pennsylvania
DEPARTMENT OF ENVIRONMENTAL PROTECTION

Technical Support Document for Long-Term Ambient Air Monitoring Project Near Permanent Marcellus Shale Gas Facilities Protocol

August 1, 2013

Commonwealth of Pennsylvania
Department of Environmental Protection

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Introduction

On July 23, 2012 the Department of Environmental Protection released the document "*Long-Term Ambient Air Monitoring Project near Permanent Marcellus Shale Gas Facilities Protocol*". The July document presented key elements of the ambient air sampling plan and study protocol developed by the Department for its one-year project to study the potential toxic air pollution near permanent facilities handling, transporting and processing unconventional natural gas extracted from the Marcellus shale formation underlying Washington County.

This Technical Support Document (TSD) provides supplemental information for the July protocol document and provides additional information on the study's sampling site locations and equipment configurations.

Section I, Study Management & Planning, provides information on the study's goals, tasks, and overall design. It also shows the management and oversight structure and identifies key Department resources that will be employed in the execution of the study.

Section II, Study and Site Design, includes detailed information on the overall study design and the design of the individual sampling sites within the study area.

Section III, Study Implementation, describes the deployment plan for the sampling sites, the selected sampling and monitoring equipment with performance specifications to be employed for the study, analysis methods, plans for data acquisition and management, and an overview of Quality Assurance / Quality Control methods and procedures.

Section IV, Data Validation, Analysis and Results Reporting, details methods and procedures to be used for validating collected data. Data analysis methods, procedures and result action items are discussed.

I. Study Management & Planning

This section will describe the study's management structure, describe the overall study goals and discuss the major tasks that the Air Quality Monitoring Division will undertake to meet those goals.

1. Study Management

This study will be managed by the Department of Environmental Protection, Bureau of Air Quality, Division of Air Quality Monitoring, Toxic Monitoring Section. The study manager is Michael Hopko, Environmental Group Manager for the Toxic Monitoring Section. Questions concerning the protocol or this technical support document can be directed to the Study Manager via mail at:

> PA Department of Environmental Protection
> Bureau of Air Quality
> Toxic Monitoring Section; Attn: Michael Hopko
> Rachel Carson State Office Building
> PO Box 8468
> Harrisburg, PA 17105-8468,

or by e-mail at:

mhopko@pa.gov

The study will incorporate staff from the entire Air Quality Monitoring (AQM) Division to complete most tasks associated with the study. Other Department and Bureau of Air Quality (BAQ) assets will be employed as needed and specified in this document. Figure 1 shows a select organizational structure of the AQM Division.

Figure 1- PA DEP Air Monitoring Division Basic Organizational Structure
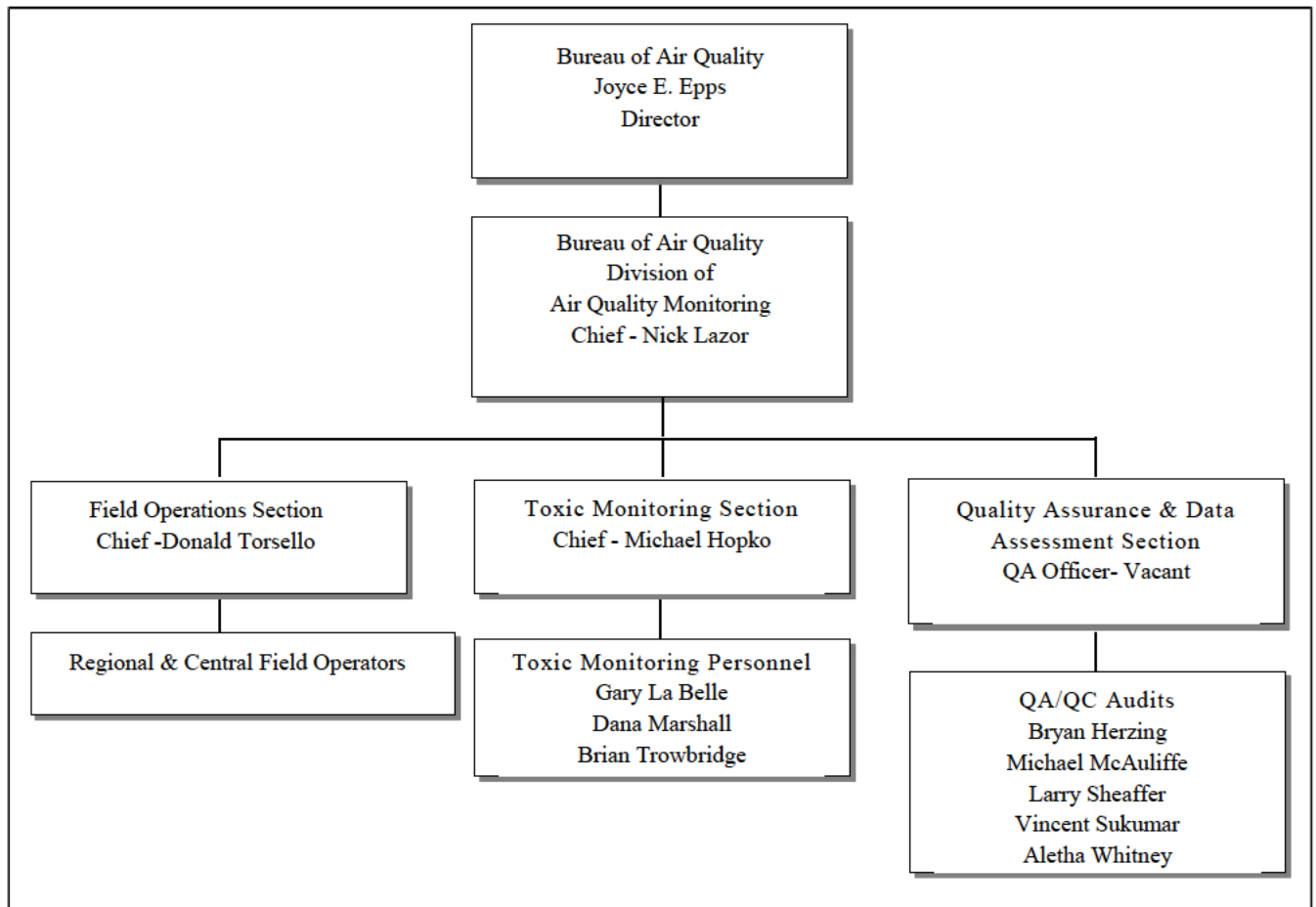
The Field Operations Section will equip and deploy all monitoring locations associated with monitoring criteria pollutants, provide field operators to operate criteria monitoring equipment, and effect field maintenance and repairs. These operators will also collect discreet samples from toxic monitoring samplers and perform basic field maintenance on toxics monitoring equipment when required, and at the direction of the Toxic Monitoring Section.

The Toxic Monitoring Section will equip and deploy all sampling and monitoring equipment associated with toxic pollutant monitoring. This section will also perform maintenance and repair functions on toxic sampling equipment that cannot be effected by Field Operators. The Toxic Monitoring Section will also

manage collected air toxics sampling data and results and perform analysis consistent with the analytical goals specified in Section I.3. of this document.

