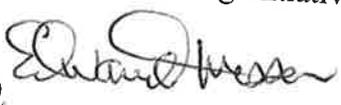
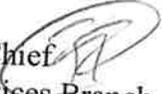




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SECTION
ENVIRONMENTAL
PROTECTION AGENCY

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY- Region III
OFFICE OF ANALYTICAL SERVICES AND QUALITY ASSURANCE
Environmental Sciences Center
701 Mapes Road
Fort Meade, Maryland 20755-5350

DATE: July 09, 2012
SUBJECT: Review of the QAPP for Natural Gas Activities Air Monitoring Initiative
FROM: Edward Messer, Environmental Scientist
OASQA, Technical Services Branch (3EA22) 
THUR: Fred Foreman, Branch Chief 
OASQA, Technical Services Branch (3EA22)
TO: Andrew Hass, Project Manager
Office of Air Monitoring and Analysis (3AP40)

As requested, I have reviewed the Quality Assurance Project Plan (QAPP) for the Natural Gas Activities Air Monitoring Initiative (NGAAMI) study in Pennsylvania.¹ This detailed QAPP was prepared by the EPA Region 3 Office of Air Monitoring & Analysis and dated June, 2012.

This detailed QAPP, including the supporting appendices and documents, encompasses all of the necessary quality assurance elements for a successful project. Therefore, I am recommending the approval of this QAPP.

If you have any questions pertaining to this QAPP review, please don't hesitate to contact me at 410-305-2744

¹ Reviewed for compliance with EPA Requirements for Quality Assurance Project Plans, EPA QA/R5, March 2001





**Quality Assurance Project Plan
EPA Region 3
Natural Gas Activities Air Monitoring
Initiative (NGAAMI)**

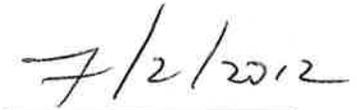
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June, 2012**

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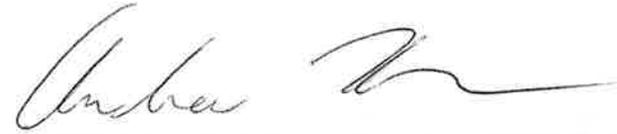
1.0 Signature Page



EPA Project Lead



Date



Air Division Quality Assurance Reviewer



Date

Acronyms and Abbreviations

ANSI	American National Standards Institute
APD	Region 3 Air Protection Division
AQS	Air Quality System
ASTM	American Society for Testing and Materials
ATSDR	Agency for Toxic Substances and Disease Registry
CAA	Clean Air Act
CFR	Code of Federal Regulations
CoC	chain of custody
CV	coefficient of variance
DAS	data acquisition system
DQA	data quality assessment
DQOs	data quality objectives
ECHD	electron capture – hall detector
EDD	electronic data deliverable
EDO	environmental data operation
EPA	Environmental Protection Agency
ERG	Eastern Research Group
ERT	Environmental Response Team
GC/MS	gas chromatography/mass spectrometry
GIS	geographical information systems
GPS	geographic positioning system
HAPs	hazardous air pollutants
HASP	health and safety plan
HPLC	high pressure liquid chromatography
ISO	International Standards Organization
IUPAC	International Union of Pure and Applied Chemists
LAN	local area network
LBC	Laboratory Branch Chief
LIMS	Laboratory Information Management System
MDL	minimum detection limit
MQOs	measurement quality objectives
NATA	National Air Toxics Assessment
NATTS	National Air Toxics Trends Stations
NGAAMI	Natural Gas Activities Air Monitoring Initiative
NIOSH	National Institute of Occupational Safety and Health
NIST	National Institute of Standards and Technology
NWS	National Weather Service
OAQPS	Office of Air Quality Planning and Standards
OASQA	Office of Analytical Services and Quality Assurance
OSHA	Occupational Safety and Health Administration
PC	personal computer
PD	percent difference

Acronyms and Abbreviations

PM _{2.5}	particulate matter – 2.5 microns
PT	proficiency testing
QA/QC	quality assurance/quality control
QA	quality assurance
QAO	Quality Assurance Officer
QAFR	quality assurance final report
QAM	quality assurance manager
QAPP	quality assurance project plan
QC	quality control
S/L	State/Local
SOP	standard operating procedure
TAD	technical assistance document
TO	toxic organic
TSA	technical system audit
UATMP	Urban Air Toxics Monitoring Program
VOC	volatile organic compound

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3.0 Project Management

3.1 Roles and Responsibilities

EPA is responsible for developing and implementing the ambient air monitoring initiative in targeted natural gas extraction host areas of Pennsylvania and/or West Virginia. EPA will be responsible for implementing the deployment and operation of monitors and the laboratory analysis of samples for this air study. It is the responsibility of Region 3 Air Protection Division (APD) to assess the overall quality of the data and take corrective action when appropriate. The responsibilities of each organization are addressed here.

3.1.1 Region 3 Air Protection Division (APD)

EPA will be responsible for:

- Coordinating “cross-agency” to implement the monitoring plan
- Examining available information from external and internal sources to create the list of sites that require monitoring;
- Ensuring that the methods and procedures used in making air pollution measurements are adequate to meet the study’s objectives and that the resulting data are of satisfactory quality;
- Communicating technical information to the necessary participants;
- Providing up-front support (i.e., equipment acquisition and procure laboratory support);
- Developing the monitoring plan, HASP, QAPP and SOPs
- Providing analysis and interpretation of the results and communicating those results to the EPA Administrator and the public at large.
- Siting the monitoring stations;
- Receiving and inspecting unexposed samples to make sure they are ready for sampling;
- Operating the monitoring samplers according to the schedule stated the NGAAMI Monitoring Plan associated with this QAPP (see Section 3.2);
- Shipping the exposed samples to the laboratory performing the analysis;
- Participating in the screening and analysis of the data, and;
- Following the field approved field SOPs when operating monitors.

3.1.2 Region 3 Office of Analytical Services and Quality Assurance (OASQA) Laboratory

The air monitoring initiative requires that air toxic samples be analyzed in accordance to strict QA/QC requirements as defined in Section 6.9. The OASQA Laboratory will be analyzing samples for this initiative and will meet the requirements as stated in Section 6.8. The ability to meet the Measurement Quality Objectives (MQOs) will be demonstrated by analyzing Proficiency Testing (PT) samples and having acceptable results.

Here is a partial list of the laboratory duties:

- Sending sample containers/filters to the field operators, following strict requirements on shipping and handling according to their SOPs;
- Receiving samples from the field;
- Analyzing the samples relative to their QA/QC procedures and SOPs;
- Troubleshooting and repairing any laboratory instruments that malfunction;
- Assessing data, including data review, prior to delivery to APD; and,
- Reporting all data to APD as required.

3.2 Sampling Frequency, Duration, and Quantity

Ambient air sampling will be conducted on a staggered schedule, so details of sampling will not be easily patterned. Start dates will vary by site as a function of monitoring setup completion and calibration. Once monitoring operations have commenced, the base (i.e., minimum amount) sampling will consist of a minimum 30 valid samples from each operating monitor. There may be cases in which the amount of samples collected is deemed to be insufficient (e.g., invalidated sample(s), insufficiently representative data, etc.) and thus monitoring will continue until the minimum amount of samples mentioned above is collected. A companion document to this QAPP, the "NGAAMI Monitoring Plan" (hereby known as The Monitoring Plan) has additional information related to this section and can be found in Appendix A.

4.0 Problem Definition/Background

4.1 Problem Statement and Background

4.1.1 Introduction

EPA will monitor air quality at a number of sites as part of an initiative to understand whether outdoor toxic air pollution poses health risks to residents living in close proximity to the natural gas operations (including drilling, completion, production, processing, and distribution). This quality assurance plan addresses one aspect of the initiative; ambient air monitoring. This ambient air monitoring initiative cannot assess all aspects of natural gas activities, and, instead, will focus directly on specific situations which may pose the potential for health risks from longer durations of exposure or higher concentrations of airborne contaminants, such as near hydraulic fracturing flow back waste impoundments and compressor stations.

EPA determined priority areas for an initial round of monitoring. EPA selected the areas based on extent of extraction operations, specific extraction operations currently underway, testimony from local residents, and consultation with state and local air regulatory agencies.

4.1.2 Project Objectives

This ambient air monitoring initiative will yield data of sufficient quality to allow a preliminary assessment for any potential air toxics impacts specific to the site at which the monitoring occurred. This preliminary assessment will be used to determine subsequent steps that may include:

1. Terminating monitoring where assessments indicate low impacts;
2. Pursuing long-term emission and risk reduction activities (such as enforcement or other actions) where monitoring data show potentially unacceptable impacts; and
3. Considering longer-term monitoring where initial data are inconclusive and additional information is needed to better characterize the potential for impacts.

4.2 Project Monitoring Design

4.2.1 Meteorological Measurements

Site specific meteorological parameters that will be measured consist of wind speed and direction data. The type of sensor provided will be of sufficient quality for its intended use. EPA is purchasing meteorological equipment and data acquisition systems that will be able to collect both scalar and vector data. Meteorological information is also gathered from the National Weather Service (NWS) stations across the state. Parameters include: temperature,

relative humidity, barometric pressure, rainfall, wind speed, wind direction, cloud type/layers, cloud cover and visibility range.

4.2.2 Hazardous Air Pollutants

There are currently 187 hazardous air pollutants (HAPs) and pollutant classes that are regulated under the Clean Air Act (CAA). These pollutants, often called air toxics, have been associated with a wide variety of adverse health effects, including cancer, neurological effects, reproductive and developmental effects. Air toxics are emitted from multiple sources, including major stationary, area, and mobile sources, resulting in population exposure to these air toxics as they occur in the environment. While in some cases the public may be exposed to an individual HAP, people more typically experience exposures to multiple HAPs from many sources.

4.2.3 PM_{2.5}

The characteristics, sources, and potential health effects of "fine" particles (smaller than 2.5 micrometers in diameter) are very different. Fine particles are generally emitted from activities such as industrial and residential combustion and from vehicle exhaust. Fine particles are also formed in the atmosphere from gases such as sulfur dioxide, nitrogen oxides, and volatile organic compounds that are emitted from combustion activities and then become particles as a result of chemical transformations in the air. These health effects include premature death and increased hospital admissions and emergency room visits (primarily among the elderly and individuals with cardiopulmonary disease); increased respiratory symptoms and disease (among children and individuals with cardiopulmonary disease such as asthma); decreased lung function (particularly in children and individuals with asthma); and alterations in lung tissue and structure and in respiratory tract defense mechanisms.

Table 4-1 lists the "classes" of compounds that will be measured for this initiative. For more information on the instruments that will be used to collect these samples, please see The Monitoring Plan in Appendix A.

Current information indicates that specific pollutants in these groups may be present due to the on-going natural gas extraction processes. While we are focusing our effort on monitoring for specific pollutants, the measurement methods used for certain classes of pollutants will detect other chemicals as well. For instance, under the class of compounds known as "VOCs," benzene is a pollutant that may be present in the areas monitored. When the laboratory performs the analysis for benzene, there are a number of other compounds that can be analyzed, such as 1, 3 butadiene. This situation exists for the other classes of compounds as well. We will report concentrations for all chemicals that the laboratory is confident in its ability to analyze.

The Monitoring Plan has the full list of compounds that will be evaluated by the methods chosen for this project. Please note that a more detailed list of compounds to be analyzed is listed in Table 6-2.

Table 4-1 List of Methods and Target Analytes

Target Analytes	Method	Sampling Media
VOCs	EPA TO-15	Air (via canister)
PM _{2.5}	Gravimetric	Filter
Meteorology	Sonic Anemometry	Wind speed and direction scalar and vector data

4.3 Location of Interest - NGAAMI Initiative



Figure 4-1 Map of monitor location

5.0 Project Task/Description

The measurement goal of this natural gas ambient air monitoring initiative is to estimate the concentration, in standard units of micrograms per cubic meter ($\mu\text{g}/\text{m}^3$) and/or parts per billion/volume (ppbv) of specific classes of chemical compounds (particulates and gases) in outdoor ambient air at specific site locations. This is accomplished by several separate collection media and analytical techniques. Activities for this project are divided into two separate, yet linked activities: field monitoring and laboratory analysis. An overview of the initiative follows.

5.1 Overview of Field Activities

Ambient air sampling devices will be placed at monitoring locations on or near properties that are adjacent to natural gas activities. Table 4-1 lists the methods and sampling media used for this project. The Monitoring Plan has the instrument specifications necessary for this project. Appendix A of the Monitoring Plan lists the site locations and the pollutants to be monitored. The sampling will occur for 24 hours +/- 1 hour to account for sample collection and set-up.

All of the equipment and instruments operated in the field will be supplied by vendors that specialize in manufacturing these sample collection devices.

Training – EPA will be utilizing its own staff to conduct the ambient air sampling for this initiative. EPA personnel expected to operate field sampling will be provided adequate training to ensure proper operation of equipment during this initiative. Prior to the commencement of sampling, EPA will support one or more monitoring-focused meetings to provide opportunities for staff to ask clarifying questions and to ensure a common understanding of procedural requirements and expectations.

Standard Operating Procedures (SOPs) - EPA will provide field SOPs for each of the methods being deployed in this air monitoring initiative, complimenting the existing laboratory SOPs that have been developed by appropriate laboratory staff. Specific details will be incorporated into field SOPs once the exact type(s) of samplers and equipment being procured is identified through the contractual process. At that time, field SOPs will be made available to EPA personnel.

5.2 Overview of Laboratory Activities

Laboratory activities for this initiative include preparing and shipping the sample canisters, receiving samples, and sample analyses. Some activities associated with these phases include,

Preparing and Shipping the Sample Canisters

- Canisters are pre-cleaned and checked at the laboratory prior to shipment to the field;
- Receiving filters, canisters or cartridges from the field personnel;
- Checking sample integrity;
- Conditioning filters, storing canisters and cartridges;
- Storing samples prior to field use;
- Packaging filters, canisters and cartridges for field use;
- Associated QA/QC activities;
- Maintaining analytical equipment at specified environmental conditions; and;
- Equipment maintenance and calibrations.

Sample Receiving

- Pre-ship check for logistics
- Receiving filters, canisters and cartridges from the field and logging into database;
- Storing filters, canisters and cartridges; and,
- Associated QA/QC activities.

Sample Analyses

- Checking filter, cartridge and canister integrity ;
- Extraction of VOCs from canisters;
- Weighing of Teflon, quartz and glass fiber filters;
- Storing filters/archiving;
- Cleaning canisters; and,
- Associated QA/QC activities and data reporting.

The details for these activities are included in various sections of this document, the applicable laboratory SOPs, and References 1- 3.

