from the sampler.
3. Confirm the sampler date is correct and the time is within ±5 minutes of the local standard time.
4. Confirm the canister being set up has a starting pressure of -28 to -30 mmHg.
5. Confirm the canister being set up has been cleaned/evacuated within 90 days up to the time it samples.
6. Once the sample is collected, the site operator will make sure the sample ran from 23 to 25 hours and the final canister pressure is 1 to 15 mmHg. Otherwise the sample is invalid.
7. For chain of custody, each canister will have 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 SUMMA canister chain-of-custody tag is below.

SUMMA Canister Chain-of-Custody Tag

IDEM/OAQ/AIR TOXIC MONITORING

Site_____ Sample Date_____
Canister #_____ Beginning Vacuum_____
Dilution Factor_____ Ending Field Pressure_____
Elapsed Sample Time_____ Final Lab Pressure_____
Beginning Flow_____ Final Flow_____
Set-up Staff Initials_____ Pick-up Staff Initials_____
Lab Staff Initials_____
Clean & Evacuated-Date_____ Initials_____

Comments_____

Below in Table 3 is a summary of the quality control (QC) checks and how the QC check affects the data.

Table 3
Quality Control Checks

QC Check	Data Status
Sampler Flow Rate ≥10.1% from transfer standard	Data is suspect back to last passing flow check
Canister cleaned more than 90 days prior to sample date	Data is invalid
Sample Time	If not 23 to 25 hours, data is invalid
Date	If just the date is incorrect but time is accurate to within 60 minutes, the sample can be reported to AQS with the corrected date. The data is valid.
Time	If the time is off between 5 minutes and 60 minutes, then adjust the time and the data is valid. If time is incorrect by more than 60 minutes, the sample is invalid.
Missing information on canister tag: Site, Flows, Sample Time All other information	Data is invalid unless information can be retrieved from the site log book or computer log entry Data is valid

4.3.2 Laboratory – Toxics Section

The Thermo GC/FID system is calibrated with a propane standard. The standard is run three times for instrument calibration. The runs are averaged and must be ±10% of 2996 ppbC. The propane standard must also be ±10% of 2996 ppbC in order for the instrument to pass the daily calibration. If instrument fails 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 P4700 Precision State Dilution System. The diluted standard is good for 30 days. A calibration curve, which consists of 7 levels ranging from 0.1 to 10 part per billion volume (ppbv), is generated, if 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 ±30% of 2.5 ppbv.

There are three QC measurements performed with each batch of canisters. Canisters 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 ±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 ±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.

An MDL study is done at least once per quarter. 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.

4.3.3 Laboratory – Ambient Monitoring Section

A sampler assembly cleanliness check is required every 6 months. The entire sampler assembly will be flushed with hot, hydrocarbon free zero-grade air for two hours at approximately 40-50 cc/min. A certified canister will then be attached and the sampler will be allowed to sample the zero–grade air until the canister is pressurized to approximately 10 psig. The canister will then be analyzed by the Air Toxics Section according to the procedure found in Section 4.2 using a GC/FID system. Cleanliness is defined as <10 ppbC TNMOC.

If a sampler fails the certification, then the cleaning process is continued until it passes the certification.

4.3.4 Data

The OAQ Toxics Data Capture (OAQTDC) Database is utilized as a sample tracking logbook for chain-of-custody. The following information is entered into document tracking of the SUMMA canister transport and subsequent VOC analysis: site information, canister check-in and cleaning dates, and TNMOC and VOC analysis data. The VOC analysis data is transferred from the GC/MS computer to OAMTDC via a flash drive. AQS obtains the VOC analysis data from

OAQTDC. QC data is recorded on the Agilent computer. The folder is C:\Air Toxics PDF Files\'Year'.