The Quality Assurance and Data Assessment Section (QA/DA) will manage criteria pollutant data by performing quality assurance / quality control (QA/QC) and ambient criteria pollutant air quality standard analysis functions for all collected criteria pollutant data consistent with the study goals specified in Section I.3 of this document.

The Department's Bureau of Laboratories will perform analyses of discreet ambient air samples collected for this project. The laboratory is an accredited environmental laboratory under the National Environmental Laboratory Accreditation Program (NELAP).

Additional information on the organizational structure and management of the Air Quality Monitoring Division can be found in the Quality Assurance Project Plans (QAPPs)[1] for the respective sections and pollutants measured.

2. *Study Planning*

Study planning commenced as results from three short-term screening studies conducted in 2010 provided insight into the general nature of emissions associated with Pennsylvania natural gas production, processing and transportation activities. Activities surrounding the establishment of study goal and task criteria, resource planning, fiscal budgeting and preliminary siting activities commenced in late 2010 and through 2011. Study implementation began in early 2012 with the first monitoring stations commencing data collection in July of 2012. The general study protocol, "*Long-Term Ambient Air Monitoring Project near Permanent Marcellus Shale Gas Facilities Protocol*" was published on the Department's website on July 23, 2012[2]

3. *Study Goals & Tasks*

The initial July 2012 protocol described a primary overall study goal and four technical objectives (goals) that were established to guide the completion of the primary goal. The ultimate completion of these goals and objectives will enhance both the Department's and the public's understanding of potential air-quality related health risks associated with air quality impacts in areas that contain sources of air pollution related to the natural gas extraction, processing and transport industry. For this document, aspects of the four protocol technical objectives have been reframed to create a more precise overall study goal with two direct secondary goals and are listed in section 3a.

One of the four technical objectives in the July 2012 protocol addressed using Forward-Looking Infra-Red (FLIR) volatile organic compound (VOC) imaging technology to "conduct visual emissions surveys of the target sources". This specific technical objective will be addressed separately in Appendix G of this document and is largely independent of the risk assessment goals described below. This is due to the fact that the FLIR technology is unable to specifically identify or quantify concentrations of compounds

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[1] QAPP documents are available upon request by contacting the Study Manager through the contact information in Section I.1.

[2] Protocol is available at http://www.dep.state.pa.us/dep/deputate/airwaste/aq/toxics/toxics.htm

observed to be emitted and will serve only to assist in study site and target source gross characterization, not in ambient air pollutant concentration measurement.

Specific study team tasks have been established in Section 3b, the completion of which will largely help the study team achieve the stated primary and secondary goals.

a. Statement of Goals

The overall goal of the study is to "determine any chronic or long-term risks to the public from individual or multiple shale gas sources"[3]. This goal includes examination of both hazardous air pollutants (HAP) and criteria pollutants[4]. Data on target pollutant concentrations are to be collected over a one-year period and analyzed using EPA-recommended or approved data-reduction, summary and risk analysis techniques.

For the purpose of this study, "shale gas sources" include, but are not limited to, permanent facilities in the study area that are associated with the extraction, treatment, transport and/or processing (including fractionation) of natural gas and natural gas liquids (NGLs) extracted from the Marcellus Shale formation underlying the Commonwealth. While the short-term studies[5] described in the study protocol did examine emissions from operations surrounding the drilling and completion of new natural gas extraction wells, the short-term duration of these activities at individual well pads (usually less than six months) can possibly bias an analysis of chronic risk that generally use an estimated one year mean ambient pollutant concentration. Study design and siting considerations are discussed in the next sections.

A second goal of the study is to identify and assess potential increases in ambient concentrations of criteria pollutants in the project area over the time period of the study and to compare observed ambient concentrations to historical data collected both in the study area and other existing monitoring locations within the Commonwealth. Collected criteria pollutant measurement data will also be compared to the current corresponding primary and secondary National Ambient Air Quality Standard (NAAQS[6]).

The final goal of the study is to assess and identify potential implications the observed results may have in other areas of the Commonwealth with varying populations and environmental conditions that may host similar facilities.

The original protocol document also included a goal to gather information on potential sources of fugitive emissions at permanent shale gas sources using mobile infra-red optical gas imaging technology. As this singular evaluation goal is significantly different from the ambient air concentration measurement described in the first two goals, the task and procedures for this goal will be discussed in Appendix G.

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[3] *Long-Term Ambient Air Monitoring Project near Permanent Marcellus Shale Gas Facilities Protocol,* PA DEP, July 23, 2012

[4] A "criteria pollutant" is one for which a NAAQS has been established by the EPA under the federal Clean Air Act. Criteria pollutants include Carbon Monoxide, Lead, Nitrogen Dioxide, Ozone, Particulate Matter (2.5 and 10 microns aerodynamic diameter), and Sulfur Dioxide.

[5] The three short-term screening studies can be found at http://www.dep.state.pa.us/dep/deputate/airwaste/aq/toxics/toxics htm

[6] Information on the National Ambient Air Quality Standards (NAAQS) can be found at http://www.epa.gov/air/criteria.html html.

b. Description of Major Tasks and Criteria

The following major tasks are required to achieve the study goals.

- Design an ambient air monitoring study that will gather systematic criteria and/or toxic pollutant concentration and accompanying meteorological data downwind from a permanent large source(s) and/or cluster of smaller permanent sources that are associated with shale gas extraction, treatment, transportation, and/or processing (including fractionation). The data collected from the study will be used for chronic risk assessment, exposure assessment, historical data / ambient standard comparative purposes and, where able, source contribution investigation.

- Create one or more sampling sites within the study area that monitor for criteria and/or toxic pollutants from representative shale gas sources. These sites will be optimized, where practicable, for sampling ambient air inhaled by a local population. One or more additional sites will collect ambient air to represent either upwind or background concentrations of ambient air pollution.

- Deploy sampling equipment and infrastructure, where practicable, that is both consistent with EPA-approved or recommended sampling/monitoring methods and the study design. Any deviations from approved or recommended methods will be documented. All monitors and samplers will systematically collect data for at least one year or such a time that sufficient data exist to estimate mean ambient concentrations of the measured pollutant with an estimated statistical confidence.

- Acquire data and document data collection in a manner that allows for sufficient quality assurance and quality control (QA/QC) to provide confidence in the quality of the data. QA/QC protocols should be consistent with either EPA required or recommended procedures where practicable.

- Analyze discreet samples using EPA, ASTM International[7], or other acceptable methods using a laboratory that is accredited through the National Environmental Laboratory Accreditation Program (NELAP). The study will use the Department's NELAP accredited Bureau of Laboratories for analytical analysis.

- Use and document data analysis methods that are consistent with scientific practice. Provide transparency on collected data and methods in order to achieve result reproducibility for the scientific community and other members of the public.

Many of these tasks have already been completed at the time of the writing of this document.

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[7] An international standards organization that until 2001 was known as the American Society of Testing and Materials. http://www.astm.org/index.shtml

II. Study and Site Design

Consistent with the goals established in the previous section, the Department designed a study to best meet the goals with available monitoring and analysis resources. Both the overall study and individual sampling site designs, where practicable, conformed to latest EPA requirements and guidance for both criteria and non-criteria pollutants. A listing of relevant study and sampling site design guidance documents are contained in the Technical References in Appendix A.