References:

1. Compendium Method for the Determination of Toxic Organic Compounds in Air, United States Environmental Protection Agency, Section TO-15, January 1999
<http://www.epa.gov/ttn/amtic/airtox.html>

2. Compendium Method for the Determination of Toxic Organic Compounds in Air, United States Environmental Protection Agency, Section TO-11A, January 1999
<http://www.epa.gov/ttn/amtic/airtox.html>
3. Quality Assurance Handbook for Air Pollution Measurement Systems – Volume IV: Meteorological Measurements Version 2.0, 2008,
<http://www.epa.gov/ttn/amtic/met.html>

6.0 Data Quality Objectives

The primary objective of the project is to collect sufficient representative empirical data on target compounds in ambient air from select natural gas activity host areas of Pennsylvania and/or West Virginia to allow regulators and health assessors to make informed decisions, conclusions and recommendations. This monitoring information will be used to assist in identifying locations hosting natural gas activities (including drilling, completion, extraction, processing, and distribution) where:

1. Actions to reduce ambient concentrations and /or exposures to ambient concentrations are needed;
2. Measured ambient concentrations do not indicate impacts of potential concern and no further monitoring is needed;
3. Additional information, including additional monitoring, is needed to inform regulators and health assessors or for other longer-term objectives related to more fully characterizing ambient concentrations and potential source influences in the area.

EPA is responsible for developing and implementing this natural gas ambient air monitoring initiative. To do this work, EPA will collect ambient air data at the identified areas. This effort will also provide information to residents that live nearby these operations with regard to potential air contaminants concerns from the nearby processes.

The DQO process described in EPA's QA/G-4 document provides a general framework for ensuring that the data collected by EPA or any environmental data operation (EDO) meets the needs of the intended decision makers and data users. The process establishes the link between the specific end use(s) of the data with the data collection process and the data quality (and quantity) needed to meet a project's goals. The following sections provide the required information for the DQO process.

6.1 The DQO Process

The DQO process is a seven-step process based on the scientific method to ensure that the data collected by EPA meet the needs of its data users and decision makers in terms of the information to be collected and, in particular, the desired quality and quantity of data. It also provides a framework for checking and evaluating the project goals to make sure they are feasible and that the data are collected efficiently. The seven steps are usually labeled as:

- State the Problem
- Identify the Decision

- Identify the Inputs to the Decision
- Define the Initiative Boundaries
- Develop a Decision Rule
- Specify Tolerable Limits on the Decision Errors
- Optimize the Design for Obtaining Data

This section presents an overview of the seven steps in EPA's QA/G-4 DQO¹ process as applied to the objectives of this project. The purpose of this section is to provide a general discussion of the specific issues that were used in developing the DQOs for this project.

Each DQO step is discussed in detail below. The pollutant specific outcomes of the DQO process are contained in Section 6.9.

6.2 State the Problem

The EPA project team developed the following problem statement:

Residents have raised outdoor air quality questions and concerns in areas that have natural gas extraction, processing and distribution activities on-going near their properties. Measuring the levels of contaminants in the air around these processes will help EPA understand whether that air quality poses any health concerns to residents living in close proximity

6.3 Identify the Decision

The decision statement should provide a link between the principal investigation question and possible actions. The decision that monitoring at these sites is intended to inform is as follows:

Data will be collected from selected areas based on information developed by or made available to the EPA. Monitoring will be performed in such a way that the resulting data will be sufficient in terms of quantity, quality and representativeness to better inform our understanding of chronic and acute contaminant concentrations in the ambient air at these areas and the influence of nearby sources. EPA will use the data collected from this monitoring initiative to assist in evaluating impacts from these operations using health based thresholds developed by EPA/ATSDR and or specific State and Local agencies. These data along with other information pertaining to air contaminants at these locations will be relied upon by EPA to identify:

1. Actions needed to reduce ambient concentrations and /or exposures to ambient concentrations;
2. Locations where measured ambient concentrations do not indicate impacts of potential concern and no further monitoring is needed;

3. Where additional information, including additional monitoring, is needed to inform regulators and health assessors, or for other longer-term objectives related to more fully characterizing ambient concentrations and potential source influences in the area.

6.4 Identify the Inputs to the Decision

This section discusses the variety of inputs that are needed to make the final DQO decision for this study. The pollutants of particular interest are listed in Table 6-2. The statements included here apply implicitly to this full list of analytes.

In addition to the monitoring results, other inputs potentially important to decision-making for this project include, but are not limited to, the following items (not listed in any priority order):

- List of target areas, the extraction process on-going at monitored areas and target compounds;
- Existing ambient air sampling methods and analytical techniques;
- NATA estimates;
- Nearby meteorological monitoring data from the National Weather Service or local airport weather data;
- Topographical information pertaining to factors influencing pollutant transport;
- Health effects information, including relevant toxicological information, and information available on the EPA web sites;
- Community concerns; and,
- Funding information.

6.5 Define the Initiative Boundaries

The specific location of the monitors should be established to represent ambient air in the proximity of the areas monitored, as described in The Monitoring Plan. Ideally, monitors should be located on the grounds of a property or adjacent property where natural gas operations are currently underway. Siting criteria that are detailed in Code of Federal Regulations (CFR) Chapter 40 Section 58, Appendix E² will be followed to the extent that is practical, as described in The Monitoring Plan. All monitoring stations will be located within Pennsylvania and/or West Virginia.

6.6 Develop a Decision Rule

The decision rule is an “if ... then” statement for how the various alternatives will be chosen.

If the ambient air monitoring data in combination with other information for an area indicate the need for action to reduce air concentrations of or exposures to air contaminants, then EPA will work with the appropriate agencies on options for such actions in outdoor air. If the available monitoring data and other information are insufficient to support a conclusion in this regard, then additional data collection may be pursued. If the available monitoring data and other information are sufficient to reach a conclusion but do not support the conclusion that further action is needed, then additional data collection will not be pursued.

6.7 Specify Tolerable Limits on the Decision Errors

Budgetary constraints are a consideration in describing the DQOs. The Region has a finite budget that affects the amount of monitoring performed in this air study. The initial monitoring will include at most 20 samples collected a week. On-site measurements will also include meteorological data such as wind direction and wind speed to help inform our consideration of this issue. At sites where the suspected impacts are associated with a particular source(s), the monitoring data set will need to include samples taken when the predominant wind direction is generally from the sources in question to the samplers in order to fully support the decision making process contemplated in this initiative.

In order to understand other aspects of the quality of the data (i.e., precision and bias) the precision estimates of each method was based on the estimates from EPA's laboratory for this initiative and other method estimates and is expressed in terms of coefficient of variance (CV). The bias was chosen from the National Air Toxics Trends Stations (NATTS) estimates². The NATTS is a long term (six-year) trends program that has been in operation since 2004. Data from proficiency testing of the laboratories within the NATTS illustrated that bias can be controlled within 25%. Data completeness will be met when a minimum of 30 valid samples are collected during the initiative. There may be cases in which the amount of samples collected is deemed to be insufficient (e.g., invalidated sample(s), insufficiently representative data, etc.) and thus monitoring will continue until the minimum amount of samples mentioned above is collected. The established minimum detection limits (MDLs) will be met in order to evaluate the resulting data in a health-based context. The MDLs are generally set at or below the concentrations of individual air contaminants for which a lifetime, continuous exposure would pose an excess lifetime cancer risk of one-in-one million or a hazard quotient of 0.1. Note: for a small number of chemicals, the laboratory analytical methodology may be insufficient to achieve such an MDL. Where the level of the MDL substantially limits our interpretation with regard to potential significance of health risk-related impacts, this will be recognized in reporting and interpreting the results.

6.8 Optimize the Design for Obtaining Data

The team decided that due to resource constraints, and to compare investigation data with other data collected within the U.S. (e.g., through the NATTS program), sampling would follow a variable “one every three days” schedule. A project goal of 100% data completeness is established for the initial monitoring. EPA will monitor at a location until the minimum required 30 valid samples are collected. See the Monitoring Plan in Appendix A for sampling schedule.

6.9 DQOs for the Natural Gas Activities Air Monitoring Initiative

This section combines all of the information gathered and states the action that will be followed given the scenarios that can occur.

In order to better evaluate potential impacts of air contaminants at some areas hosting natural gas activities in Pennsylvania and/or West Virginia, monitoring will commence at select locations. If the following criteria are met, the data will be considered of sufficient quantity and quality for the decision-making to commence as described in section 6.3:

- 1. Data are collected with a coefficient of variance (precision) and bias as stated in Tables 6-1;*
- 2. Data completeness is 100% ;*
- 3. MDLs are at or below those specified in Table 6-2 and;*
- 4. Where applicable, sufficient samples are collected when the predominant wind direction is from the source(s) in question, providing sufficient representativeness from the overall dataset to evaluate acute and/or chronic exposure scenarios.*

Once a DQO is established, the quality of the data must be evaluated and controlled to ensure that it is maintained within the established acceptance criteria. Measurement Quality Objectives (MQOs) are designed to evaluate and control various phases (i.e., sampling, preparation, and analysis) of the measurement process to ensure that total measurement uncertainty is within the range prescribed by the DQOs. The MQOs can be defined below:

Precision - a measure of mutual agreement among individual measurements of the same property usually under prescribed similar conditions. This is the random component of error. Precision is estimated by various statistical techniques using some derivation of the standard deviation.

Bias - the systematic or persistent distortion of a measurement process which causes error in one direction. Bias will be determined by estimating the positive and negative deviation from the true value as a percentage of the true value using the PT samples.

Representativeness - a measure of the degree which data accurately and precisely represent a characteristic of a population, parameter variations at a sampling point, a process condition, or an environmental condition.

Comparability - a measure of confidence with which one data set can be compared to another.

Completeness - a measure of the amount of valid data obtained from a measurement system compared to the amount that was expected to be obtained under correct, normal conditions.

Detectability- the determination of the low range critical value of a characteristic that a method specific procedure can reliably discern.

In theory, if these MQOs are met, measurement uncertainty should be controlled to the levels required by the DQO. Table 6-1 lists the MQOs for pollutants of concern that will be measured for this initiative. More detailed descriptions of these MQOs and how they will be used to control and assess measurement uncertainty is described in Section 18.0. Data within these tables reflect the MQOs needed to meet the DQOs for this study. The laboratory analyzing samples for the NAAGMI must demonstrate the ability to meet the PT MQO before the laboratory can analyze samples for this project.

Table 6-1 MQOs for certain compounds

Pollutant Group	Reporting Units	Precision (CV) ³	Bias ²	Representativeness	Comparability/ Method Selection	Completeness
VOCs	ug/m3	30%	25%	Micro, Middle, and/or Neighborhood Scale	GC-MS/TO-15	30 samples
PM _{2.5}	ug/m3	10%	10%	Micro, Middle, and/or Neighborhood Scale	Gravimetric	30 samples

Table 6-2 MDL for certain compounds

Target Compound	CAS	Lab MDL Full Scan (ppbv)	Lab Reporting Limit (RL) (ppbv)
1,1-Dichloroethane	75-34-3	0.034	0.5
1,1-Dichloroethene	75-35-4	0.035	0.5
1,1,1-Trichloroethane	71-55-6	0.017	0.5
1,1,2-Trichloroethane	79-00-5	0.022	0.5
1,1,2,2-Tetrachloroethane	79-34-5	0.022	0.5
1,2-Dibromoethane	106-93-4	0.025	0.5
1,2-Dichlorobenzene	95-50-1	0.04	0.5
1,2-Dichloroethane	107-06-2	0.022	0.5
1,2-Dichloropropane	78-87-5	0.024	0.5
1,2,4-Trichlorobenzene	120-82-1	0.099	0.5
1,2,4-Trimethylbenzene	95-63-6	0.047	0.5
1,3-Butadiene	106-99-0	0.051	0.5
1,3-Dichlorobenzene	541-73-1	0.054	0.5
1,3,5-Trimethylbenzene	108-67-8	0.036	0.5
1,4-Dichlorobenzene	106-46-7	0.025	0.5
2-Butanone	78-73-3	0.036	0.5
4-Methyl-2-pentanone	108-10-1	0.022	0.5
Benzene	71-43-2	0.017	0.5
Benzyl chloride	100-44-7	0.034	0.5
Bromodichloromethane	75-27-4	0.018	0.5
Bromoform	75-25-2	0.012	0.5
Bromomethane	74-83-9	0.042	0.5
Carbon disulfide	75-15-0	0.018	0.5
Carbon tetrachloride	56-23-5	0.015	0.5
Chlorobenzene	108-90-7	0.012	0.5
Chloroethane	75-00-3	0.022	0.5
Chloroform	67-66-3	0.024	0.5
Chloromethane	74-87-3	0.036	0.5
cis-1,3-Dichloropropene	10061-01-5	0.031	0.5
cis-1,2-Dichloroethene	156-59-2	0.034	0.5
Dibromochloromethane	124-48-1	0.024	0.5
Dichlorodifluoromethane	75-71-8	0.043	0.5
Dichlorotetrafluoroethane	76-14-2	0.035	0.5
Ethanol	64-17-5	0.094	0.5

Target Compound	CAS	Lab MDL Full Scan (ppbv)	Lab Reporting Limit (RL) (ppbv)
Ethylbenzene	100-41-4	0.031	0.5
Hexachlorobutadiene	87-68-3	0.067	0.5
m,p-Xylene	108-38-3/ 106-42-3	0.107	1.0
Methyl tert-butyl ether	1634-04-4	0.015	0.5
Methylene chloride	75-09-2	0.018	0.5
Naphthalene	91-20-3	0.089	0.5
o-Xylene	95-47-6	0.017	0.5
Propylene	115-07-1	0.071	0.5
Styrene	100-42-5	0.035	0.5
Tetrachloroethene	127-18-4	0.015	0.5
Toluene	108-88-3	0.024	0.5
trans-1,2-Dichloroethene	156-60-5	0.022	0.5
trans-1,3-Dichloropropene	10061-02- 6	0.017	0.5
Trichloroethene	79-01-6	0.018	0.5
Trichlorofluoromethane	75-69-4	0.035	0.5
Trichlorotrifluoroethane (Freon 113)	76-13-1	0.030	0.5
Vinyl chloride	75-01-4	0.061	0.5

***Please note MDL's are subject to change**

Table 6.3 Cancer-based and Noncancer-based Long Term Comparison values

Target Compound	CAS	Individual (ppbv)	Long Term-NonCancer (ppbv)	Long Term-Cancer (ppbv)
1,1-Dichloroethane	75-34-3	1266.6		18.1
1,1-Dichloroethene	75-35-4	20.2	50.4	
1,1,1-Trichloroethane	71-55-6	1832.6	916.3	
1,1,2-Trichloroethane	79-00-5	80.6	73.3	1.2
1,1,2,2-Tetrachloroethane	79-34-5	17.5	0.2	