4.4 Quality Assurance

4.4.1 Field

A zero check is performed annually at each site. The zero air check is performed by either hooking up a clean air cylinder or a hydrocarbon trap to the system, which is collected in a canister. The zero air check is performed over a 24 hour period, usually from mid-day the first day into the next day. If possible, the zero air is introduced into the sample inlet located outside. Using the inlet, all of the line and the equipment is subject to the zero air check. Once the zero air check is completed, the canister is sent to the toxics laboratory for analysis. The limit should be approximately 10 ppbC TNMOC. Values much greater than this, such as >20 ppbC, will warrant some action on the site operator, such as sample line replacement or cleaning of the sampler. An additional QA zero check may be performed to confirm results or as a follow-up to any action taken by the site operator.

4.4.2 Laboratory

The rotameters used to measure the sampler's canister flow are certified annual by the IDEM, OAQ, Quality Assurance Certification Facility.

4.4.3 Data

QC checked data ready to be entered into AQS is submitted to the Quality Assurance Section for review. Screened data consists of calibration data on the GC, canister analysis data, and field data. Listed below in Table 4 are the types of data and specifications that must be met.

Table 4
Data Specifications

Laboratory Data Review	Field Data Review
BFB criteria (see verify file for PASS value)	Pressures (-28 to -30 starting vacuum; +1 to 15 ending)
TO-15 criteria (90% must be ±30% of 2.5, which is 1.75 to 3.25 so no more than 6) (M+P-xylenes max value of 6.50)	Elapsed time (1380 to 1500 mins)
Blank criteria (if 6 or more > 0.05, then fail)	Canister used within 90 days of cleaning/evacuation
Lab standard cylinder ≤ 30 days old	Chain of custody (all required blanks filled)
Samples analyzed within 30 days of sample collection	

4.5 Canister Cleaning

Once staff have verified and confirmed all analyses on a canister are complete, it will be cleaned. Canister cleaning and certification are critical to ensure the highest possible quality of data from canister sampling and analysis. Each canister goes through 20 cleaning cycles, which consist of evacuating 3 minutes and pressurization for 8 minutes in an oven. The procedure for cleaning is further described in the SOP, Canister Cleaning and Certification.

A clean canister is certified for use up to 90 days. Staff will re-clean any canister that is not used within 60 days.

4.5.1 Quality Control

A maximum of eight canisters can be cleaned at one time. After the cleaning procedure is complete, at least one of the eight canisters must be tested on the Thermo Scientific Trace GC 1310 for TNMOC. The TNMOC concentration must be less than 5.0 ppb. If the canister fails, then all eight of the canisters are re-cleaned and tested again.

Staff will re-clean any canister that has exceeded 60 days on the shelf.

5.0 Carbonyls

Carbonyl monitoring is required as one of the components of the PAMS monitoring program. Carbonyl data are collected using Method TO-11A of the USEPA's Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air. Currently, Indiana uses the ATEC 2200 2C for one-in-six day sampling at the Indianapolis – Washington Park site (AQS# 180970078). On June 1, 2018 Indiana increases the monitoring frequency to three 8-hour samples on a one-in-three day basis as part of the early adoption of the PAMS program. Samples are collected by drawing a known volume of air through a cartridge filled with silica gel coated with activated 2,4-Dinitrophenylhydrazine (DNPH). These samples are analyzed using HPLC with a UV absorption detector.

5.1 Sample Collection

Ozone interferes with carbonyl sampling, so provisions must be made to remove ozone from the sample path. Either a denuder or cartridge ozone scrubber must be a component of the sampling apparatus. If used, ozone scrubber cartridges need to be replaced every three weeks. Sampling of carbonyl compounds is carried out by pulling ambient air through Waters Sep-Pak DNPH-Silica cartridges using an ATEC model 2200 toxic air sampler. The pre-coated DNPH cartridges are purchased from Waters, Inc. Waters Sep-Pak DNPH-Silica cartridges consist of DNPH-coated silica packed in Waters Sep-pak plus cartridges equipped with end caps and plugs. The caps and plugs must be kept on the DNPH cartridges and the cartridges stored refrigerated until they are installed in the sampler. Also, cartridges must remain sealed in their original packaging and protected from light (foil pouch or similar opaque container) until they are installed for sample collection or prepared as QC samples. Light may degrade the DNPH derivatives. The physical/chemical properties of the cartridges are as follows:

- Hold-up volume 0.7 ml
- Particle size 55 to 105 µm
- Collection efficiency >95% for sampling rates up to 2 l/min
- Capacity Approximately 75 µg formaldehyde
- Quantity of DNPH Silica 0.35 g/cartridge (1.0 mg DNPH)
- Operating temperature l0-100 °C
- Dimensions 4.3 cm total length; 1.0 cm I.D.; 0.9 cm bed length

The sampler is capable of collecting duplicate carbonyl samples. Prior to sample collection, the sampling unit inlet line is purged with approximately 10 air changes of ambient air.

All exposed cartridges should be collected as soon as possible after the conclusion of sampling in order to minimize degradation of the carbonyl-DNPH derivatives. Exposed cartridges are collected within 72 hours of the end of sample collection. The person who handles the cartridges must wear latex gloves or similar. The cartridges must be extracted within 14 days of the sample date. The exposed sample must be refrigerated after removal from the sampler until time of analysis. It is important that exposed samples are kept at 4° C or colder after collection and during shipping. A certified thermometer or similar temperature device, used during storage, confirms the temperature requirements are met. Perform analysis as soon as possible after the lab receives the cartridges and no later than 30 days after the sample has been extracted. Performance and logging of lab calibrations, and the analysis of blanks and spiked control samples will be done by the contract laboratory.

Listed below are general steps for the carbonyl monitoring and handling of DNPH cartridges. Specific details are listed in the SOP, Carbonyl Cartridge Pickup and Setup, available from the IDEM OAQ AMB.

For set-up:
1. Wearing latex gloves, take the cartridge from the pouch.
2. Remove and save the end caps and plugs.
3. Connect the cartridge to the sampler with flexible plastic tubing.
4. Perform a leak check.
5. Schedule the sample date and time. Also confirm the current sampler date is correct and the time is within ±5 minutes of the actual local standard time.
6. Fill out an Eastern Research Group (ERG) Carbonyl Compounds Data Form.
7. Record information in logbook and/or if available an electronic log.

For pick-up:
1. Wearing latex gloves, remove the cartridge from sampler.
2. Place the plugs on the ends of the cartridge.
3. Store the cartridge in the user pouch.
4. Print a sample label from the carbonyl sampler and affix the label onto pouch.
5. Place the cartridge in a refrigerated cooler.
6. Ensure the cartridge is kept in the cooler, up to and including shipping to the contract

laboratory for analysis.

7. Finish filling out the ERG Carbonyl Compounds Data Sheet upon completion of sample analysis.
8. Record information in logbook and/or if available an electronic log.

Additional Info:

Field blanks: Once a month, attach one of the cartridges onto the sequential sampler without flow. The field blank is setup, collected, and analyzed the same way as a sample. Follow USEPA's monitoring schedule, if provided.

Duplicates: A number of cartridges, equal to 10% of the total number of samples, should be run as duplicate samples. IDEM runs a duplicate samples approximately every fifth sample day. The duplicates attached to an empty port on the same sampler as the normal sample and programed to run at the same time as the sample. The duplicate sample is marked appropriately for sample analysis.

5.2 Sample Analysis

Upon completion of sampling, the cartridges are sent to a suitable contract laboratory for analysis. The laboratory performs solvent extractions of the cartridges. The resulting extract is analyzed for various carbonyl DNPH derivatives using high performance liquid chromatography (HPLC). A cartridge's refrigerated shelf life is six months. After six months, background traces begin to increase. Therefore, any cartridges stored longer than six months are invalid.

5.3 Quality Control

5.3.1 Field

During routine sample pickup or setup, a leak check is performed. Confirm the sample date is correct and the time is within ±5 minutes of the actual local standard time. A flow calibration is performed annually. The standard flow limit is ±10.0%. Table 5 summarizes the QC checks and results' effects on the data.