1. Overall Study Design

As indicated in the sampling protocol, the short-term screening studies informed the Department's decision to choose a location in the Pennsylvania portion of the Marcellus play as the focus for the long-term study. Given the association of HAPs with the chemical components of natural gas liquids and the abundance of these liquids in the "wet-gas" held below the Southwestern region of the Commonwealth, the Southwestern region of Pennsylvania, coupled with its rapidly developing associated infrastructure for extracting, processing and transporting this gas and associated liquids, provided the most suitable area for a long-term study.

Washington County (Figure 2) was ultimately specifically chosen as it was the first county to commence extraction from the Marcellus shale in Pennsylvania and, with that county's continued natural gas field development, has significant permanent gathering and treatment infrastructure either in place or in late term development. Furthermore Washington County has more historic ambient air monitoring stations than most other counties of the region. These previously existing stations can provide both existing infrastructure for new monitors and historic ambient concentration data for target criteria pollutants. Appendix B provides additional information on the history and distribution of natural gas field development across Pennsylvania.

Figure 2 - Washington County in Pennsylvania
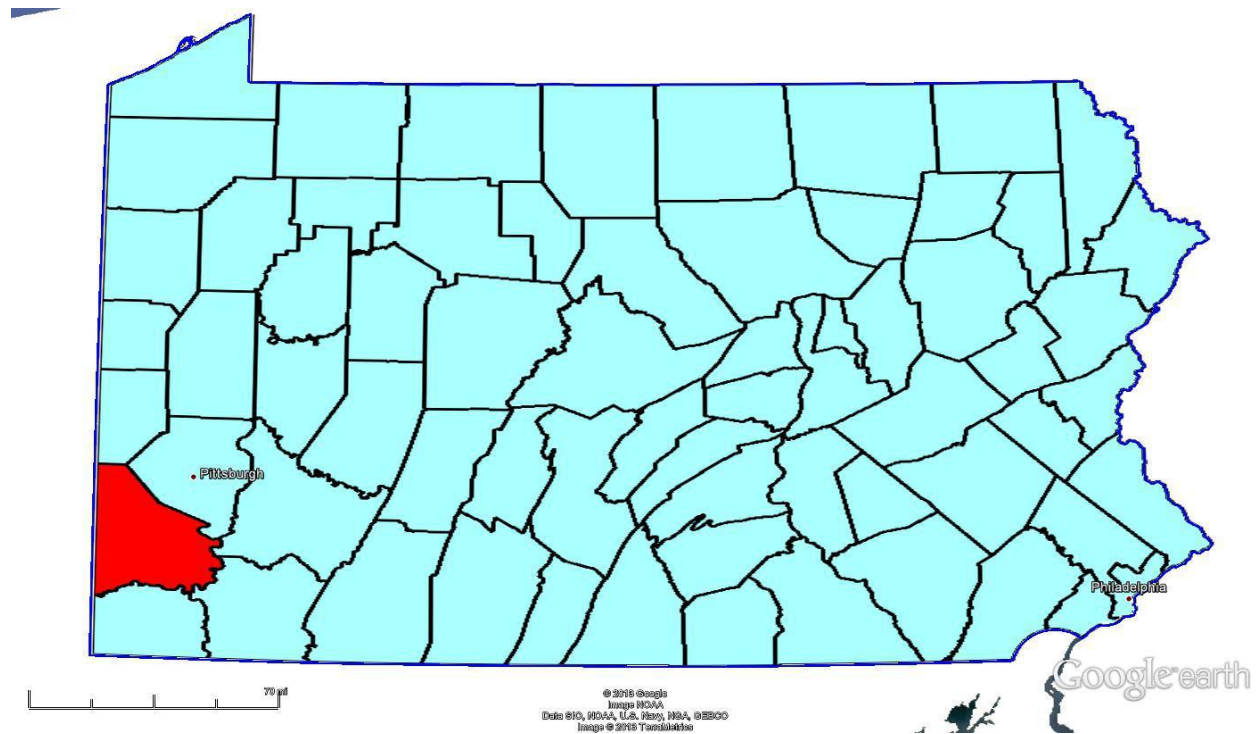
Figure 3 shows the general location of the study area, the location of the Commonwealth's historic ambient monitoring stations, and the positions of both active (producing) and inactive (not completed or completed but not producing) wells in addition to active or planned permitted unconventional gas facilities in Washington County. Due to the scale of the image, single dots for wells may represent multiple wells on a single well pad.

Figure 3 - Washington County Study Site Overview and Historical Ambient Monitoring Stations
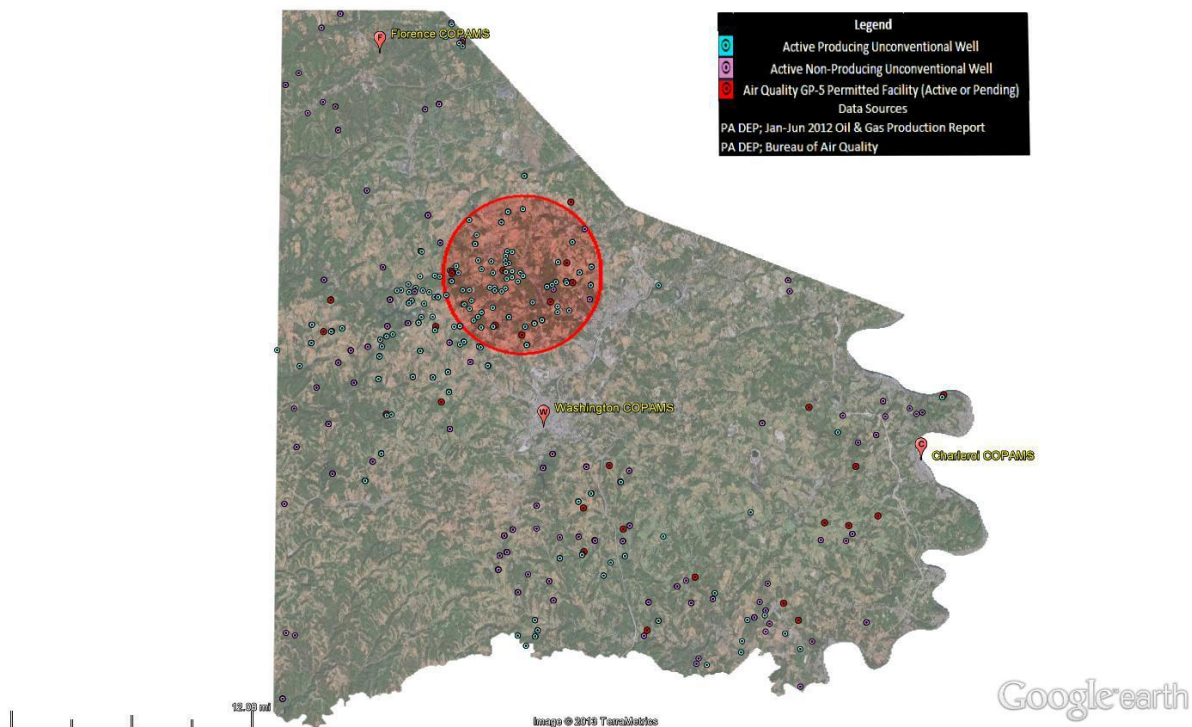
The overall study will consist of multiple sampling sites within Washington County that will measure downwind ambient concentrations of toxic and/or criteria pollutants from permanent shale gas air pollution sources. The primary permanent facilities of interest within the study area (red area in Figure 3) include:

- newly established natural gas compressor stations or gas treatment facilities (dewatering) that transport freshly extracted combined natural gas and gas liquids,

- two natural gas processing and fractionation facilities, and

- a number of actively producing well pads with associated wet gas handling equipment (e.g. small dehydrators, condensate collection tanks, etc.).