Target Compound	CAS	Individual (ppbv)	Long Term-NonCancer (ppbv)	Long Term-Cancer (ppbv)
1,2-Dibromoethane	106-93-4	1.6	1.2	0.0
1,2-Dichloroethane	107-06-2	66.7	593.0	0.9
1,2-Dichloropropane	78-87-5	43.3	0.9	1.1
1,2,4-Trichlorobenzene	120-82-1	269.5	26.9	
1,2,4-Trimethylbenzene	95-63-6	2034.3		
1,3-Butadiene	106-99-0	9.0	0.9	1.5
1,3-Dichlorobenzene	541-73-1	6.7		
1,3,5-Trimethylbenzene	108-67-8	2034.3		
1,4-Dichlorobenzene	106-46-7	1663.3	133.1	0.4
Benzene	71-43-2	9.4	9.4	4.1
Benzyl chloride	100-44-7	27.0		0.4
Bromodichloromethane	75-27-4	104.5		
Bromoform	75-25-2	1648.0		23.4
Bromomethane	74-83-9	51.5	1.3	
Carbon disulfide	75-15-0	2247.8	224.8	
Carbon tetrachloride	56-23-5	31.9	303.2	1.1
Chlorobenzene	108-90-7	2172.4	217.2	
Chloroethane	75-00-3	15160.4	3790.1	
Chloroform	67-66-3	102.4	20.1	
Chloromethane	74-87-3	484.3	43.6	
cis-1,3-Dichloropropene	10061-01-5	3.1		
Dibromochloromethane	124-48-1	105.7		
Dichlorodifluoromethane	75-71-8	475172.5		
Ethylbenzene	100-41-4	9212.5	230.3	9.2
Hexachlorobutadiene	87-68-3	30.0	8.4	0.4
m,p-Xylene	108-38-3/ 106-42-3	690.9	23.0	
Methyl tert-butyl ether	1634-04-4	1941.6	832.1	105.4

Target Compound	CAS	Individual (ppbv)	Long Term-NonCancer (ppbv)	Long Term-Cancer (ppbv)
Methylene chloride	75-09-2	575.8	287.9	60.5
Naphthalene	91-20-3	5.7	0.6	0.6
o-Xylene	95-47-6	2072.8	23.0	
Propylene	115-07-1	17431.1		
Styrene	100-42-5	2113.0	234.8	
Tetrachloroethene	127-18-4	206.4	2.5	39.8
Toluene	108-88-3	1061.4	1326.8	
trans-1,2-Dichloroethene	156-60-5	201.8		
trans-1,3-Dichloropropene	10061-02-6	3.1		
Trichloroethene	79-01-6	1875.0	112.5	9.4
Trichlorofluoromethane	75-69-4	355972.9		
Vinyl chloride	75-01-4	391.2	39.1	4.3
Target Compound	CAS	TCEQ short-term ESL (ppbv)	TCEQ long-term ESL (ppbv)	
cis-1,2-Dichloroethene	156-59-2	2000	200	
Dichlorotetrafluoroethane	76-14-2	10000	1000	
Ethanol	64-17-5	10000	1000	
Trichlorotrifluoroethane	76-13-1	5000	500	

*****Please note comparison values are subject to change**

References:

1. Guidance on Systematic Planning using the Data Quality Objectives Process (QA/G-4) EPA/240/B-06/001 February 2006, http://www.epa.gov/quality/qa_docs.html
2. Schools Air Toxics Ambient Monitoring Plan, April 2, 2009, Appendix B

7.0 Documentation and Records

The following information describes the documents and records that will be kept on file for the ambient air monitoring initiative.

7.1 Routine Record Data Activities

Table 7-1 includes the documents and records that will be filed according to the statute of limitations discussed in Section 7.3.

Table 7-1 NGAAMI Data and Records Storage

Categories	Record/Document Types	Responsible Party
Site Information	Network description Site characterization file Site maps Site Pictures	APD
Field Operations Information	QA Project Plan Standard operating procedures (SOPs) Field and laboratory notebooks Sample handling/custody records Inspection/Maintenance records	APD
Laboratory Data	Any original data (routine and QC data) including data entry forms Electronic deliverables of summary analytical and associated QC and calibration runs per instrument Control charts Chromatograms and spreadsheets with raw unadjusted data	ESC Laboratory Allegheny County (PA) PM _{2.5} weighing lab
Quality Assurance Information	Network siting and reviews Data quality assessments QA reports Response/Corrective action reports	APD

7.2 EPA Data and Document Control

Table 7-1 represents the documents and records, at a minimum, that must be filed. These documents, including draft and intermediate versions of significant importance to the project records, will be stored and maintained consistent with EPA records management policies¹.

On-Site Notebooks - The NGAAMI will utilize sampling site notebooks. These will be 3-ring binders that will contain the appropriate data forms for routine operations as well as inspection and maintenance forms and SOPs. Additional notes, such as weather conditions, will be noted whenever the site technician arrives.

Field Notebooks – Each field technician may utilize a notebook to document any activity deemed necessary. Although the samples will have a Chain of Custody (CoC) form with each sample, the notebooks will be used to record additional information about the operations. All field notebooks will be bound and paginated so that individual pages cannot be removed unnoticeably.

Lab Notebooks - These notebooks will be uniquely numbered. One notebook will be available for general comments/notes; others will be associated with, the temperature and humidity recording instruments, the refrigerator, calibration equipment/standards, and the analytical balances and instruments used for this project.

Electronic data collection – In order to reduce the potential for data entry errors, automated systems will be utilized where appropriate and will record the same information that is found on data entry forms. In order to provide a back-up, a hardcopy of automated data collection information will be stored for the appropriate time frame in project files.

7.3 Data Reports, Archiving and Retrieval

In general, all the information listed in Table 7-1 will be retained for 5 years. However, if any litigation, claim, negotiation, audit or other action involving the records has been started before the expiration of the 5-year period, the records will be retained until completion of the action.

References:

1. US EPA, Records Management Policy, CIO 2155.1, June 8, 2009, http://www.epa.gov/records/policy/2155/rm_policy_cio_2155_1_2.pdf.
2. US EPA, Records Management Manual, <http://www.epa.gov/records/policy/manual/index.htm>.
3. US EPA, Records Schedule, <http://www.epa.gov/records/policy/schedule/index.htm>.

Section 8.0 Sampling Design

8.1 Scheduled Project Activities, Including Measurement Activities

This section will discuss the operation and installation of samplers for the NGAAMI initiative. Table 8-1 represents the activities associated with the ordering and deployment of the primary and collocated samplers. Please note this schedule may change due to unforeseen circumstances beyond the control of EPA.

Table 8-1 Scheduled Monitoring Activities

Activity	Due Date	Comments
QAPP Development	Spring 2012	Input taken and incorporated into official document.
Monitoring Plan Development	Spring 2012	Monitoring Plan vetted through official channels.
Sampler siting/testing	April-June 2012	Establishment of sites and preliminary testing of samplers.
QAPP Finalized	Spring/ Summer 2012	QAPP finalized.
Field and Laboratory Assessment and Support	Spring 2012	Field and laboratory orientation and assessment.
Sampling Begins	Summer 2012	Sampler testing completed and media shipped to monitoring locations.
Laboratory Analysis Begins	Summer 2012	Samples received and analysis begins.
Sampling Ends	TBD	Consideration of additional monitoring, areas of interest to monitor as well as funding will determine when sampling ends

8.2 Rationale for the Design

8.2.1 Network Siting

In identifying specific monitoring locations in areas impacted by natural gas operations, EPA will consider the following types of information:

- Site evaluation;
- Best professional judgment;
- GIS updates;
- Access and safety issues; and,
- Meteorology.

8.2.2 Primary Samplers

To determine whether the data are of sufficient quality, the ambient air monitoring initiative must address sampler type, sampling frequency, and sampler siting. By employing samplers that are described in the appropriate EPA TO-15 Compendium the data collected will be comparable to standard methods.

By selecting sampler locations using the rules in *Network Design and Site Exposure Criteria for Selected Noncriteria Air Pollutants*,¹ and 40 CFR Part 58 Appendix E², the EPA NAAGMI can be confident that the samplers are sited in a similar fashion. The sampling instruments are detailed in The Monitoring Plan. Sampling frequency is discussed in Section 6.8 and 9.2, while siting and exposure are further described in Sections 8.3 – 8.4.

8.2.3 Collocated Samplers

The purpose of collocated samplers is to estimate the precision of the various samplers. The goal is to have concentrations measured by a sampler having a CV of less than 30% for most systems. Table 6-1 lists the individual precision CV objectives. To estimate the level of precision being achieved in the field, the ambient air monitoring initiative will operate collocated samplers for all samplers, but not at every site. It is estimated that 15% of the network have collocated samplers. The collocated samplers will be set, run and collected every other sample on the same day as the primary samplers. Section 12.1.3 outlines the equations that will be used to determine precision. There will be two samples from each instrument that will be used to determine the precision.

8.3 Design Assumptions

The sampling design is based on the assumption that following the rules and guidance provided in 40 CFR Part 58 Appendix E¹ and using the guidance in the *Network Design and Site Exposure Criteria for Selected Noncriteria Air Pollutants*² will result in data that can be used to document air concentrations during the monitoring period. This information will be used in considering the potential impacts of air contaminant emissions into the ambient air on residential properties. The siting design assumes that location of the monitors is within the micro, middle or neighborhood scale, as defined in 40 CFR Part 58 Appendix D³.

8.4 Procedure for Locating and Selecting Environmental Samples

8.4.1 Sampling Design

The design of the air contaminant sampling network must achieve the monitoring objective. For the NGAAMI, the objective is to:

Collect information on ambient air concentrations of target compounds at a targeted list of areas in Pennsylvania and/or West Virginia natural gas activity host communities during a defined monitoring period.

The procedure for siting the samplers in host areas is based on best-case judgment by EPA. The best-case decisions will use data from existing monitoring networks, knowledge of source emissions and population distribution, and inference from analyses of meteorology to select optimal sampler locations. In addition, a Geographic Information System (GIS) software package will also be utilized to help locate the samplers.

8.5 Classification of Measurements as Critical/Noncritical

The ambient concentration and site location data will be provided to the SCRIBE database. Information about the SCRIBE database is presented in Section 16.4. The information collected at collocated samplers is the same as that presented in Tables 6-1 and 6-2 for primary samplers. All of the measurements in these tables are considered critical because they form the basis for estimating precision, bias and detectability which is critical to appropriate interpretation of the monitoring data.

References:

1. Network Design and Site Exposure Criteria for Selected Noncriteria Air Pollutants, 1984, EPA document: EPA-450/4-84-022
2. Code of Federal Regulations, Title 40 Part 58 , Appendix D&E

9.0 Sampling Methods Requirements

9.1 Purpose/Background

The methods described herein provide for measurement of the concentrations of hazardous air pollutants (HAPs) in ambient air for a 24-hour sampling period. Each sampler collects a discrete sample that requires extraction and analysis performed in the laboratory. Table 9-1 lists the classes of target analytes for this project.

Table 9-1 List of Target Analytes

Target Analytes	Method	Sampling Media
VOCs	EPA TO-15	Air (via canister)
PM _{2.5}	Gravimetric	Filters

9.2 Sample Collection and Preparation

Sample preparation is an essential portion of this initiative. The following tasks are required for sample preparation:

- PM_{2.5} - filter receipt and inspection, filter numbering, conditioning and storage;
- VOC - cleaning, testing, verification and storage of canisters and sampler certification

Sample set-up of the air toxics and particulate samplers for the ambient air monitoring initiative should take place at the same time as the exposed sample has been recovered. For instance, on a Sunday - Thursday sample day set-up when 1 in 6 day sampling is required, the pickup occurs the day after the run. However, on Friday and Saturday run dates, the pick-up may be the following Monday depending on personnel schedules. Since the ambient air monitoring initiative has collocated samplers, the second monitor will be set up to run at a sample frequency of every other sample run days and will take place on the same day as the primary sampler.

Please note: Once monitoring operations have commenced, the base (i.e., minimum amount) sampling will consist of a minimum 30 valid samples from each operating monitor. There may be cases in which the amount of samples collected is deemed to be insufficient (e.g., invalidated sample(s), insufficiently representative data, etc.) and thus monitoring will continue until the minimum amount of samples mentioned above is collected.

9.2.2 Sample Recovery

Sample preparation is an essential portion of this initiative. The following tasks are required for sample preparation:

- PM_{2.5} - filter receipt and inspection, filter numbering, conditioning and storage;
- VOC - cleaning, testing, verification and storage of canisters and sampler certification

9.3 Support Facilities for Sampling Methods

Support for sampling will come from the EPA Region 3 APD offices, the Region 3 OASQA laboratory in Ft. Meade and ACHD laboratory staff. Table 9-2 lists some of the supplies that will be stored at each support facility.

Table 9-2 Field Supplies

Item	Quantity	Notes
Powder Free Gloves	Box	<i>Material must be inert and powder free</i>
Flow rate standards	1 for each sampler	<i>NIST Traceable</i>
Sampler Operations Manual	1 per model	
Flow rate verification filter	2	For PM _{2.5} sampler
Tools	1	<i>One Tool kit with various wrenches, screwdrivers, etc.</i>
Filter Cassettes	1 box	<i>For use with flow rate check filter or non-permeable membrane</i>
Sample tubing	1	
Power/extension cords	1 per site (as needed)	
Various fittings	1 Box	<i>Of the type specified in the sampler manual</i>
Pumps	1 Box	<i>Of the type specified in the sampler manual</i>
VOC transport cases	TBD	<i>For shipping VOC canisters to/from the lab</i>

The items in Table 9-2 are just some of the supplies that may be needed during this initiative. In addition, there are other items that the field operator may need during a site visit that are not expected to be at each site, the operator is expected to bring these items with him/her.

9.4 Sampling Corrective Action

Corrective action measures in the NGAAMI will be taken to ensure that the MQOs are attained. Please see the method descriptions in reference section of Chapter 5 for information on corrective actions that may be encountered in the network.

9.5 Sampling Equipment, Preservation, and Holding Time

This section details the requirements needed to prevent sample contamination, the volume of air to be sampled, how to protect the sample, temperature preservation requirements, and the permissible holding times to protect ensure against degradation of sample integrity.

9.5.1 Sample Contamination Prevention

The quality system has rigid requirements for preventing sample contamination. Powder free gloves are worn while handling filters, and filter cassettes. Filter and cartridges are to be stored in storage containers (static resistant zip lock bags) as provided by the sampler manufacturer during transport to and from the laboratory.

9.5.2 Sample Volume

The volume of air to be sampled is detailed in the manufacturers and method specifications for the canisters. The different methods specify that certain minimum volumes must be collected. All samples are expected to be collected for 24 hours; therefore, the site operators must set the flow rates to collect sufficient sample to obtain the minimum sample volume. In some cases a shorter sample period may occur due to power outages, travel time, etc. If the sample period is less than 23 hours or greater than 25 hours, the sample will be flagged and the analytical laboratory notified via a phone call and by filling out the Chain of Custody (CoC) form.

9.5.3 Temperature Preservation and Holding Time Requirements

The temperature requirements of the samples vary between methods. During transport from the laboratory to the sample location, there are no specific requirements for temperature control for the glass fiber filters. Filters will be located in their protective container and in the transport container. Excessive heat must be avoided (e.g., do not leave in direct sunlight or a closed-up car during summer). The temperature requirements are detailed here:

Table 9-3 Temperature Requirements

Item	Temperature Requirement	Reference
VOC canister pre and post sampling	Avoid excessive heat (i.e., do not leave in direct sunlight or in a closed vehicle)	TO-15
Glass fiber filter temperature control pre-sampling.	Avoid excessive heat (i.e., do not leave in direct sunlight or in a closed vehicle)	Gravimetric

Table 9-4 Holding Times

Item	Holding Time	From	To	Reference
VOC canister	<30 days	Completion of sample period	Time of analysis	TO-15 Compendium Section 9.4.2.1
Glass Fiber Filter for PM _{2.5}	30 days in a refrigerator at 6° C or less	Sample end date/time	Time of analysis	NAAQS PM _{2.5} QAPP

For detailed reference information, please see the reference section of Chapter 5 of this QAPP.