Table 5
Quality Control Checks

QC Check	Data Status
Cartridge Shelf Life – manufacturer expiration date	If past the date, the cartridge/sample is void/invalid.
Leak Check – pass/fail	Failure, invalidates data back to the last passing leak check.
Date – incorrect	If the time is accurate to within 60 minutes, the sample can be reported to AQS with the correct date of sampling. The data is valid.
Time – > 5 min < 60 min Time – > 60 min	Adjust and data is valid. The sample is invalid.
Flow – more than ±10.0% from the standard flow device	The data is invalid back to the last accurate flow check, unless there is proof, such as a failed leak check, to determine when the sampler's flow went out of specifications.
Sample Temperature - ≥ 4° C prior to sampling, from end of sampling through shipment, and up to analysis.	Data will be invalid anytime the sample goes above this limit, once it has been conditioned after sampling.

The site operator replaces the sample line on a 1 to 2 year cycle, depending on how dirty the line becomes or failing zero air checks performed by the QAS.

5.3.2 Laboratory

The contract laboratory does the analysis. QC checks for the laboratory consist of data being obtained from field blanks, as well as any internal checks performed by ERG.

5.3.3 Data

Once analysis is completed by ERG, the data is uploaded into AQS and also sent to the Ambient Monitoring Section. The data is reviewed for completeness, accuracy, and for potential outliers. Data from the field blank and duplicate samples are screened to determine whether the results warrant additional analysis of the actual reported concentrations or any sampler maintenance is required.

5.4 Quality Assurance

5.4.1 Field

A quarterly flow audit is performed. The standard flow limit is ±10.0%. A leak check is also performed. The date is confirmed to be correct. The time is confirmed to within ±5 minutes of local standard time. See Table 5 above for status of data based on these checks.

An annual zero air check is performed on the sampler. Either a clean air cylinder is connected or a cartridge is placed on the sampler inlet, and the sampler is programmed to run for a 24 hour

period. The zero air check carbonyl cartridge is then sent to the contract laboratory, and is treated as a normal sample. Each target carbonyl should be ≤ 0.2 ppb above the reference sample. The test results assist the site operator concerning the presence of any sample line contamination. Test results provide useful information in regards to how the sample is handled and analyzed.

5.4.2 Laboratory

Annually, a support contractor prepares a DNPH cartridge sample spiked with known amounts of target compounds. The contract laboratory extracts and analyzes the cartridge per their standard procedures. The concentrations of the target compounds are blind to the laboratory. The monitoring agency then reports the measured results to the support contractor. The support contractor compiles the reported concentrations, and evaluates them against the nominal spiked values and against the overall PAMS required network average (with outliers removed). The limit is ±25% of the target value. Corrective action is required when the proficiency test fails.

5.4.3 Data

Once the Ambient Monitoring Section receives the data and completes their QC checks, the data is forwarded to the QAS. The QAS performs similar checks on the data stated in Section 5.3.3 of this chapter. An example of this form is below.

Form 1
Toxics - Carbonyl Data Check Form

Site:	Indianapolis Washington Park - 180970078	Month/Year	April 2017
Parameter:	Toxics – Carbonyl		

		S	U	NA	Notes
1.	Cartridge extracted within 14 days of sample date	x			
2.	Cartridge analyzed within 30 days of sample date	x			
3.	Sample time 23 to 25 hours	x			
4.	Blank Cartridge values show: Acetaldehyde < 0.10 µg Formaldehyde < 0.15 µg Acetone < 0.30 µg Other Compounds < 0.10 µg	x			
5.	Duplicate Cartridge concentration within 20% of reported	x			
6.	Total collection volume 1.0 to 2.2 m^3 at standard conditions				Sampler in field set to run at lower flow rate resulting in lower volume– will confirm this is accurate

Additional Comments:
Data Check Completed Date: 6/30/17
Data Check Performed By: JWW