As can be seen in Figure 3, Washington County also has a number of other permanent gas facilities in addition to the ones included in the red study area. These facilities, largely compressor stations, will also contribute emissions in the area which can also be reflected in ambient air sampling. The study will not attempt to make conclusions about the relative contribution of specific sources to the observed results.

Some of the permanent facilities in the county transport gas from conventional, shallow gas reserves (i.e. non-Marcellus, non-shale gas reserves). The facilities are largely in the southeastern portion of the county and are not the focus of this study. While the study will attempt to isolate ambient pollutant concentration contributions from permanent shale gas extraction facilities, monitors and samplers

employed in the COPAMS network cannot differentiate between emissions from unconventional versus conventional permanent facilities.

Toxic pollutant sampling equipment and monitors for the study will be placed to collect data to represent the anticipated highest mean ambient pollutant concentration that might be observed by a local population. These mean concentrations will then form the basis for toxic cancer risk and non-cancer hazard assessments of the impacted population. Criteria pollutant analyzers will be sited to best capture representative concentration data for the area for comparison to primary and secondary NAAQS.

It is important to note that the purpose of this study is not to determine mean ambient concentrations of pollutants across the entire county or for all areas in the county in which unconventional natural gas extraction is occurring. The design does not include sufficient sampling site spatial distribution or number of sampling locations to confidently estimate those mean concentrations and is outside of the scope of this study. The study will contain specific site areas with monitors and/or samplers sited to characterize ambient air concentrations of criteria and toxic pollutants in those areas consistent with the study's goals listed previously in Section I.3.

Figure 4 shows the general study area in more detail. It identifies the permanent shale gas facilities, and shows the distribution of unconventional wells.

Figure 4 - Long-Term Study Area Overview
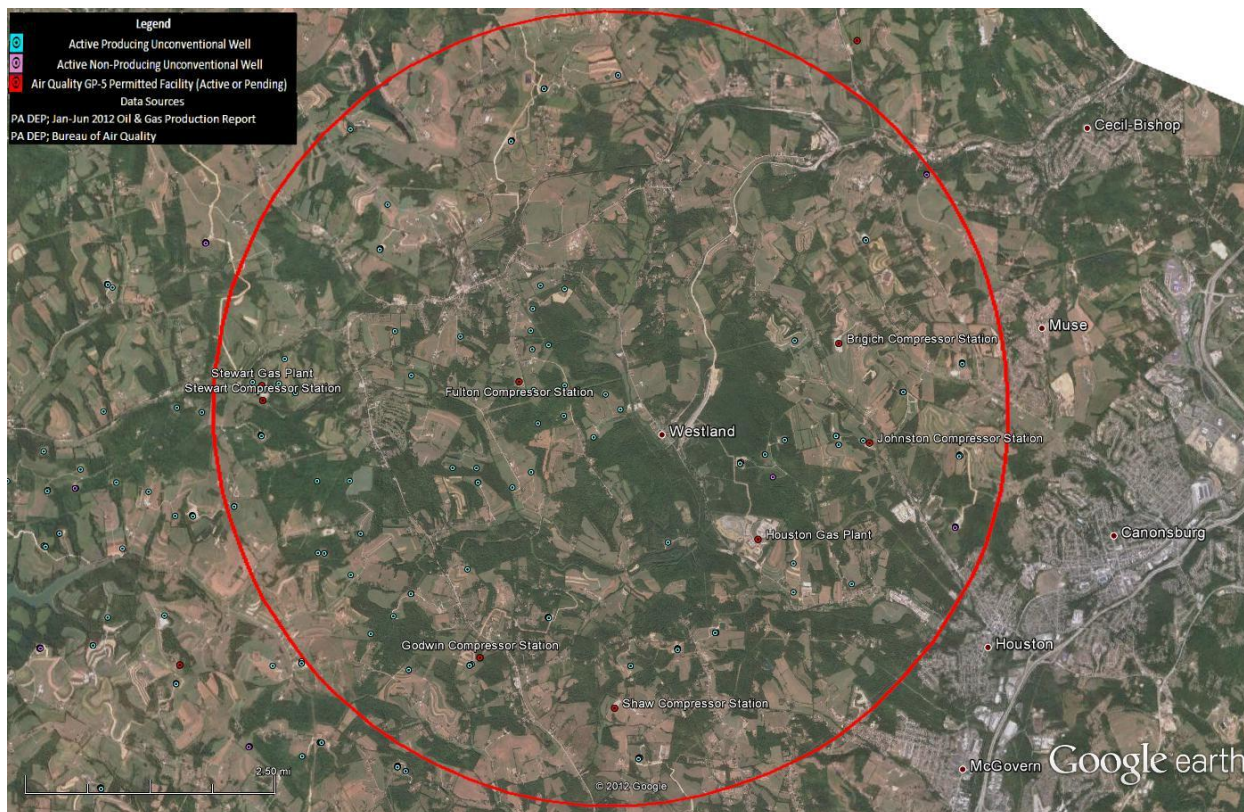
2. *Sampling Site Design*

Three study sites have been designed, where practicable, in accordance with either EPA regulation concerning monitoring for criteria pollutants[8] or recommended design protocols for non-criteria / toxic pollutants[9]. All criteria pollutant samples and measurements are collected using Federal Reference Method / Federal Equivalence Method (FRM/FEM) equipment and protocols. Deviations from recommended or required protocols will be documented in the final report.

a. *Primary Study Site*

The Department has designated the study's primary site as the location that houses both criteria and toxic pollutant monitors and samplers located generally downwind of a large natural gas liquid fractionation plant. This facility, owned by MarkWest Liberty Midstream Resources, LLC ("MarkWest"), separates high value natural gas liquids from the "wet" natural gas for subsequent sale. It also possesses sources on site that could, in addition their stack emissions, possess a higher rate of fugitive emissions through routine operations as compared to a compressor station or well pad gas conditioning infrastructure. The facility also gathers wet gas from numerous producing wells in the region thus leading to a higher rate of gas throughput than a single well pad or compressor station alone.

This facility is a permitted Natural Minor source for criteria pollutants, VOC and Hazardous Air Pollutants (HAPs). It is a Clean Air Act Title V Major Source for Greenhouse Gas emissions. The facility has an estimated annual air emissions based on operational data, source specifications and control device efficiencies using data collected by the company, provided by source manufacturers, and/or EPA approved emissions estimation methods. The facility reported to DEP the estimated emissions for their operations in 2011. The facility's 2011 reported emissions are summarized in Table 3.

Concentrations of criteria pollutants observed at the primary downwind site will be compared to applicable concentrations observed at the historical county monitoring stations at Florence, Washington, Charleroi and other Commonwealth ambient air monitoring sites with and without permanent shale gas facilities. Chronic cancer risk and non-cancer hazard assessment estimates will be determined using systematically collected toxic air pollutant data, however the sampler siting will not be driven by locating to sample within a large local population but estimating mean concentration of select HAPs near to and downwind from the fractionation plant. A summary of study background and comparison sites is provided in Table 2.