Section 10.0 Sample Handling and Custody

10.1 Sample Custody

Sample custody is an important aspect of this project. Sample custody procedures must be followed in order to assure safe and secure samples are delivered both from and to the field. The next sections outline the NGAAMI sample handling regime. Figures 10-1, 10-2 and 10-3 illustrate examples of chain of custody (CoC) forms, canister tags, and the PM_{2.5} Sample Data Sheet that will be used in this project. Sample custody procedures must be followed in order to assure safe and secure samples are delivered both from and to the field. All shipping to and from the NAAGMI sites will be handled by UPS. The next sections outline the NGAAMI sample handling regime.

10.1.1 Canister Sampling Field Data Forms

The sample is given a unique identification (ID) number and tagged; see Figure 10-2, noting the site location and the sample collection date. A canister sample CoC form is shipped with each 6-liter canister to the NAAGMI lab. If duplicate samples are to be taken, two canisters and two data sheets are sent in the shipping container to the site. When a sample is taken, the site operator fills out the field data form and sends the CoC with the canister in the shipping container to the analytical laboratory. The sample ID number on the canister tag must match the ID number noted on all copies of the data sheet.

Upon receipt, the sample canister vacuum/pressure is compared against the field documented vacuum/pressure to ensure the canister remained airtight during transport. If any leaks are detected, the sample is voided. The CoC is stored with the canister until analysis is complete and then stored chronologically in a designated file cabinet.

More detailed sample receipt procedures and sample acceptance policies are presented in the OASQA Laboratory SOP R3QA051-011812. The sample specific information from the CoC sheets and sample tag is then entered into the Laboratory Information Management System (LIMS) for Case File generation, as described in OASQA SOP R3QA066-080311.

10.1.2 Invalid Canister Sample

The canister sample CoC form may indicate that the sample sent from a site is invalid. When a sample is designated as invalid, the assigned lab ID number is voided and is invalidated on the individual respective chain of custody form. The sites will be notified in the analytical reports of any invalid samples.

10.1.3 PM2.5 Filter Data Forms

Each sample filter must be accompanied by an individual sample sheet which will stay with the sample filter from the pre-weighing, through sampling and on to post weighing and archiving of the sample in the laboratory cold storage area. The first and last block on this form will be completed by the laboratory responsible for pre and post weighing activities. All three middle blocks must be filled in completely by the field technician. The first of these blocks, entitled *field setup visit*, is to be completed for each filter. Each technician will maintain all sample sheets for filters which are currently inside of each monitor.

Figure 10.3 PM_{2.5} Sample Data Sheet

LABORATORY PRE SAMPLE ACTIVITIES		WEIGHING PERFORMED BY	
FILTER ID #		CASSETTE #	
DATE / TIME WEIGHED		USE BY DATE	
RELATIVE HUMIDITY		TEMPERATURE	
INITIAL WEIGHT		BATCH #	
FILTER TYPE	ROUTINE FILTER []	FIELD BLANK []	

FIELD SETUP VISIT		PERFORMED BY	
SITE NAME		AIRS ID#	
DATE/TIME OF SETUP		SAMPLER MODEL #	
WINS IMPACTOR #		WINS LAST CLEANED	(DATE)
SAMPLER INDICATED Pa	mmHg	SAMPLER INDICATED Ta	(°C)
EXPECTED SAMPLING DATE / TIME	START	STOP	

POST SAMPLING VISIT * SAMPLE MUST BE REMOVED FROM SAMPLER WITHIN 177 HOURS (7 DAYS, 9 HOURS) AFTER
END OF SAMPLING RUN*

SAMPLE REMOVAL DATE / TIME	
SAMPLE TUBE ID #	
SAMPLE SHIP DATE / TIME	
COOLER TEMP PRIOR TO SAMPLE ADDITION	°C

INITIAL AND FINAL CONDITIONS (FROM SAMPLER OR DATA STORAGE)		
	START RUN	END RUN
SAMPLING DATE / TIME		
INDICATED Pa	mmHg	mmHg
INDICATED Ta	°C	°C
INDICATED FLOW (Q)	L/MIN	L/MIN
INDICATED FLOW (Q) AVE	L/MIN
INDICATED (Q cv)	
VOLUME SAMPLED	M ³
QUESTIONABLE SAMPLE?		

LABORATORY POST SAMPLE ACTIVITIES	PERFORMED BY
SAMPLE RECEIPT DATE / TIME	
MAXIMUM TRANSPORT TEMPERATURE (CHECK ONE)	4 °C or under <input type="radio"/> 25 °C or under <input type="radio"/> Over 25 °C <input type="radio"/>
MUST BE WEIGHED WITHIN (CHECK ONE)	30 DAYS <input type="radio"/> 10 DAYS <input type="radio"/>
BALANCE ROOM RELATIVE HUMIDITY	BALANCE ROOM TEMPERATURE
FINAL WEIGHING DATE/TIME	
FINAL WEIGHT (Mg)	
CALCULATED CONCENTRATION (ug / M ³)	
QUESTIONABLE SAMPLE?	

10.2 Analytical Laboratory Data

All analytical laboratories will provide sample tracking forms, narratives describing any anomalies and any modifications to analytical procedures, data and sample handling records, and laboratory notes for inclusion in the final report. All laboratory electronic records will be recorded for archive, and all hardcopies of raw data will be included in the project archive file. All records generated by measurement activities are signed or initialed by the person performing the work and reviewed by an appropriate supervisor. Measurement results become part of a project report which is reviewed by a technical reviewer. All notebooks are kept in ink, dated and signed by the person making the entries, and routinely inspected by the appropriate supervisor, as evidenced by his/her initials and date of inspection.

10.3 Sampling Monitoring Data

All data sheets from the monitoring sites will be collected at the end of each monitoring episode and maintained in the laboratory/field office throughout the monitoring study. If corrective action is required during the field monitoring activities, the reason for the correction and action taken will be documented on a corrective action report form. All forms will be written on with indelible ink. If correction is required on the form, a single line will be drawn through the erroneous entry, and the correction will be dated and initialed. Any blank spaces will have a line drawn through to ensure that the space is not filled in later.

11.0 Analytical Methods Requirements

11.1 VOCs

The analytical instruments for this project are: gas chromatograph – mass spectroscopy (GC/MS) for VOCs and gravimetric micro-balance weighing for PM_{2.5} samples. All analytical method SOPs concerning the VOC analysis are on file at OASQA Laboratory in Ft. Meade, MD.

Analytical method for air canisters is performed following Region 3 SOP R3QA230-041912 as listed on file. All instrument conditions and performance criteria can also be found in the referenced SOP. The referenced SOP, R3QA230-041912, was prepared based on Region 3 Quality Manual Version 8. Due to the nature of the air canister samples, the exceptions to the Region 3 Quality Manual are noted below:

- Trip blank(s) are not recommended for this method.
- Field blank(s) are not recommended since they do not serve their purpose for this method.
- Sample storage is at room temperature and in the laboratory where TO-15 instrument is located.
- Sample canisters will be cleaned and certified once the report is submitted.
- Instead of batch blank(s), one (1) daily method blank is performed subjected to passing QC requirement.

Air canister cleaning is referenced by Region 3 SOP R3QA231. Each canister will be certified by GC/MS analysis to ensure cleanliness for its intended use.

11.2 PM_{2.5}

ACHD will perform PM_{2.5} gravimetric on the filter collected at the designated NGAAMI site. The net mass of a filter is obtained by taking the difference between the tare and gross weights of that filter. Tare weight is the weight of the specific filter after it has been conditioned and before it is sampled. The gross weight is the weight of the specific filter after it has been sampled and after it has again been conditioned. Both procedures are done in the laboratory.

Details of the procedure can be found in Appendix B of this QAPP.

References:

1. US EPA, Region 3 Environmental Science Center, Laboratory Quality Manual, Version 8, February 3, 2011.
2. US EPA, Region 3 Environmental Science Center, Analysis of Volatile Organic Compounds in Air Samples Using Silco/Summa Canisters, R3QA230-041912, April 19, 2012.
3. US EPA, Region 3 Environmental Science Center, Procedure for Cleaning Canisters used for Volatile Organic Compounds in Air Analyses, R3QA231-042810, April 28, 2010.

12.0 Quality Control Requirements

Quality Control (QC) is the overall system of technical activities that measures the attributes and performance of a process. In the case of the NGAAMI, QC activities are used to ensure that measurement uncertainty, as discussed in Chapter 6, is maintained within acceptance criteria for the attainment of the DQO.

12.1 QC Procedures

Day-to-day QC is implemented through the use of various checks on the samplers. These checks are used to verify that the sampler is operating properly. The procedures for the methods section are described in Sections 9 (field) and 11 (laboratory), respectively. The following information provides some additional descriptions of these QC activities, how they will be used in the evaluation process, and what corrective actions will be taken when they do not meet acceptance criteria.

12.1.1 Calibrations

Calibration is the comparison of a measurement standard or instrument with another standard or instrument to report, or eliminate by adjustment, any variation (deviation) in the accuracy of the item being compared. The purpose of calibration is to minimize bias.

Calibration activities for air contaminants samplers follow a two-step process:

1. Certifying the calibration standard and/or transfer standard against an authoritative standard; and,
2. Comparing the calibration standard and/ or transfer standard against the routine sampling/analytical instruments.

Calibration requirements for the critical field and laboratory equipment are discussed in Section 14 of this QAPP. More detailed procedures are found in the respective instrument and sampler SOPs.

12.1.2 Blanks

Blank samples are used to determine contamination arising from principally four sources: the environment from which the sample was collected/analyzed, the reagents used in the analysis, the apparatus used, and the operator/analyst performing the analysis. Three types of blanks will be implemented during this initiative:

Lot blanks – occurs when shipments of filters are periodically sent from the vendor to appropriate lab. Each shipment must be tested to determine the length of time it takes the filters to stabilize. Upon arrival of each shipment, three lot blanks will be randomly selected for the shipment and be subjected to the conditioning/pre-sampling procedures. *NOTE: Lot blanks do not apply to VOC canisters.*

Field blanks - provides an estimate of total measurement system contamination. By comparing information from laboratory blanks against the field blanks, one can assess contamination from field activities. Field blanks will be utilized for all samples with the exception of canister sampling. *NOTE: Field blanks cannot be utilized with the VOC canisters since they arrive in the field under vacuum.*

Lab blanks -provides an estimate of contamination occurring at the analysis facility. Details of the use of the lab blanks can be found in the SOPs. Lab blanks will be utilized for the VOCs. Lab blanks for VOCs are generated by the canister cleaning system.

12.1.3 Precision Checks

Precision is the measure of mutual agreement among individual measurements of the same property, usually under prescribed similar conditions. In order to meet the data quality objectives for precision, EPA must ensure the entire measurement process is within statistical control. Precision measurements will be obtained using collocated monitoring.

Evaluation of Collocated Data- All collocated data will be reported to SCRIBE, per procedures described in Section 16.4. The following algorithms will be used to evaluate collocated data. Collocated measurement pairs are selected for use in the precision calculations only when both measurements are within the acceptance criteria.

The relative percentage difference, d_i , for each check is calculated by using the following equation, where X_i represents the concentration produced from the primary sampler and Y_i represents the concentration reported for the duplicate sampler.

$$d_i = \frac{Y_i - X_i}{(Y_i + X_i)/2} \times 100$$

Estimate of Precision - In 2008, the EPA changed the calculations that derive precision, i.e., precision is expressed as coefficient of variance (CV). The following equation is used to calculate the CV. The precision estimate is used to assess the one-point QC checks for gaseous pollutants described in section 3.2.1 of CFR Part 58, Appendix A¹. The precision estimator is the coefficient of variation upper bound and is calculated as follows:

$$CV = \sqrt{\frac{n \cdot \sum_{i=1}^n d_i^2 - \left(\sum_{i=1}^n d_i\right)^2}{n(n-1)}} \cdot \sqrt{\frac{n-1}{\chi_{0.1, n-1}^2}}$$

Where $\chi_{0.1, n-1}^2$ is the 10th percentile of a chi-squared distribution with $n-1$ degrees of freedom.

Table 12-1 illustrates several issues that will preclude collocated data from being used for precision calculations.

Table 12-1 Sample Invalidation Criteria for Collocated Data

Parameter	Decision
Both samples did not run 24 hours +/- 10 min.	Do not use for precision calculations
One or both filters are damaged or exhibit a pinhole or tear	Do not use for precision calculations
One or both samplers has erratic flow pattern	Do not use for precision calculations
The difference in the pressure of the VOC canisters is > 2 psig	Do not use for precision calculations
One or both samples are not kept within the holding and storage temperature requirements for any length of time	Do not use for precision calculations

Estimate of Bias - For the NGAAMI initiative, EPA’s independent PT laboratories will create single blind TO-15 PT samples. The appropriate analysis labs will analyze the samples and send the results to the independent lab that generated the TO-15 PT sample. The audit sample for each system will be mailed directly to the appropriate analytical laboratory. The results will then be sent to the EPA. The equation used to define percentage difference (d_i) for each individual compound audit i is calculated. Where X_i represents the audit standard concentration from a certified laboratory (known) and Y_i represents the indicated value obtained from the laboratory.

$$d_i = \frac{Y_i - X_i}{X_i} \times 100$$

12.2 Proficiency Testing

TO-15 Laboratory bias will be determined by the analysis of known reference analytes prepared by independent laboratories, i.e., the PT samples. The participating laboratories supporting the monitoring initiative will be required to participate in the national PT program that supports the NATTS and non-NATTS laboratories.

The PT is an assessment tool for the laboratory operations only. An EPA’s Contract laboratory independent from the NGAAMITO-15 laboratory creates “blind” samples. Upon receipt, the laboratory logs in the samples and performs the normal handling routines as any other sample.

The PT is analyzed in accordance with the SOPs. Then the results are reported to the EPA. The contract laboratory that creates the PT samples will write PT report and sends a copy of the results to the laboratory and the EPA OAQPS QA coordinator. Any results outside of the EPA’s acceptance criteria are then noted in the PT report. The acceptance criteria is detailed in the “bias” row of table 6.1 of this QAPP

Table12-2 Proficiency Testing

Assessing Agency	Type of Assessment	Agency Assessed	Frequency
EPA	PTs*	TO-15 Analytical Laboratory and/or their subcontract lab	At least once during the monitoring

*PT samples are created, supplied and analyzed by Battle, Inc. as part of an EPA national contract for the National Air Toxic Trends Station program.

Reference:

1. Code of Federal Regulations, Title 40 Part 58 , Appendix A
2. EPA Guidance on Technical Audits and Related Assessments for Environmental Data Operations (QA/G-7), May 2006. http://www.epa.gov/quality/qa_docs.html

13.0 Instrument/Equipment Testing, Inspection, and Maintenance

13.1 Purpose/Background

The purpose of this section in the ambient air monitoring initiative QAPP is to discuss the procedures used to verify that all instruments and equipment are maintained in sound operating condition and are capable of operating at acceptable performance levels.