A second site systematically sampling for toxic VOC's is situated upwind from the fractionation plant. It is hoped that this site will allow for meaningful comparison to sampled downwind analytes and concentrations to help determine, at a gross level, if there exists significant ambient contribution of toxic VOC's between the two locations. This site will also provide data for comparison to other VOC sampling sites within the study area and across the Commonwealth. This information will help inform the Department if further detailed study is needed. This site is situated to minimize excessive localized influence from other sources as practicable.

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[8] 40 CFR Part 58

[9] Information on toxic air pollutant monitoring and analytical methods can be found on EPA's website at http://www.epa.gov/ttn/amtic/airtox.html

Meteorological data will also be collected at both sites. Wind for this area is predominately from the southwest quadrant. Figure 5 gives an aerial overview of the Primary study site.

Figure 5 - Primary and Upwind Site Overview with Shale Gas Sources
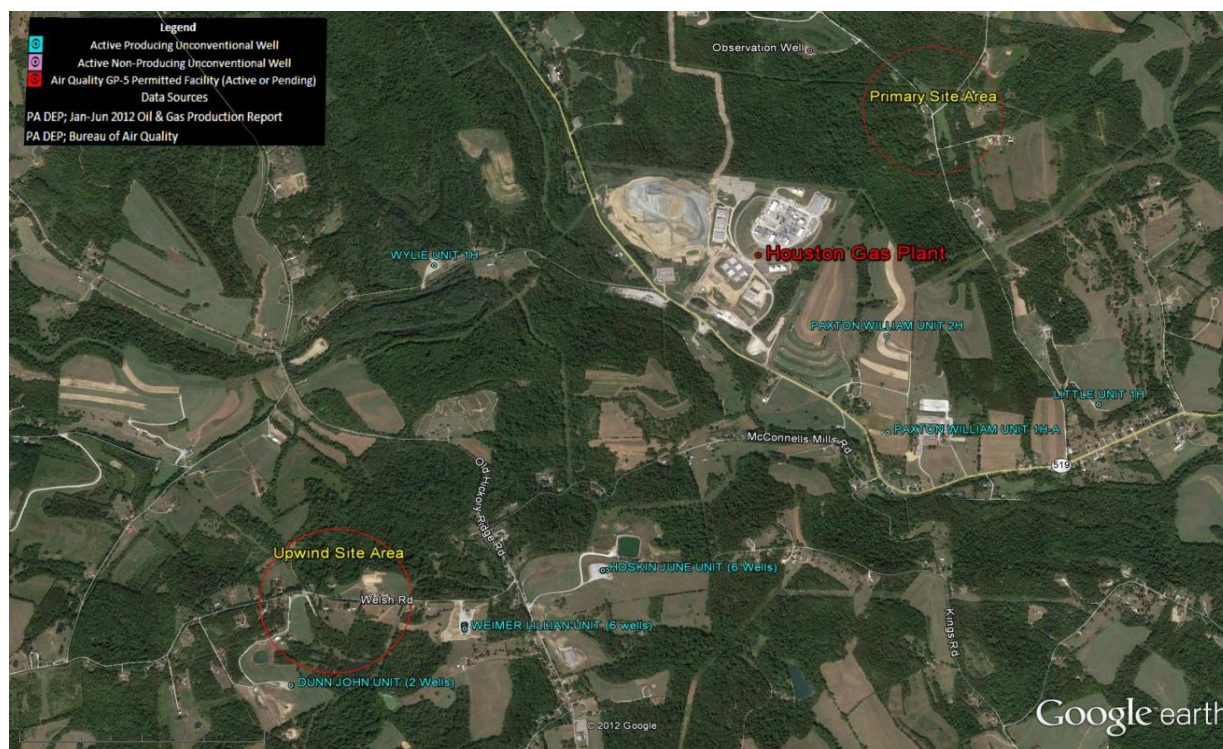
The primary site monitors and collects samples for HAPs, Carbonyls, Ozone, NO$_x$, Carbon Monoxide (CO), PM$_{2.5}$, Methane, Total Non-Methane Hydrocarbons, H$_2$S, Wind Speed, Wind Direction and Temperature. Appendix C lists the specific toxic organic analytes for which will be sampled. VOC and carbonyl samples will be collected over 24 hours every sixth day. The upwind site samples for toxic VOCs and measures Wind Speed, Wind Direction and Temperature. A VOC sample is collected over 24 hours every sixth day. Table 1 summarizes the pollutants to be measured at all the sampling sites for the study.

b. *"Brigich" Study Site*

This site is designed to determine downwind ambient concentrations of toxic organic chemicals emitted from the "Brigich" natural gas compressor station. This compressor station, owned by MarkWest, is located approximately 2.2 miles (3.5 km) NNW of the fractionation plant and moves natural gas and associated NGLs from nearby well pads to the plant for processing. The single sampler for this site is located sufficiently downwind to capture potential emissions from the compressor station while minimizing excessive influences from other potential emissions sources in the area.

This facility's reported 2011 estimated emissions are summarized in Table 3. 2012 emissions were not reported at the time of this writing

Concentrations of pollutants measured at the "Brigich" site will be compared to applicable concentrations observed at the other study sites, historical monitoring stations at Florence, Charleroi and other Commonwealth ambient air monitoring sites with and without permanent shale gas facilities. A summary of study's background and comparison sampling sites is provided in Table 2.

Meteorological data is collected at this site. Figure 6 gives an aerial overview of the "Brigich" Study site. Wind in this area is predominately from the west and southwest.