13.2 Testing

All samplers used for sample collection will be similar to the instruments in the appropriate methods. Prior to field installation, field operators will assemble and run the instrumentation. The field operators will perform checks on the instrumentation. If any of these checks are out of specification, the field technicians will attempt to correct them. If the problem is beyond their expertise, the field manager will contact the vendor for guidance. If the vendor does not provide sufficient support, then the instrument will be returned to the vendor. Once installed at the site, the field operators will run the tests at least one more time. If the sampling instrument meets the acceptance criteria, it will be assumed to be operating properly.

13.3 Inspection

Inspection of various equipment and components are provided here. The inspections section is subdivided into two sections: one pertaining to laboratory issues; and one associated with field activities.

13.3.1 Inspection in Laboratory

Table 13-1 lists several items that require inspections and how to appropriately document the inspection. Other inspections will be documented in the individual SOPs and QAPPs.

Table 13-1 Inspections in the Laboratory

Item	Inspection Frequency	Inspection Parameter	Action if Item Fails Inspection	Documentation Requirement
GC/MS Room Temperature	Daily	20 - 30 ⁰ C	1) Check HVAC System 2) Call service provider that holds maintenance agreement	Document in Logbook
GC/MS Cleanliness	Monthly, or as needed	Use glove and visually inspect	Clean room and remove clutter put canisters back into rack	Document in Log Book
PM _{2.5} weigh room temp and humidity	Daily	Per PM _{2.5} weigh room SOP	1.) Check HVAC System 2.) Call service provider that holds maintenance agreement	Document in Log Book

13.3.2 Inspection of Field Items

There are several items to inspect in the field before and after a sample has been taken. Please refer to the instrument manufacturer's operation manuals.

13.4 Maintenance

There are many items associated with appropriate preventive maintenance of a successful field study. Please refer to the manufacturer's operating manual and the field SOPs for detail on maintenance items for individual samplers.

14.0 Instrument Calibration and Frequency

All instrument and automated samplers in this study will be calibrated using National Institutes of Standards and Technology (NIST) traceable standards. The field and laboratory technician that operate and maintain the instruments should also perform verifications/calibrations as necessary. For the NAAGMI, the calibrations are divided into the field and analytical laboratory portions.

14.1 Field Calibrations

The following calibrations are performed in the lab:

- calibration of canister flow controller against the working standard;

The following section will give more details on how these procedures are performed. Please reference the individual SOPs and/or manufacturer's operating manual.

14.2 Calibration Method

This section describes generalized calibration procedures that will be used by the laboratories and field technicians.

14.2.1 Canister Flow Controller Calibration

Please see the TO-15 laboratory SOP and/or flow controller Operating Manual for calibrating the canister flow controller.

14.2.2 Wind Sensor Calibration

The NAAGMI will utilize sonic anemometers in the field. Sonic anemometry is a relatively new technology that is gaining national acceptance, due to lower levels of detection and no moving parts. However, because the sensors do not have any moving parts, calibration of these sensors can be challenging. In general, sonic anemometers must be mounted so they are level. The Columbia Magellan sonic anemometer will automatically align itself North upon installation. Please reference the instrument manufacturer's operating manual for further information. Additional background information on wind direction alignment can be obtained in the EPA's QA Handbook, Volume IV: Meteorological Measurements².

14.3 Calibration Standard Materials and Apparatus

Flow Rate - The flow rate standard apparatus used for flow-rate calibration (field- NIST-traceable, piston-type volumetric flow rate meter; laboratory -NIST-traceable manual soap bubble flow meter and time monitor) has its own certification and is traceable to other standards for volume or flow rate which are themselves NIST-traceable. A calibration relationship for the flow-rate standard, such as an equation, curve, or family of curves, is established by the manufacturer (and verified if needed) that is accurate to within 2% over the expected range of ambient temperatures and pressures at which the flow-rate standard is used. The flow rate standard will be recalibrated and recertified at least annually.

The actual frequency with which this recertification process must be completed depends on the type of flow rate standard; some are much more likely to be stable than others. In addition to providing excellent documentation of the certification of the standard, a control chart also gives a good indication of the stability of the standard. If the two standard-deviation control limits are close together, the chart indicates that the standard is very stable and could be certified less frequently. The minimum recertification frequency is 1 year. On the other hand, if the limits are wide, the chart would indicate a less stable standard that will be recertified more often.

Calibration Frequency - Since the NGAAMI initiative has a limited duration, calibrations must be performed at the beginning and at the end of the sampling, or if the instrument malfunctions or is repaired. More frequent calibrations are encouraged, but not required and are left to the field operator's discretion. These events, as well as sampler equipment maintenance and inspections will be documented in field data records (i.e., CoC forms) and notebooks. The records will normally be controlled by the individual agency field managers, and located in the labs or field sites when in use or at the manager's offices when being reviewed or used for data validation.

14.4 Laboratory Instruments

Please see the applicable laboratory SOPs for calibration requirements.

References:

1. ASTM. 1977. Standard test methods for measuring surface atmospheric pressure. American Society for Testing and Materials. Philadelphia, PA. Standard D 3631-84.
2. EPA. 2008. Quality Assurance Handbook for Air Pollution Measurement Systems Volume IV: Meteorological Measurements. U.S. Environmental Protection Agency. Document No. EPA/454/B-08-002. <http://www.epa.gov/ttn/amtic/met.html>

15.0 Non-Direct Measurement Data Acquisition Requirements

This section addresses data not obtained by direct measurement from the ambient air monitoring. This includes both outside data and historical monitoring data. Non-monitoring data and historical monitoring data can be used by personnel working on the ambient air monitoring in a variety of ways. The procedures described in this section apply both to data acquired through the NAAGMI and to information previously acquired and/or acquired from outside sources.

15.1 Acquisition of Non-Direct Measurement Data

EPA will rely on data that are generated through field and laboratory operations; however, other significant data are obtained from sources outside the EPA or from historical records.

15.1.1 Chemical and Physical Properties Data

Physical and chemical properties data and conversion constants are often required in the processing of raw data into reporting units. This type of information that has not already been specified in the monitoring regulations will be obtained from nationally and internationally recognized sources.

- National Institute of Standards and Technology (NIST);
- International Standards Organization (ISO),
- International Union of Pure and Applied Chemists (IUPAC),
- American National Standards Institute (ANSI),
- U.S. EPA;
- other widely-recognized national and international standards organizations; and
- Operating instrument manuals and SOPs.

15.1.2 Sampler Operation and Manufacturers' Literature

Another important source of information needed for sampler operation is manufacturers' literature. Operations manuals and users' manuals frequently provide numerical information and equations pertaining to specific equipment. Field personnel are cautioned that such information is sometimes in error, and appropriate cross-checks will be made to verify the reasonableness of information contained in manuals.

15.1.3 Other Ancillary Data

Other data, such as GIS and satellite mapping data are useful for siting and analysis of the data collected for this project. Here is a partial list of some data that will be useful to this study.

- Standard Google Earth™ layers;
- Markers for sites to be monitored, with pop-up box indicating name, address, and pollutants to be monitored;
- Other natural gas extraction processes in the area;
- Demographics of the area.

15.1.4 National Weather Service Data

Meteorological information is gathered from the U.S. Weather Service stations across the nation. Parameters include: temperature, relative humidity, barometric pressure, rainfall, wind speed, wind direction, cloud type/layers, cloud cover and visibility range.

16.0 Data Assessment and Management

16.1 Background and Overview

The data management and quality assurance of the VOC canister data will be handled by the EPA OASQA Laboratory in Ft. Meade, MD. The quality assurance of the PM_{2.5} filter samples will be handled by the Allegheny County (PA) laboratory.

16.2 OASQA Laboratory Data Assessment

Analytical data generated by the EPA Office of Analytical Services and Quality Assurance (OASQA) Laboratory will be reviewed and assessed in accordance with standard procedures. As outlined in the Laboratory's Quality Manual (version 8 02-03-1) the OASQA laboratory performs three levels of data review for every report prior to release. Data generated by the laboratory are reviewed internally prior to distribution to ensure validity of the reported data and this internal process consists of data generation, reduction, and three levels of review.

- The first level of review is done by the primary analyst, who is responsible for data generation and reduction. The primary analyst ensures that the data are correct and complete, and that all supporting documentation is organized and available in the case file record.
- The second level of peer review is done by an analyst to assure that the reported data are free from transcription and calculation errors, and that manual calculations including manual integrations are properly performed. Additionally, the secondary reviewer verifies that the data is properly entered in the laboratory's information management system (LIMS), and that improper or fraudulent practices are not occurring. The peer reviewer evaluates the data to ensure conformance to the associated analytical SOP and that the analysis can be reconstructed and verified. The recalculation of results during the peer review verifies that the laboratory software programs are reliable.
- The third and final level of review for OASQA data is completed by one of the following: Laboratory Branch Chief (LBC), Laboratory Technical Director and/or the Quality Assurance Officer (QAO). This final level of review is performed on the entire consolidated data report prior to delivery to the customer. This review ensures that all sections of the report are complete, that the case file is properly assembled and that the requirements of the client were met.

For any analytical data that is generated by contractors or externally of EPA, it is highly recommended that this data be assessed and/or validated independently of the data generator.

All results will undergo a project-level review to ensure results meet project data quality objectives. Any results not meeting data quality objectives will be qualified in the final report.

16.3 Allegheny County Laboratory Data Assessment

ACHD data assessment is checking that data processing operations have been carried out correctly and monitoring the quality of the field operations. Data assessment can identify problems in either of these areas. Once problems are identified, the data can be corrected or invalidated, and corrective actions can be taken for field or laboratory operations. Numerical data stored in the PM_{2.5} DAS are never internally overwritten by condition flags. Flags denoting error conditions or QA status are saved as separate fields in the database, so that it is possible to recover the original data.

The following data assessment functions are incorporated into the PM_{2.5} DAS to ensure quality of data entry and data processing operations:

- **Duplicate Key Entry** - the following data are subjected to duplicate entry by different operators: filter weight reports, field data sheets, chain of custody sheets. The results of duplicate key entry are compared and errors are corrected at biweekly intervals.
- **Range Checks** - almost all monitored parameters have simple range checks programmed in. For example, valid times must be between 00:00 and 23:59, summer temperatures must be between 10 and 50 degrees Celsius, etc. The data entry operator is notified immediately when an entry is out of range. The operator has the option of correcting the entry or overriding the range limit. The specific values used for range checks may vary depending on season and other factors. Since these range limits for data input are not regulatory requirements, the Air Division QA Officer may adjust them from time to time to better meet quality goals.
- **Completeness Checks** - When the data are processed certain completeness criteria must be met. For example, each filter must have a start time, an end time, an average flow rate, dates weighed, and operator and technician names. The data entry operator will be notified if an incomplete record has been entered before the record can be closed.
- **Internal Consistency and Other Reasonableness Checks** - Several other internal consistency checks are built into the PM_{2.5} DAS. For example, the end time of a filter must be greater than the start time. Computed filter volume (integrated flow) must be approximately equal to the exposure time multiplied by the nominal flow. Additional

consistency and other checks will be implemented as the result of problems encountered during data screening.

- **Data Retention** - Raw data sheets are retained on file in the Air Protection Division office for a minimum of five years, and are readily available for audits and data verification activities. After five years, hardcopy records and computer backup media are cataloged and boxed for storage. Physical samples such as filters shall be discarded with appropriate attention to proper disposal of potentially hazardous materials.
- **Statistical Data Checks** - Errors found during statistical screening will be traced back to original data entry files and to the raw data sheets, if necessary.
- **Sample Batch Data Verification** - have associated flags that are generated by QC values outside of acceptance criteria, with a sample batch. Batches containing too many flags would be rerun and or invalidated.

Table 16-1 summarizes the assessment checks applicable to the PM_{2.5} data.

Table 16-1 Assessment Check Summaries

Type of Data Check	Electronic Transmission and Storage	Manual Checks	Automated Checks
Data Parity and Transmission Protocol Checks	√		
Duplicate Key Entry		√	
Date and Time Consistency		√	√
Completeness of Required Fields		√	√
Range Checking			√
Statistical Outlier Checking			√
Manual Inspection of Charts and Reports		√	
Sample Batch Data Validation			√

16.4 EPA Data Management

EPA will be utilizing SCRIBE for storing data associated w/ the NAAGMI. SCRIBE is a software tool developed by the EPA's Environmental Response Team (ERT) to assist in the process of managing environmental data. SCRIBE captures sampling, observational, and monitoring field data. Examples of SCRIBE field tasks include air sampling, soil sampling, and

water sampling. SCRIBE can import electronic data including analytical lab result data as an electronic data deliverable (EDD) and sampling location data such as latitude and longitude from Global Positioning Systems (GPS).

SCRIBE outputs include labels for collected samples, chain of custody generation and analytical lab result data reports. SCRIBE provides a flexible user interface to manage, query and view all this information. SCRIBE supports exporting electronic data for user services such as Geographic Information System (GIS) tools and spreadsheets so sampling data may be further analyzed and incorporated into report writing and deliverables.

16.5 Data Tracking

The appropriate lab database (i.e., LIMS) contains the necessary input functions and reports appropriate to track and account for the whereabouts of specific samples during processing operations. The following input locations are used to track sample location and status:

- Laboratory (initial receipt)
- Sample receipt;
- Canister number (VOC only);
- Filter package for the laboratory (filter numbers in each package are recorded);
- Laboratory (receipt from field)
- Package receipt (package is opened and contents are logged in);
- Samples are stored in correct locations (i.e., canisters are stored in the laboratory); and,
- Refrigerator, by refrigerator number.

Security of the data in the NGAAMI SCRIBE database is ensured by the following controls:

- Password protection on the data base that defines three levels of access to the data;
- Password changes as necessary
- Logging of all incoming communication sessions, including the originating telephone number, the user's ID, and connect times; and
- Storage of media including backup tapes in locked, restricted access areas.

17.0 Reports to Management

This section describes the quality-related reports and communications to management necessary to support the NGAAMI and the associated data acquisition, assessment, and reporting. Since this is envisioned to be a short term project for multiple locations, a report will be issued for each area monitored by EPA.

17.1 QA Final Report

After the monitoring has been completed, EPA staff will gather PT data, and precision, bias and completeness information from the collocated monitoring and perform a Data Quality Assessment (DQA). The DQA process is discussed in Section 20.0 of this QAPP. Please reference that section for details.

18.0 Project-Level Data Assessment

18.1 Data Interpretation

Many of the processes for verifying and assessing the measurement phases of the data collection operation have been discussed in Section 16. Laboratories will be responsible for verifying and assessing data after laboratory analyses.

After a reporting batch is completed, a thorough review of the data will be conducted for completeness and manual and electronic data entry accuracy. For the chromatographic data, the entries are reviewed to reduce the possibility of entry and transcription errors. Once the data are transferred to the LIMS database, the data will be reviewed for routine data outliers and data outside acceptance criteria. These data will be flagged appropriately. Appropriate data qualifiers or flags can be found in applicable laboratory SOPs.