Figure 6 - Brigich Site Overview with Shale Gas Sources
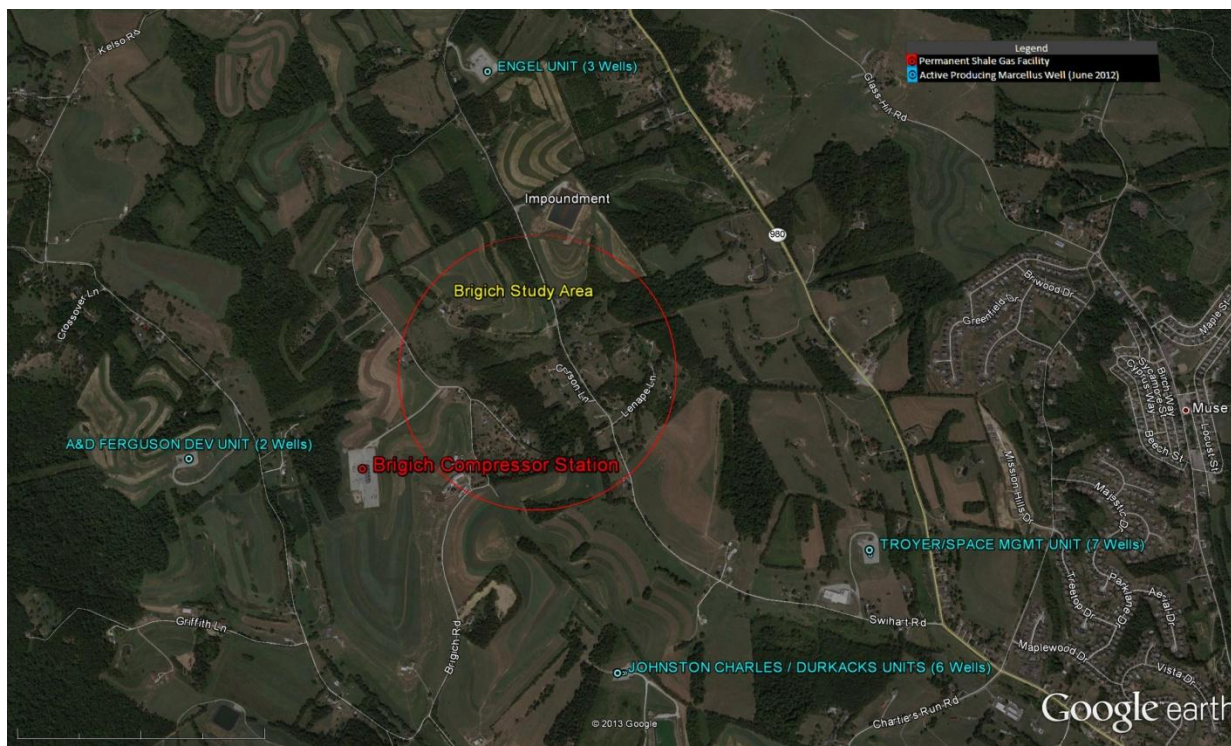
The Brigich site collects samples for HAPs and measures Wind Speed, Wind Direction and Temperature. HAP samples are collected over a 24 hour period every sixth day consistent with the national ambient sampling network schedule. Table 1 summarizes the pollutants to be measured at all study sites.

c. "Stewart" Study Site

This site is designed to determine downwind ambient concentrations of HAPs and carbonyls emitted from two closely collocated permanent shale gas facilities (compressor station and compressor station/de-watering plant). These stations are located approximately 6.2 miles (10 km) west of the fractionation plant. Unlike the Brigich site that samples to estimate downwind concentrations of toxic organic chemicals emanating from the compressor station itself, the sampler for the Stewart site is located in a downwind location in a populated area for the purpose of estimating potential total increased cancer and

non-cancer risk and hazard for the local population in the sampling area. The sampler is located to have no natural gas wells or permanent natural gas infrastructure within the immediate area (0.5 mile radius).

Facility 1 is the Nancy Stewart Booster Station owned by Markwest. Facility 2, located approximately 500 feet (150 meters) north of the Nancy Stewart Booster Station, is the Stewart Gas Plant, a gas liquid fractionation facility, owned by Laurel Mountain Midstream, LLC. These facilities operate independently and are not interconnected. Table 3 summarizes these facilities 2011 reported estimated emissions. Additionally within 0.5 miles (0.8 km) of the two permanent facilities there exist 10 producing Marcellus Shale gas wells and associated on site sources that could contribute to downwind pollutant concentrations.

Concentrations of pollutants measured at the "Stewart" site will be compared to the other study sites, historical monitoring stations at Florence, Charleroi and other Commonwealth ambient air monitoring sites with and without permanent shale gas facilities. Table 2 summarizes the study's comparison and background sites.

Meteorological data is collected at this site. Wind direction is predominately from the west and southwest. Discreet HAP and carbonyl samples are collected over a 24 hour period every six days and will coincide with the national and Commonwealth ambient monitoring network schedule. H_2S is monitored continuously. Figure 7 provides an aerial overview of the "Stewart" Study site.

Figure 7 - Overview of the Stewart Site and Shale Gas Sources
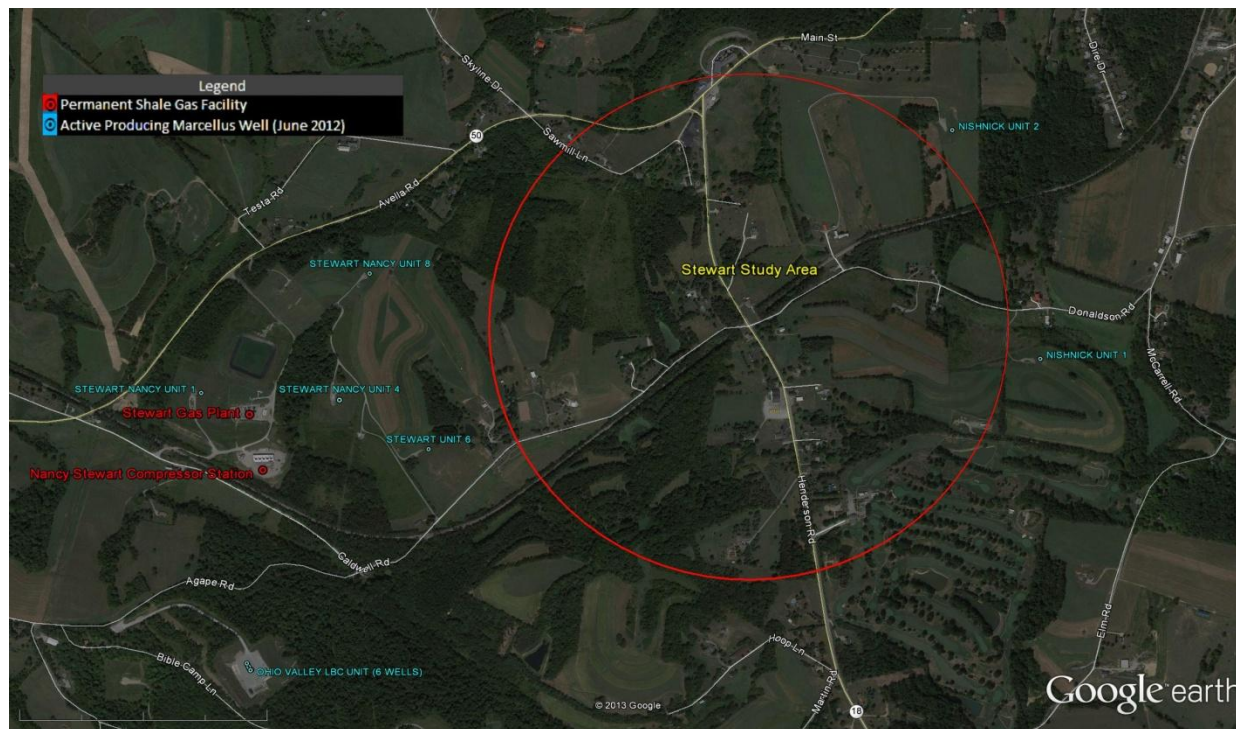
The Stewart study site collects samples for Toxic VOC's, Carbonyls and measure H_2S, Wind Speed, Wind Direction and Temperature. Table 1 summarizes the pollutants to be measured at all study sites.

d. Study Site Pollutant Measurement Summary

Table 1 is a summary of the pollutants to be measured and/or sampled at the three study sites comprising the study.

Table 1- Study Site Pollutant Measurement Summary

Study Site Name	VOC's	Carbonyl	Ozone	NOx	CO	PM$_{2.5}$	Methane /NMHC	H$_2$S	Met
Primary	X	X	X	X	X	X	X	X	X
Upwind	X								X
Brigich	X								X
Stewart	X	X						X	X

Discreet samples (i.e. HAP VOC and carbonyls) will be collected over a 24 hour period once every six days coinciding with the national and Commonwealth ambient monitoring network schedule. All other measurements will be continuous or semi-continuous.

e. Background & Comparison Sites

The Department will use existing ambient air monitoring stations[10] both in the study area and throughout the Commonwealth with which to compare collected ambient concentration data. Additionally, sampling equipment has been added to a local existing station to supplement collected VOC data. Where able, comparisons of ambient pollutant concentration data will be made using both temporally consistent and historic long-term averages (e.g. three to five year averages). Table 2 summarizes likely background and comparison sites, with pollutants / analytes either to be additionally measured or for which exists comparable historical data.

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[10] Additional information on the background and comparison sites can be found on the Department's Air Monitoring webpage at http://www.ahs2.dep.state.pa.us/aq_apps/aadata/.

Table 2 - Background/Comparison Site Pollutant Measurement Summary

COPAMS Station	County	Type	AQS Site Code[11]	VOC's	Carbonyl	Ozone	NOx	CO	PM2.5	Met
Florence	Washington	Rural	42-125-5001	X					X	X
Washington	Washington	Urban	42-125-0200			X			X	X
Charleroi	Washington	Urban	42-125-0005	X		X	X	X	X	X
Arendtsville	Adams	Rural	42-001-0001	X	X		X	X	X	X
Lancaster	Lancaster	Urban	42-071-0007	X	X	X	X		X	X
Marcus Hook	Delaware	Urban	42-045-0109	X						
Chester	Delaware	Urban	42-045-0002	X		X	X		X	X
Perry County	Perry	Rural	42-099-0301			X	X			X

Where able, collected toxic organic data will also be compared to contemporaneous and historical air toxics data collected at stations comprising the National Air Toxics Trends Stations (NAATS) program network.

All stations collect data using the same or equivalent methods and on the same schedule as the study sites so relevant comparisons can be made.

f.   Study Area Permanent Shale Gas Facility Reported Emissions

Table 3 summarizes the GP5 permitted facility reported non-greenhouse gas and toxic air emissions for 2011. Emissions estimates for permanent shale gas facilities were submitted to the Department for the first time in 2012 for the 2011 calendar year. The estimates are calculated by the companies using a combination of federally approved air pollution source emissions factors (e.g. AP-42), source manufacturer provided emissions rates, or engineering based estimation procedures.

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[11] AQS site codes are monitoring station identifiers used in the U.S. EPA Air Quality System (AQS). The AQS is a national repository of ambient air quality data. More information on AQS can be found at http://www.epa.gov/ttn/airs/airsaqs/

Table 3 - Permanent Shale Gas Facility 2011 Reported Annual Pollutant Emissions (Tons per Year)

Pollutant	Facility Name			
	Houston Gas Plant (TPY)	Brigich Comp. Sta. (TPY)	Stewart Gas Plant (TPY)	Nancy Stewart Comp. Sta. (TPY)
CO	53.1	14.7	19.8	16.1
NOx	47.1	56.2	11.1	60.7
PM10	6.0	2.1	0.7	1.9
PM2.5	6.0	2.1	0.7	1.9
SOx	0.6	0.1	0.04	0.1
VOC	29.9	22.7	12.0	25.4
Total HAPs[12]	6.1	4.5	5.4	4.0
Speciated HAPs				
Benzene	0.17	0.08	0.11	0.07
Ethyl Benzene	0.07	0.01	0.07	0.01
Formaldehyde	0.07	3.36	4.39	3.34
Toluene	1.04	0.27	0.13	0.13
Xylene	2.39	0.49	0.10	0.16
2,2,4-Trimethylpentane[13]	0.13	0.01	0.02	0.01
n-Hexane	2.24	0.27	0.53	0.30

III.   Project Implementation

This section will provide an overview of the physical deployment of the equipment for the study and additional detailed information on sampling/measurement equipment specifications, methods of analysis, data acquisition, and quality assurance goals and methods.

1. Sampler Siting and Equipment Deployment

Staff from both the Toxic Monitoring and Field Operations Sections has performed all required sampling site screening, field verification, and equipment deployment. Agreements with landowners for new sampling locations were secured prior to deployment with the assumption that equipment deployment and data collection at these sites will be for at least one year. Staff from the Field Operations Section will maintain all sites and collect discreet samples for the duration of the study. Staff from the Toxics Monitoring Section will perform advanced maintenance, troubleshooting and calibration of toxics

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[12] Total Hazardous Air Pollutants (HAPs) equals the sum of the speciated HAPs.

[13] 2,2,4-Trimethylpentate is also commonly known as Isooctane.

monitoring and sampling equipment when applicable. Sampler and analyzer auditing will be conducted by the Division's Quality Assurance & Data Assessment Section.

All monitoring and sampling equipment have been deployed, and will be operated and maintained consistent with standard operating procedures for each monitor/sampler.

An example of a typical site agreement for an ambient monitoring/sampling station is included in Appendix D.

2. *Operation/Analysis Methods & Equipment Specifications*

All monitoring and sampling equipment will be operated in accordance with the applicable standard operating procedure (SOP) for each type and model of equipment. All equipment field operators have been trained in the applicable SOP for equipment for which they are responsible in accordance with field operations training protocols contained in the respective SOP's and Quality Assurance Program Plan's (QAPP)[14].

Table 4 details the monitoring / sampling equipment that will be deployed for this study, their type, and the associated analysis or monitoring method that will be used for each. Federal Reference and Equivalence Methods (FRM/FEM) specify manufacturers and models of equipment and the parameters for operation.

All discreet samples for VOC/HAP, Carbonyls and $PM_{2.5}$ will be analyzed by the Department's Bureau of Laboratories using approved analysis methods in accordance with the laboratory's standard operating procedures[15]. The Department's laboratory is accredited under the National Environmental Laboratory Accreditation Program (NELAP). Additional information on the Bureau of Laboratories can be found online at http://www.portal.state.pa.us/portal/server.pt/community/labs/13780.

All HAP and non-criteria pollutant sampling and analysis equipment used in this study meets, at minimum, specifications for performance that will help ensure collected data is accurate, reliable and usable for quantitative ambient emissions concentration estimation.

Minimum specifications for HAP and carbonyl samplers and associated meteorological equipment at the Primary upwind, Brigich and Stewart sites are contained in Appendix E. Meteorological equipment specifications for criteria pollutant monitoring at the Primary site are consistent with the requirements established for primary and secondary NAAQS special purpose monitoring.

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[14] This project will employ existing standard operating procedures (SOP) and Quality Assurance Program Plans (QAPP) specific to the equipment used or pollutant measured. The AQM Division will collect and analyze data for this project consistent with the Division's existing ambient air criteria and toxics monitoring networks. Fixed-point monitor H_2S and Methane/Non-methane Hydrocarbon protocols have been developed specifically for this project but will rely on existing quality assurance protocols already in place for continuously monitored gaseous pollutants. Specific SOPs and QAPPs are available on request by contacting the Study Manager through the contact information contained in Section I.1

[15] Bureau of Laboratories analysis standard operating procedures are available upon request by contacting the Study Manager through the contact information provided in Section I.1.