Records of all samples will be retained on file for 5 years, valid or invalid. Information will include a brief summary of why the sample was invalidated along with the associated flags. This record will be available on stored electronic media. Certain criteria based upon the laboratory analyst's judgment have been developed that will be used to invalidate a sample or measurement (i.e., water in cartridges, vacuum on canister too low, etc.). In all cases the sample will be returned to the laboratory for further examination. When the laboratory analyst reviews the CoC forms, he/she will look for possible problems. Filters that have flags related to obvious contamination, filter damage, or field accidents will be examined immediately. Upon concurrence of the associated laboratory analyst and the Analytical Coordinator, these samples will be invalidated.

Although there are a large number of parameters to analyze, many of these parameters present similar characteristics. The following describe software programs that help with analysis of the data.

Spreadsheets - Spreadsheets allow the user to input data and statistically analyze, plot and graph linear data. This type of analysis will allow the user to see if there are any variations in the data sets. In addition, various statistical tests such as tests for linearity, slope, intercept or correlation coefficient can be generated between two strings of data. Time series plots can help identify the trends. Large jumps or dips in concentrations, periodicity of peaks, and expected or unexpected relationships among species.

18.2 Reconciling Results with DQOs

The DQOs for the NGAAMI were developed in Section 6. The following is excerpted from Section 6.9.

In order to better evaluate potential impacts of air contaminants at some areas hosting natural gas activities in Pennsylvania and/or West Virginia, monitoring will commence at select locations. If the following criteria are met, the data will be considered of sufficient quantity and quality for the decision-making to commence as described in Section 6.3:

- 1. Data are collected with a coefficient of variance (precision) and bias as stated in Tables 6-1;*
- 2. Data completeness is 100%;*
- 3. MDLs are at or below those specified in Tables 6-2 and;*
- 4. Where applicable, sufficient samples are collected when the predominant wind direction is from the source(s) in question, providing sufficient representativeness from the overall dataset to evaluate acute and/or chronic exposure scenarios.*

This section of the QAPP will outline the assessment procedures that EPA staff will follow to determine whether the data complies with the stated goals by performing a Data Quality Assessment (DQA) that is described in *EPA QA/G-9: Guidance for Data Quality Assessment*¹. The DQA will be detailed in the QA Final Report that is discussed in Section 17, Reports to Management.

18.3 Five Steps of DQA Process

For the stated DQO, the assessment process must follow statistical routines. As described in *EPA QA/G-9*, the DQA process is comprised of five steps. The steps are detailed below.

Step 1: Review DQOs and Sampling Design - Section 6 of this QAPP contains the details for the DQOs, including defining the objectives of the NGAAMI and stating the MQOs. Section 8.0 of this QAPP contains the details for the sampling design, including the rationale for the design, the design assumptions, and the sampling locations and frequency.

Step 2: Conduct Preliminary Data Review - A preliminary data review will be performed to uncover potential limitations to using the data, to reveal outliers, and generally to explore the

basic structure of the data. The first step is to calculate basic summary statistics, generate graphical presentations of the data, and review these summary statistics and graphs.

Step 3: Select the Statistical Test – EPA staff will generate summary statistics for each of its primary and QA samples. The summary statistics will be calculated from only valid samples. The following statistical tests will be performed:

- Examination of precision of the data as described in Section 12.1.3;
- Examination of bias from the PT data.

Step 4: Draw Conclusions from the Data - If the MQOs are met, and the initiative design acceptable, then it can be assumed that the project QA objectives have been met. This conclusion can be included in the QA Final Report. If any MQOs are not met, then these will be noted in the QA Final Report, as well.

Step 5: Action Plan Based on Conclusions from DQA - The QA Final Report will be presented to EPA management and analysis staff when completed. It is outside of the scope of the QAPP or QA Final Report what actions might follow this initiative. However, the information from this project will be used in considering and undertaking any additional initiative or mitigation actions, if needed.

References:

1. Guidance for the Data Quality Assessment Process EPA QA/G-9 U.S. Environmental Protection Agency, QAD EPA/600/R-96/084, July 1996.

APPENDIX A

Natural Gas Ambient Air Monitoring Initiative Monitoring Plan

June, 2012

Introduction

Purpose: Environmental Protection Agency (EPA) Region 3 will conduct ambient air sampling for volatile organic compounds (VOCs) and particulate matter (PM_{2.5}) nearby Marcellus Shale hydrofracking and drilling operations in southwestern and northeastern Pennsylvania (PA). Six (6) L canisters will be used for the collection of ambient air and laboratory analysis of VOCs. A lightweight, portable instrument will be used to collect PM_{2.5} and the filter subsequently sent for laboratory weighing. Field work will be carried out by EPA Region 3 personnel.

Background: The Marcellus Shale is a rock formation that underlies approximately two-thirds of Pennsylvania and portions of the states of New York (NY), West Virginia (WV), Maryland (MD), and Ohio (OH) at a depth of 5,000 to 8,000 feet and is believed to hold trillions of cubic feet of natural gas and has long been considered prohibitively expensive to access. Recent advances in drilling technology and rising natural gas prices have attracted new interest in this previously untapped formation. The geology of the Marcellus formation suggests that areas in the southwestern, north-central and northeastern regions of Pennsylvania that have not traditionally seen much gas well drilling may be especially productive.

Extracting natural gas from the Marcellus Shale formation requires both vertical and horizontal drilling, combined with a process known as hydraulic fracturing or hydrofracking. After the well is drilled, cased and cemented to protect groundwater and the escape of natural gas and other fluids, drillers pump large amounts of water mixed with sand and other fluids into the shale formation under high pressure to fracture the shale around the well, which allows the natural gas to flow freely to the well bore. The amount of water typically required for hydraulic fracturing ranges from about one million gallons for a vertical well to approximately five million gallons for a vertical well with a horizontal lateral.

Project Objectives

EPA will collect ambient air monitoring samples to determine if concentrations of certain VOCs and PM_{2.5} are at or above levels of concern. A priority of the NAAGMI is for the samples to be collected on residential properties that are nearby, or adjacent to, a longer-term natural gas extraction processes/facilities. Longer-term operating facilities are the focus of this initiative compared to an active drill site which may only be active for a month or two. Once monitors are sited and samples are collected the data is intended to be used for: 1) determining impacts,

if any, on the air quality at residential areas that are in close proximity to natural gas extraction processes; 2) determining if additional action is necessary by EPA, state, and/or local agencies to ensure the levels of pollutants are detected at safe levels.

Project Design

Site Selection: EPA has chosen a sampling location in Southwest PA (Washington Co.) to collect VOC and PM_{2.5} samples. Please see the map in Attachment A to see the sites in Google Earth. The location will be at a compressor station. At the sampling location, there will be three monitoring sites collecting samples. For QA purposes, one monitoring site will be collocated. A background site will be selected and collect samples for both VOC and PM_{2.5}. A meteorological 3m tower will be operating at one site per sampling location.

Monitor Siting: There may be cases where following CFR siting criteria may not be practical. However, effort must be made to follow siting criteria in 40CFR, Part 58 App. E as much as possible. Considerations must be made to:

- Avoid siting a monitor where sampling will be impacted by nearby influences other than the compressor station or frack-water impoundment.
- Avoid monitoring in an area where flow is obstructed.
- Place sampler inlets at a representative height
- Site the monitors in the best possible, practical location for security of equipment

VOC Canister Sampling and Analysis: EPA personnel will deploy and collect 24-hour ambient air samples from pre-designated monitoring site locations using 6L canisters. Each canister will be equipped with a restrictive orifice at a flow range between 2-4 mL/min and sample for a duration of 24 hours. An in-line timer will also be used to ensure samples start and stop at the same time. All samples will be submitted to the EPA Region 3 Office of Analytical Services and Quality Assurance (OASQA) laboratory in Fort Meade, MD for VOC analysis. There will be at least 8 canisters delivered to the lab after each scheduled sampling day. The OASQA lab has a list of determined Minimum Detection Limits (MDL) for the compounds to be analyzed by EPA Compendium Method TO-15. The OASQA lab has also set the reporting limit at 0.5ppbv. All canisters and flow rate orifices will be certified clean by the OASQA lab prior to being shipped back out to the field.

PM_{2.5} Sampling and Analysis: EPA personnel will collect 24-hour PM_{2.5} samples from (1) predetermined air monitoring sites at the compressor station location. One of the PM_{2.5} monitoring sites at the compressor station location will be collocated. PM_{2.5} samples will be collected using Airmetrics MiniVol™ TAS. Ambient air will be sampled at 5 liters/per minute

and PM_{2.5} will be collected on a PM_{2.5} membrane, polytetrafluoroethylene (PTFE) teflon 46.2 millimeter (mm) filter. All sample filters will be submitted to the Allegheny County Health Department (ACHD) in Pittsburgh, PA for filter mass measurement.

Meteorological Monitoring: Meteorological data will be collected by EPA personnel using a portable 3-meter tower sited at one of the three monitoring sites in each sampling location. Ambient temperature, relative humidity, wind speed, wind direction, and station pressure readings will be collected and stored in 5-minute averages. Data is stored in data logger until downloaded to a lap top by EPA personnel. Manufacturer specifications detail that the meteorological tower battery has a charge-life of 60 hrs. Meteorological data will be running continuously. However, it may be necessary to conserve the battery life so there could be times during non-sampling days that the no meteorological data will be collected. As with siting the ambient air samplers, it is important to follow good practices for the meteorology equipment as best as possible.

Sampling Schedule: Monitors at NGAAMI sites will collect samples on a 1 in every 3 day schedule. At times it may be necessary to stagger the 1 in 3 day schedule in order to make it less obvious of the days when the monitors are operating. Sampling is expected to last approximately 3-4 months or until at least 30 valid samples are collected at each sampling location

Site Surveying: All locations will be logged using Global Positioning System (GPS) technology. GPS coordinates will be plotted in Google Earth. Digital photographs will be taken to identify the location and to document the air monitor location(s) for reference.

Document, Pack, and Ship Samples: Personnel will prepare sampling labels and chain of custody (COC) records using SCRIBE. EPA's Environmental Response Team (ERT) developed SCRIBE to assist in the process of managing environmental data. VOC samples will be packed and shipped to the OASQA Laboratory for EPA Method TO-15 VOC analysis. The canisters are shipped in a 2-canister shipping case using the OAQSA lab UPS shipping account. PM_{2.5} filter samples will be packed and driven to ACHD where they will be weighed for filter mass.

Quality Assurance

Prior to sampling, an approved NAAGMI QAPP will be in place outlining QA requirement and activities associated with the monitoring. This is consistent with EPA data collection requirements. In addition, there will be designated collocated monitors at each sampling location for both PM_{2.5} and VOC. In addition, the TO-15 lab will participate in a Proficiency Test "blind" sample to determine if the bias in the analysis is within acceptable ranges.

Data reporting

Quality assured and verified data collected for the NAAGMI will be housed in the SCRIBE database. Data will be input in the SCRIBE data as soon as possible after receipt from the appropriate labs. All data will be reported, even if the concentrations detected fall below the determined MDL's. No data substituting will be allowed. VOC data and PM2.5 samples will be reported in $\mu\text{g}/\text{m}^3$. All data will be reported under local conditions. The list Null and QA flags can be found in Section 5 of the NATTS TAD at:
<http://www.epa.gov/ttn/amtic/airtox.html>.

ATTACHMENT A -- Site

Brigich Compressor Station, Chartiers Township, PA



Location #1 = Brigich Road

Location #2 = Jasper Way

Location #3 = Plum Run Road

ATTACHMENT B -- Monitoring Approaches

VOCs

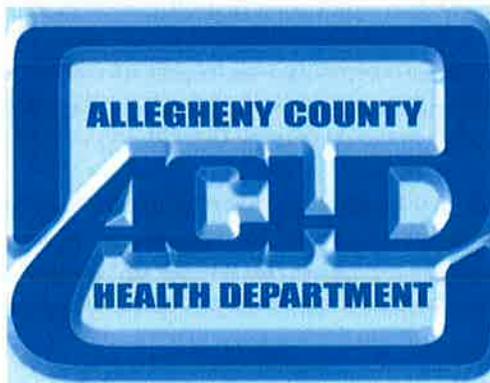
- Passive Canisters
 - o Small, portable easy to site on property
 - o Canister, flow regulator, and timer should be shielded from direct sunlight if possible
 - o Inlet should be at ~2m so the canisters may need to be elevated
 - o Equipment Specifications:
 - Canister
 - 6L internal volume Summa
 - Silonite valve
 - ¼ inch tube fitting sample line connection
 - Passive Air Vacuum Regulators
 - ¼" silonite treated inlet
 - o 2-micon frit of filter and washer located at critical orifice
 - o Orifice size .0012" (flow range b/t 2-4cc/min)
 - Canister Air Sampling Timer/Solenoid Valve
 - o Compatible w/ any canister and passive flow controller
 - o 7-day/24-hour programmable timer capable of automated sampling
 - o Battery operated capable of accommodating a 24-hour sample
 - o 1/4 " Swagelock® inlet and outlet fittings
 - o Waterproof exterior
 - o Sampling duration and rate: 24 hours and 3.5 cc/min
 - o Sampling medium: ambient air canister
 - o Sampling Analysis: TO-15 (GC-MS)

PM_{2.5}

- Low-volume particulate sampler with PM_{2.5} size selection inlet
 - o No shelter requirements
 - o Inlet should be at ~2m so the samplers may need to be elevated
 - o Battery operated
 - o Equipment specifications
 - Programmable timer
 - 47mm Teflon filter
 - o Field calibration kit
 - o Analysis method: Gravimetric weighing

APPENDIX B

**ALLEGHENY COUNTY HEALTH DEPARTMENT
AIR QUALITY PROGRAM
MONITORING SECTION
PITTSBURGH, PENNSYLVANIA**



Analytical Standard Operating Procedures

February 2012

PM2.5 Analysis

I. Scope and Application:

The objective of the PM2.5 Project is to provide ambient data that supports the NGAAMI. This method is useful for determining the PM2.5 fine particle concentration in the atmosphere at various predetermined area locations. New filters are labeled, conditioned, weighed and sent to the site. The Field Personnel (or other Agency Personnel) place the filters within the sampler to collect sample, then return the filters to the laboratory where the Laboratory Personnel condition and weigh the exposed filters

II. Method Summary

The overall goal of the PM2.5 Project is to provide data as PM2.5 (particulates with an aerodynamic diameter of 2.5μ or less) net weight filter values collected from the various predetermined sites. This net mass value can be obtained through using both the tare and gross weight of a filter. The Field Personnel are to supply additional data as needed, which along with the net weight (tare and gross weight) enable the calculation of PM2.5 Concentration.

The net mass of a filter is obtained by taking the difference between the tare and gross weights of that filter. Tare weight is the weight of the specific filter after it has been conditioned and before it is sampled. The gross weight is the weight of the specific filter after it has been sampled and after it has again been conditioned. Both procedures are done in the laboratory.

III. Interferences

A. Safety in Laboratory - Refer to Laboratory Safety Manual

1. Health & Safety Warnings

Standard Laboratory protective clothing, lab coat and eye protection are not required, but recommended and wearing powder-free gloves while handling filters is required. The Laboratory personnel will wear an anti-static lab coat and gloves when handling the filters. Refer to Section A3.

2. Cautions

Observing proper filter handling, discussed earlier, is necessary. This involves wearing powder free gloves (which is required) and smooth, stainless steel, non-serrated forceps to handle the filters. Never let the gloves or the skin come in contact with the filter. This could affect the final mass measurements. The filters are extremely delicate and are to be treated as so, never be rough with the filters because this could cause loss of sample or loss of filter integrity (tear, separation of ring, etc....).

Always handle the mass reference standards with smooth, non-metallic forceps and store the standards within the conditioning room. By handling the mass standards in this manner it prevents them from corroding and it helps maintain the integrity of the standards. The Laboratory personnel will keep the laboratory standards separate from the working standards. The Laboratory personnel will clearly label the standards "Working" or Laboratory to alleviate any errors that may occur. The working standards are calibrated against the laboratory standards and both sets are to be calibrated according to the manufacturer's recommendation (Denver Instruments).

Cleaning the working standards weight forceps and the filter forceps before their use is necessary. The filter handling forceps and mass reference forceps are to be cleaned with alcohol and lint free wipes. The Laboratory personnel will use moistened alcohol wipes and Kimwipes™ to clean the forceps.

The Conditioning Room is to be kept in order, clean and free of dust. By maintaining cleanliness of the room, it eliminates any contamination that may occur to the filters during their conditioning period and weighing session. No non-approved cleaning solution is allowed to be used in the conditioning room, only anti-static solution may be used.

Weight loss is an important part of the monitoring program. Weight loss can result from a number of different areas: the evaporation of semi-volatile organic compounds the loss of water, thermal or chemical decomposition. These weight losses are controlled by keeping the sample cool during transport to the analytical laboratory. The appropriate temperature for transport, if samples are to be conditioned and post-weighed within 10 days of the end of the sampling session, is $< 25^{\circ}\text{C}$ (77°F). Filters must be stored at $\leq 4^{\circ}\text{C}$ (39.2°F), if they are to be weighed between 10 and 30 days after sampling. In both instances, one must allow the filters to warm up to the conditioning room's temperature. If this is not done,

condensation can occur within the petri dish causing grounds for voiding of a sample.

3. Interference's

Several factors may interfere with accurate and precise results within the PM2.5 measurement process. One such factor is static, which is a force or charge that could build up on the filters during the weighing and sampling procedure and cause incorrect and unstable weight readings. Filters are susceptible to static and can be difficult to weigh at times. Static makes samples difficult to handle and at times, even cause degradation of the sample by attracting contaminating particles. With these problems associated with static, the PM2.5 Project calls for an anti-static agent, such as an anti-static strip. These anti-static units neutralize the surface charged, either positively or negatively, simply by bringing filter an inch from the anti-static agent for a few seconds. The Laboratory Personnel will be using static masters. The filter will be placed on the static master (which is a ²¹⁰Po Strip) for about 30 seconds, it will then be placed on the balance pan where three (3) static master strips are placed.

Another interference involved in the PM2.5 Project is the conditioning environment. Being conditioned before both pre- and post-weighing sessions at a constant temperature and humidity is necessary for the filters. How much time a filter is to be conditioned is determined by using a lot blank. If the filter is not conditioned for the proper amount of time, this affects the reproducibility of the weight measurements. In other words, a drift in weights can be seen when replicate measurements are taken, which presents concerning data integrity and validity.

B. Troubleshooting

Troubleshooting involves taking corrective action if a part of the PM2.5 Monitoring Project happens to not go as planned. Such corrective action with respect to the laboratory includes:

- ◇ Weigh Room Humidity Out of Specification - Check HVAC system
- ◇ Weigh Room Temperature Out of Specification - Check HVAC system
- ◇ Balance Internal Calibration Unstable - Recheck working standards
- ◇ Balance zero Unstable - Recheck and look for drafts
- ◇ Balance Working Standards Out of Specification - Check Working Standards with Laboratory Standards
- ◇ Balance Filter Weighing Unstable - Check Lab Blanks, because it could be that the filters were not conditioned long enough and Document in Log Filter Book

- ◇ **Balance Working Standards Out of Specification - Re-zero Balance and recalibrate, Recheck Working standards; if still out of specification, it is necessary to have the working standards calibrated by the manufacturer (Denver Instrument Company).**

C. Temperature and Humidity Control System

HVAC contractor shall provide 100 percent full parts and service through May 31, 2004. Service will be provided within two working days of notification. Semi-annual preventive maintenance visits will be conducted, at six (6) month intervals, each of the four (4) years.

D. Electrostatic Charge Neutralization

Electrostatic charge build-up will prevent a Microbalance from operating properly. Static charge is the accumulation of electrical charges on the surface of a non-conductive material. Common symptoms of this problem, include a noisy readout, drift and sudden readout shifts. To reduce static charge within the balance, three (3) radioactive anti-static strips are placed in the weighing chamber of the Microbalance. Every filter is held over two (2) anti-static strips for a minimum of at least thirty (30) seconds before weighing.

Anti-static strips are used to reduce electrostatic build-up in the Microbalance's weighing chamber and on individual filters by charge neutralization. They neutralize electrostatic charges on items brought within an inch of them. Change the anti-static strips every six (6) months and dispose of the old strips according to the manufacturer's recommendations. Anti-static solution on a cloth is used, as needed, on all counter tops in the balance room area.

Do not assume that grounding eliminates all electrostatic build-up, because the electrical ground may not be perfect. Eventhough a filter weight be stabilize within thirty (30) to sixty (60) seconds and no there no weight drift is observed during that period, the Microbalance may still be influenced by some electrostatic build-up.

IV. Sample Handling and Preservation

A. Blanks

Laboratory blanks should be kept inside the conditioning chamber except during weighing sessions.

B. Exposed

After postsampling conditioning and weighing all filters (routine filters and blanks) will be placed in their respective petri slides and will be numerically stored at 4°C or below, in a petri slide holder. Previously voided filters will also be stored. The completed filters will be picked up periodically by Field Personnel for final storage by Field Personnel. The PM 2.5 Exposed Filter Storage form will be filled out (Form #5).

V. Apparatus

- A. Zymate Robotics System
- B. MX5 Microbalance
- C. Dataloggers

VI. Reagents

No reagents are required.

VII. Procedure & Analysis

A. PM2.5 Start-up Procedure

1. Conditioning Room

Three (3) Dickson Brand NIST traceable data loggers and a chart recorder are used to monitor daily room Temperature and Relative Humidity (RH). The Conditioning Room requirements are as follows:

Temperature Range:	20-23° C (24-hour mean)
Temperature Control:	± 2° C over 24 hours
Relative Humidity Range:	30%-40% (24-hour mean)
Humidity Control:	±5% over 24 hours

Every day the Laboratory Personnel are to monitor temperature and relative humidity to ensure they fall within the required guidelines (Form #9). A Data Logger Acquisition System will monitor the Temperature and Relative Humidity within the Conditioning Room.

The Data Logger Acquisition System is designed to collect, process and store data from three (3) areas in the room. They are located in the conditioning area, near the Microbalance and across the room. The data loggers are set to collect data at two (2) minute intervals. Data stored in data loggers are downloaded at 24-hour intervals and

evaluated to determine if the environmental conditions are within the control limits. Charts generated from the data are printed and stored (Form # 1). NIST traceable annual calibration of the data loggers is performed. Verification, using saturated salt solution, is done quarterly.

The operation of the Data Logger Acquisition System is discussed in its User's Manual. The specifics will not be discussed in this SOP.

2. Turn on the Computer, Monitor and Microbalance

A Mettler Toledo MX-5 Microbalance with resolution of 1 µg and repeatability of 1 µg is used. It is linked to a computer for automatic weight data transfer. The Microbalance is on "stand-by" when not in use.

3. Calibrate Microbalance

The Microbalance is to be calibrated by Laboratory Personnel prior to every weighing session using its internal calibration mechanism, as well as, mass reference standards (to check balance repeatability). The Microbalance is calibrated annually by a Mettler Service Technician and maintained according to the manufacturer's recommendations. If it is out of calibration, a Microbalance Service Technician is contacted. Microbalances are vulnerable to relatively small changes in physical environmental conditions, such as vibration, electrostatic charge buildup, temperature and relative humidity (RH).

The Microbalance is located in the same controlled environment in which the filters are conditioned. The Microbalance is located in a climate-controlled, draft-free, positive-pressure room to minimize human traffic effects and to stabilize the conditions of the weighing environment. The room is only used for weighing and conditioning filters; no chemicals are permitted in this room. Dust contamination will be minimized by taking clean room measures such as cleaning the weighing area daily and wearing clean laboratory clothing.

A. Microbalance Internal Calibration

- 1. Ensure balance is turned on.**
- 2. Clean balance and area surrounding balance using a fine brush.**
- 3. Check to see if the balance is level by checking bubble level on top of balance; the bubble should be at the center of the bubble level indicator.**
- 4. Calibrate balance using calibration mechanisms; an internal calibration within the balance which is performed every time the balance is used.**
- 5. Zero balance by pressing "tare" bar located on balance (on/off) bar.**

B. Microbalance Standardization

Using NIST traceable weights, Microbalance Standardization is done prior to each weighing session. Weigh the Working Standards which include 100 mg and 200 mg working standard weights, with a tolerance of no more than 0.003 mg. Record results of balance standardization in the balance log book (Form #2). If standardization does not meet specification, the proper troubleshooting actions are to be taken:

1. Verify weights.
2. Recalibrate the Microbalance.
3. Examine the weights for dirt and/or damage.
4. Clean the Microbalance.
5. Check the Working Mass Standards against the Laboratory Mass Standards.
6. Call for service.

<u>NIST Traceable Weight</u>	<u>Specifications</u>
100.000 mg	± 0.003
200.00 mg	± 0.003

The mass reference is re-certified at least annually with a NIST certificate of traceability.

Two (2) separate sets of mass reference standards are used. Working Standards is used for routine filter weighing and kept next to the Microbalance in a protective container. Laboratory Calibration Standards are handled very carefully and should be kept in a locked compartment. The Working Standards' masses are verified against the Laboratory Standards every 3 months to check for mass shifts associated with handling or contamination. The verified values of the Working standards as measured relative to the Laboratory Standard are recorded in a QC notebook and used to check the calibration of the Microbalance (Form #2).

Always use smooth, nonmetallic forceps for handling mass reference standards. The standards are handled only with these forceps, which are not used for any other purpose. Mark these forceps to distinguish them from the forceps used to handle filters. Forceps are cleaned with alcohol and lint-free wipes before handling standards and then should be allowed to air-dry. Handle the standards carefully to avoid damage that may alter masses.

B. Initial Examination of PM2.5 Filters

1. Inspection

Whenever filters are handled, the analyst must wear anti-static, powder-free gloves; these gloves act as an effective contamination barrier. Certified powder-free gloves that are free of chlorides, nitrates and sulfates are used. The filters are handled carefully by the support ring, rather than by the filter material, with smooth, non-seriated forceps that are used only for that purpose. Forceps are cleaned with alcohol and lint-free wipes before handling filters and then allowed to air-dry. These precautions reduce the potential effect from body moisture or oils contacting the filters and subsequently affecting the measured weights.

In the laboratory, each filter is transferred from its sealed manufacturer's packaging to a clean Millipore petri slide. The filter remains in this container, except for weighing, until it is loaded into a filter cassette prior to sampling. The manufacturer stamps each filter with its own unique identification number. The filter number is transcribed on the petri slide and bar code label is generated and placed on the back of the petri slide.

All filters are visually inspected for defects before the initial weighing. Filters are inspected over a light box with the filters handled with Teflon coated forceps. If any defects are found, label the petri slide with the relevant code number and the term *VOID*. Return any lot of filters containing a high number of defects to the supplier. Specific filter defects to look for are the following:

<u>VOID CODE</u>	<u>REASON</u>	<u>EXPLANATION</u>
1	Pinhole	A small hole appearing (a) as a distinct and obvious bright point of light when examined over a light table or screen, or (b) as a spot when viewed over a dark surface.
2	Separation of Ring	Any separation or lack seal between the filter border reinforcing the ring.

<u>VOID CODE</u>	<u>REASON</u>	<u>EXPLANATION</u>
3	Chaff or Flashing	Any extra material on reinforcing ring or on the heat seal area that would prevent an airtight seal during sampling.
4	Loose Material	Any extra material or dirt particles on the filter.
5	Discoloration	Any obvious discoloration that might be evidence of contamination.
6	Filter Nonuniformity	Any obvious visible nonuniformity in the appearance of filter when viewed over a bright table or black surface that might indicate gradations in porosity or density across the face of the filter.
7	Other	A filter with any imperfection not described above such, irregular surfaces or other results of poor workmanship. Lab accidents are included under this category.
8	Other	Any reason to void filters by Field Personnel. Exposed filters only.

2. Conditioning

New filters are stored in the manufacturer's packaging in the balance room until they are conditioned prior to use. Filters must be conditioned immediately before both the pre- and postsampling weighings. Conditioning time is determined by performing a stability check (Lot Blanks). Ten (10) random filters from each "Lot" will be weighed at daily intervals for a two (2) week period. Filters will be considered conditioned when they show <15 µg change in any 24-hour period.

Filters must be conditioned at the same conditions before the pre- and postsampling weighings. Mean RH must be held between 30 and 40%, with a variability of not more than $\pm 5\%$ over a 24 hour period. Mean temperature should be held between 20 and 23°C, with a variability of not more than $\pm 2^\circ\text{C}$ over 24 hours. RH and temperature is measured and recorded on a continuous basis during filter conditioning (by a recording hygrothermograph and by an electronic instrument). Refer to section A1.

If spikes of temperature or RH occur during the conditioning period, the QA/QC or Lab Manager is to evaluate all relevant data and decide if the spikes are significant enough to compromise the conditioning period. The evaluation also includes the significance of the timing of the spike in relation to the time of the weighing; the closer to the weighing, the more significant the effect on the weight. Filters weighed during these periods of spiking are re-weighed under acceptable conditions and evaluated relevant to all results. The one (1) Microbalance assigned uniquely for the weighings, has its own internal temperature compensator for minor changes. When activated calibration of internal standards occurs automatically when extreme temperature changes occur.

The environmental recording devices used, continuously display temperature and %RH readings with periodical interval. The data is stored in the logger until downloaded, saved to file and cleared. In this situation, the data evaluator will use a rolling (accumulative) average for the 24 hour period.

The conditioning chamber for all filters consists of a covered rack that will allow air to circulate over the filters, while reducing the likelihood of air-borne material settling onto the filters. This chamber is located within the "controlled" environment. Blank filters occupy the upper shelves, while exposed filters occupy the lower shelves. All filters being conditioned are contained in their petri slides with their lids ajar for ventilation. The lids rest on the appropriate petri slide base. Clean filters are arranged in their particular groups in filter number order. Exposed filters are arranged in filter number order according to their "weigh by dates," which is determined by the sample date and storage temperature.

3. Weighing

The Microbalance must be located in the same controlled environment in which the filters are conditioned. The filters must be weighed without intermediate or transient exposure to other conditions or environments. The reference method (EPA 1997) requires that the pre-sample filter weighing be conducted within thirty (30) days of the sampling period.

The following steps are followed during pre-sampling filter weighing:

- 1. Record the RH and temperature of the balance room in the QC notebook.**
- 2. Clean the Microbalance's weighing chamber with a fine brush used for this purpose only.**
- 3. Clean the surfaces near the Microbalance with anti-static solution and a lint free cloth.**
- 4. Clean filter forceps with an alcohol-moistened disposable laboratory wipes. Allow the forceps to air-dry. Make sure the forceps are thoroughly dry before use.**
- 5. To ensure maximum stability, the Microbalance is on at all times. After use the balance is put in "Stand-by" condition by lifting up on the tare bar.**
- 6. Level the balance using the air-bubble window and adjusting the two (2) feet. Zero and activate the internal calibration by pressing the menu button, then pressing the tare button. Wait until the calibration is completed.**
- 7. Using smooth, non-serrated, non-metallic forceps found within the working standard weight containers, weigh two (2) working mass reference standards carefully. Avoid damage that may alter the masses. Use the "print" key that automatically selects the stable reading. Record the observed values of these standards in the Laboratory QC notebook and compare these values with their certified values. Observed weights must be $\pm 3 \mu\text{g}$ of their certified weight.**
- 8. Exercise Zymate System according to the manufacturer's directions.**
- 9. Take a filter from its filter-handling container (petri slide) by gently slipping the filter-handling forceps under the outer polyolefin- supporting ring. Set up the filters in numeric order in the racks of the Zymate System. The first (1st) filter is always a Lab Blank (Working Mass Standard). Be sure when setting up tare weights that a blank space is left for voided filters which are not weighed.**

10. Weigh the filters. Operate the Zymate System according to the manufacturer's direction. One (1) anti-static strip should be inside the weighing chamber.
11. After every ten (10) filters, the first filter (LB) is re-weighed as a "Working Mass Standard". If the "standard" is not within the QC limits, re-weigh the standard. If after the re-weigh the "standard" is still out of range, perform corrective action (pp 6.B.1-6) and re-weigh the previous ten (10) filters.
12. An analyst performs Quality Control. Every third (3rd) filter is re-weighed. The difference between the "tare" and "QC" weights must be within $\pm 15\mu\text{g}$. If this value exceeds the $15\mu\text{g}$ limit, first verify the weight, then refer to Section 3B (1-6) for corrective action and re-weigh the previous three (3) filters. The results are recorded in the database and on the PM2.5 Pre-Sample Filter Data Sheet (Form #7) or Post-sample Weigh Log Sheet (Form #6).
13. Return the filters to the filter-handling container (petri slide) and replace the lid to seal the filter. Information is added to the labeled petri slide, including the date weighed, station location number and filter description (such as, LB, FB, TB or TFB). The filters are placed back into the petri slide holder.
14. Transfer the data according to the manufacturer's directions into the appropriate database (i.e. pre-weight, pre-weight QC, post-weight, post-weight QC or 5-Day QC).
15. The filters are ready for packing and transport.

Both pre- and postsampling filter weighings are performed on the same Microbalance.

4. Documentation

The Chain of Custody form will supply all or some of information which includes the following elements:

- ⇒ Tare/Gross Weight Analyst
- ⇒ Tare/Gross Weight Date
- ⇒ Tare/Gross Weight Time
- ⇒ Filter ID Numbers
- ⇒ Filter Type
- ⇒ Sampling Date
- ⇒ Voids

- ⇒ **Sample sender/receipt analyst, date and time**
- ⇒ **Actual/Minimum/Maximum transport temperature**

Filter flags and necessary notes The station names and numbers, number of filters per station (lab blanks, the number of routine filters and a field blank) are as follows:

The form will supply all or some of the following information elements:

- ⇒ **Conditioning Date**
- ⇒ **Weigh Date**
- ⇒ **Use by Date**
- ⇒ **Lot Number of filters used**
- ⇒ **Filter Numbers**
- ⇒ **Station Numbers**
- ⇒ **Filter Type**
- ⇒ **Voids**
- ⇒ **Tare Weight of Filters**
- ⇒ **Replicate filter weights (every three (3) filters)**
- ⇒ **Zero and Working mass standards after every tenth weighing**
- ⇒ **Cassette Numbers**
- ⇒ **Weighing Analyst's initials**
- ⇒ **Relative Humidity and Temperature of Conditioning Room just prior to each weighing session**
- ⇒ **Batch/Station Number**
- ⇒ **Sample receipt date**
- ⇒ **Maximum transport temperature**
- ⇒ **Must be weighed within 30 DAYS or 10 DAYS**
- ⇒ **Filter flags and necessary notes**
- ⇒ **Gross Weight of the Filters**
- ⇒ **Difference of post-sampling and pre-sampling weights**
- ⇒ **5-Day QC reweigh**

C. Packaging of PM2.5 Filters

1. Petri Slides

The filter will be received in the manufacturer's packaging. Prior to conditioning, the filter is examined for defects and is placed in the petri slide. The petri slide will be labeled with the Filter Identification Number. The lid is to remain on the petri slide, except during conditioning and weighing periods, in which case the lid is removed and placed ajar on the petrislide.

Immediately following the weighing session the lid is to be placed on the petri slide and the filter is to be prepared for shipment and/or archival.

2. Cassettes/Cylinders/Metal Boxes

Cassettes, and Metal Boxes are used to transport filters to their pre-determined sites. Check the filter cassettes and the backing screens for fractures, crack, evidence of wear or contamination. Clean or replace as necessary. Physically damaged screens can be used as holders for field, transfer or trip blanks, because they do not sample in the field monitors. All components of the used cassettes are cleaned in a dishwasher and then rinsed with deionized water.

When the filters are to be used at the sites (use must occur within thirty (30) days of the initial weighing), install each filter in a filter cassette. The filter cassette is arranged so that the manufacturer's filter numbers are up and screen numbers down. Record the cassette ID number (from the screen) in the database and on the PM2.5 Pre-Sample Filter Data Sheet. The filter/cassette assembly is then placed into a cylinder for transport (which is labeled with the following information: station number, filter numbers in numerical order and special features (FB, TFB or TB)*. The filters are picked up by Field Personnel on a weekly basis.

The filter cassette holds the filter in the sampler during Sampling Period. Sample collection includes placing the filters within the sampler, collecting sample, removing filters from the sampler and returning the filters to the analytical laboratory. Sample Collection is the responsibility of the Field Personnel.

D. Receipt of PM2.5 Filters

1. Check Paperwork

Upon receipt of the samples from the field, the analyst examines the PM2.5 Monitoring Program Chain of Custody Form. Determine whether all data needed to verify sample validity (e.g., sampling date, any reason to flag the filter from the field) are provided. If data are missing, out of range, unobtainable from a field operator or if sampler malfunction is evident, save the filter for inspection and record on the PM2.5 Monitoring Program Chain of Custody Form that the sample has been flagged and the reason. Check to see if the filters were sampled within thirty (30) days of the "tare weight date". Check to see if the filter numbers match what is on the paperwork and petri slide.

2. Check Filters

All filters must be transported to the laboratory in coolers. The temperature in the coolers must be maintained between 4° - 25°C. The transport temperature will be verified by using a min/max thermometer. Field Personnel will record the min/max temperature during transport at the time of delivery to the laboratory. If the protective container is cold, allow it to warm to the filter conditioning environment's temperature before opening to preclude water condensation on a cold filter. Remove the filter cassette from its protective container and examine the container. If particulate matter or debris is found in the protective container after the filter has been removed, record that the sample has been flagged as questionable and state the reason as a remark at the bottom of the Laboratory data form. Save the filter for inspection and notify the QA/QC Manager and/or Lab Manager.

Confirm the information on the PM2.5 Monitoring Program Chain of Custody Form. Confirm the filter number which is stamped on the filter's support ring with the information on the PM2.5 Monitoring Program Chain of Custody Form. Filters that are voided by Field Personnel are labeled "VOID 8." Inspect the filters for defects and record any on the PM2.5 Monitoring Program Chain of Custody Form under "questionable sample" Record the "weigh by date" (WB) on the petri slide.

Transfer the filters in their petri slides to the conditioning chamber racks with lids ajar. Lab blanks are also prepared for conditioning. If the filters are to be stored $\leq 4^{\circ}\text{C}$, transfer the filters in their (sealed) petri slides to the designated refrigerator. Both filter storage methods require a minimum of 24-hours of conditioning before post-sampling weighing.

3. Documentation

On the PM2.5 Monitoring Program Chain of Custody Form record the date received, initials and actual/minimum/maximum transport temperature. In the database record refrigerated (Y/N), date received, and the date by which the exposed filter must be weighed. Any irregularities noted by the field or laboratory personnel are noted under "questionable sample."

4. Storage

Filter storage involves monitoring the time a filter is stored within the laboratory before shipping to site and post-weighing. A filter must be sampled no longer than 30 days after its tare weighing. The postsampling conditioning and

weighing shall be completed within 240 hours (10 days) after the end of the sampling period, unless the filter is maintained at 4°C or below during the entire time between retrieval from the sampler and the start of the conditioning, in which case the period shall not exceed 30 days. The “refrigerator/freezer” temperature will be checked and recorded daily (Form #4).

E. Processing Exposed PM2.5 Filters

1. Inspection

The same rules apply for inspecting exposed filters as they do for pre-exposed filters (See Section B.1).

2. Conditioning

The same rules apply for conditioning exposed filters as they do for pre-exposed filters (See Section B.2).

3. Weighing

The same rules apply for weighing exposed filters as they do for pre-exposed filters (See Section B.3).

4. Documentation

The same rules apply for documentation of exposed filters as they do for pre-exposed filters (See Section B.4).

F. Storage of Exposed PM2.5 Filters

1. Blanks

Laboratory blanks should be kept inside the conditioning chamber except during weighing sessions.

2. Exposed

After postsampling conditioning and weighing all filters (routine filters and blanks) will be placed in their respective petri slides and will be numerically stored at 4°C or below, in a petri slide holder. Previously voided filters will also be stored. The completed filters will be picked up periodically by Field Personnel for final storage by Field Personnel. The PM 2.5 Exposed Filter Storage form will be filled out.

VIII. Calculations

No calculations are required.

IX. Quality Control

1. Internal Quality Control

Laboratory QC binders and a database (with disk backups), is kept which contains QC data, including Microbalance and standard weights calibration and maintenance information, Hygrometer readings and maintenance information, data loggers, sample shipping and receiving, routine internal QC checks of mass reference standards and laboratory and field blanks. Quality Control within the weighing session is documented on the relevant Laboratory Data Forms and Conditioning Room QC is plotted and placed within a binder to document environmental conditions.

At the beginning of each weighing session, after the analyst has completed calibrating the Microbalance and weighing the two (2) working standards, weigh laboratory and field blanks. Weigh one (1) laboratory blank (LB) during a presampling weighing session to provide one (1) laboratory blank during each subsequent postsampling weighing session. These filters are packaged, taken to the designated field location (done on a rotating basis), then returned to be reweighed. Reweigh 10% plus 1 of the exposed, sampled filters five (5) days after the postsampling session. The 5-Day QC verifies that the filters have stabilized after their initial conditioning.

Record the working standard (every 10 filters, alternating 100 mg and 200 mg weights), blank and replicate weights (every 3 filters) on the Laboratory data form and in the laboratory QC notebook and database. If the working standard weights differ from the verified values of the presampling values by more than $3\mu\text{g}$, repeat the working standard weight. If the laboratory blanks differ from the presampling values or previous postsampling values by more than $15\mu\text{g}$, repeat the blank weight. If the pre- and postsampling weights for the field blanks disagree by more than $30\mu\text{g}$, repeat the weight. If any two (2) weights still disagree, re-weigh all the filters from that station and make a note that the filters are flagged. Weights for sampled filters shall not be corrected to account for blank measurements. High blank values should not cause the automatic invalidation of sampled filters that were measured during the same weighing session. Instead, high blank values will trigger troubleshooting to discover and correct the cause.

QC Limits/Criteria

<u>Criteria</u>	<u>Limits</u>
Field Blanks	$\pm 30 \mu\text{g}$ difference
Laboratory Blanks	$\pm 15 \mu\text{g}$ difference

Lot Blanks	$\pm 15 \mu\text{g}$ difference
Laboratory Temperature Calibration	$\pm 2^\circ\text{C}$
Laboratory Humidity Calibration	$\pm 5\%$
Working Mass Standards	$\pm 3 \mu\text{g}$
Primary Mass Standards	$\pm 3 \mu\text{g}$
Duplicate Filter Weighings	$\pm 15 \mu\text{g}$ difference
Balance Check	$\pm 3 \mu\text{g}$

2. Review of Data

PM_{2.5} Monitoring Program Chain of Custody Form will be reviewed by the analyst and the Laboratory Manager. Each will review the Laboratory data sheets for completion, acceptable filter weighings and QC checks. The QC/QA Manager will prepare a monthly report of all QC and will submit it to the Laboratory Manger.

3. Documentation/Reporting of Data

All Laboratory Data Information (QC and samples) will be sent monthly (via e-mail) to the proper Personnel. Hard copies will be made from the database and kept in storage.

X. References

- A. Data will be stored on a computer hard drive with a daily tape back-up. Also, hard copies will be stored of all data sheets.**
- B. Reference Section**
 - 1.) Quality Assurance Handbook, Vol. II, Part II (2-12 Monitoring PM_{2.5} in Ambient Air Using Designated Reference or Class I Equivalent Methods - 2.12 (7.0 Filter Preparation and Analysis)). November 1998.**

FORM #1

**BALANCE ROOM
PM 2.5
Environmental Conditions**

Period Ending
6-20-00

Logger *W*

Temperature		% Relative Humidity	
Mean	21.66277174	Mean	35.81413043
Standard Error	0.032519644	Standard Error	0.083824635
Median	21.6	Median	36
Mode	20.9	Mode	37.6
Standard Deviation	0.882235831	Standard Deviation	2.274105354
Sample Variance	0.778340062	Sample Variance	5.171555161
Kurtosis	-0.567277172	Kurtosis	-0.681571763
Skewness	0.430737651	Skewness	-0.278772973
Range	3.8	Range	10.5
Minimum	20.1	Minimum	30.1
Maximum	23.9	Maximum	40.6
Sum	15943.8	Sum	26359.2
Count	736	Count	736
Confidence Level(95.0%)	0.063842529	Confidence Level(95.0%)	0.164564431

Limits:

Temperature:

The 24 Hr. mean must not exceed the range of 20°C to 23°C

The 24Hr. Standard deviation must be $\leq 2^\circ\text{C}$ @ the 95% confidence limit

% Relative Humidity:

The 24 Hr. mean must not exceed the range of 30% to 40% RH

The 24 Hr. standard deviation must be $\leq 5\%$ RH @ the 95% confidence limit

Environmental conditions **MEET** / **EXCEED** allowable limits.

Reviewer *M*

Date *6-20-00*

FORM #2

QC LOG Year PAGE #
 Balance Calibration
 Working Mass Verification
 Balance S/N

Working Mass Verification					Month	Cal Analyst	Working STD: 100 mg	Working STD: 200 mg
Date	Temp	% R.H.	Analyst	DAY				
	Primary std: 100 mg	Working std: 100 mg	Primary std: 200 mg	Working std: 200 mg				
W:1					1			
W:2					2			
W:3					3			
X:W					4			
					5			
					6			
					7			
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Date	Corrective Action							