Table 4 - Project Measurement and Sampling Equipment and Analysis Methods by Pollutant

Pollutant	Sampler/Analyzer	Type/Description	Analysis / Monitoring Method
HAP's	ATEC 2200-12	2 channel canister, discreet 24 hr	TO-15[16] & TICs[17]
	ATEC 2200-102	3 channel canister, discreet 24 hr	TO-15 & TICs
	Entech CS1200ES4[18]	Passive Flow Control, discreet 24 hr	TO-15 & TICs
Carbonyl	ATEC 2200-102	2 DNPH cartridge capacity	TO-11A[19]
	Xontech Model 925	8 DNPH cartridge capacity (3 used)	TO-11A
Ozone	Teledyne API 400E	Ultraviolet Absorption	Federal Equivalence Method[20] - Ozone
NOx	Teledyne API 200A	Chemiluminescent Photodetection	Federal Equivalence Method[21] - NOx
CO	Teledyne API 300	Infrared Absorption	Federal Equivalence Method[22] - CO
H_2S	Teledyne API 101E	Ultraviolet Fluorescence	PA DEP / Manufacturer
	Jerome X651	Fixed Point Monitor with Model 631-X Gold film electrical resistance monitor[23]	PA DEP / Manufacturer
$PM_{2.5}$	R&P Partisol Plus 2025	Gravimetric, Discreet 47 mm Filter	Federal Reference

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[16] Determination Of Volatile Organic Compounds (VOCs) In Air Collected In Specially-Prepared Canisters And Analyzed By Gas Chromatography/Mass Spectrometry (GC/MS), U.S. EPA, January 1999: 6 liter canister.

[17] Tentatively Identified Compounds – An analysis of the collected ambient air sample via Gas Chromatograph/Mass Spectrometer where organic analytes are tentatively identified using existing chromatographic libraries. The analysis, while quantitative, is not performed using a NELAP certified method however can provide a reasonable quantitative estimate of organic analytes not included in the TO-15 toxics standard.

[18] Includes an Entech Model TM1100 timer system

[19] Determination of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed by High Performance Liquid Chromatography (HPLC) [Active Sampling Methodology], U.S. EPA, January 1999: Using Sigma-Aldrich S10L DNPH cartridges.

[20] Automated Equivalent Method: EQOA-0992-087; *Federal Register: Vol. 57, page 44565, 09/28/92; Vol. 63, page 31992, 06/11/98; Federal Register: Vol. 67, page 57811, 09/12/2002; Latest Modification: 08/2010*

[21] Automated Reference Method: RFNA-1194-099; *Federal Register: Vol. 59, page 61892, 12/02/94 Latest modifications: 03/2009; 08/2010*

[22] Automated Reference Method: RFCA-1093-093; *Federal Register: Vol. 58, page 58166, 10/29/93; Latest Modification: 08/2010*

[23] The Jerome X651 H_2S analyzer will sample every 30 minutes.

			Method - PM2.5[24]
Methane / Non-Methane Hydrocarbon	Synspec Alpha 114	Continuous Gas Chromatography	PA DEP / Manufacturer
Wind Speed / Direction	Climatronics	Sonimometer / Mechanical Vane/ Cup Anemometer	U.S. EPA[25]
Temperature	Climatronics	Themistor Sensor	See Wind Speed/Direction

Appendix C lists the HAPs and carbonyls to be analyzed using the TO-15 and TO-11A methods and their respective current laboratory Method Detection Limits (MDLs)[26].

3. *Data Generation, Acquisition, and Management*

Data for this project will be generated from a number of sources including:

- Both the study's and the Commonwealth's historically sited continuous analyzers / monitors,

- From samples collected via the study's and the Commonwealth's historically sited sampling equipment analyzed by the Department's analytical laboratory, or

- Nationally collected data from other state or national ambient air monitoring networks.

All data will be acquired and managed in accordance with the QAPP for the respective analyzer or sampler network.[27]

Data generated from continuous analyzers will be acquired using digital data loggers and data storage units. Some continuously monitored data will be available remotely without the need for operators to collect the data from the sampling site (e.g. continuous data from the primary downwind site). Other data will require an operator to physically download stored data to portable storage media and transmit to project data analysis staff (e.g. meteorological data from new sites downwind of the compressor stations).

For equipment that samples for a discreet period of time, an operator is required to retrieve the sample media (i.e. summa canister or particulate filter cassette) and send to the Department's laboratory for

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[24] Manual Reference Method: RFPS-0498-118; *Federal Register: Vol. 63, page 18911, 04/16/98*

[25] U.S. EPA. *QA Handbook for Air Pollution Measurement Systems: Volume IV: Meteorological Measurements Version 2.0(Final)*, U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Air Quality Analysis Division, Measurement Technology and Ambient Air Monitoring Groups, Research Triangle Park, NC. EPA-454/B-08-002, March 2008.

[26] The Method Detection Limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte – 40 CFR Part 136 Appendix B

[27] QAPPs for the project study are available upon request by contacting the Study Manager through the contact information provided in Section I.1.

analysis. Results of the analysis are then transferred to Department data systems for retrieval by project analysis staff.

Data from other state or national ambient air monitoring networks can be retrieved from either individual states or from national data clearinghouses (e.g. EPA's AIRNow and AQS systems).

4. Continued Quality Assurance

Collecting quality data with good precision and reduced bias is one of the most important tasks of the study as it helps ensure that analysts can make confident conclusions drawn from real world observations with minimum errors.

Study quality assurance goals and procedures are enumerated in the specific QAPPs for the pollutant monitored. These documents detail both Data Quality Objectives (DQOs) and Measurement Quality Objectives (MQOs) for both continuous criteria pollutant and toxic pollutant monitoring programs.

In general all data collected for this study will meet the following DQOs:

- All data should be traceable to a National Institute of Science and Technology (NIST) primary standard.
- All data shall be of a known and documented quality. The level of quality required for each specific monitoring parameter will be established and will depend upon the data's intended use. Two major measurements used to define quality are precision and bias. These quality measurements are defined in the measured pollutant's respective QAPP.
- All data shall be comparable. This means all data shall be produced in a similar and scientific manner. The use of the standard methodologies for sampling, calibration, audition, etc. found in the QAPP and operating procedures should achieve this goal.
- All data shall be representative of the parameters being measured with respect to time, location, and the conditions from which the data are obtained. The use of federally-approved standard sampling methodologies and QA procedures should ensure that the data generated are representative of actual ambient concentrations. Specific MQOs and acceptance criteria are listed in their respective pollutant QAPPs prepared by PADEP and approved by EPA.
- For toxics measurements, the QAPP assumes that DQO's will be met if the monitoring sites satisfy the goal of one-in-six day sampling, 85% data completeness and 15% measurement coefficient of variance (CV).

MQO's for gaseous criteria pollutants are contained in EPA's Quality Assurance handbook[28]. Additional detail on criteria pollutant MQO's and how they will be used to control and assess measurement uncertainty may also be described in the individual pollutant SOPs. MQO's for $PM_{2.5}$ and toxic pollutants are contained in those pollutant's respective QAPPs.

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[28] *Quality Assurance Handbook for Air Pollution Measurement Systems, Volume II Ambient Air Quality Monitoring Program*, EPA-454/B-08-003, December, 2008

IV.   Data Validation, Analysis and Results Reporting

Data generated and collected through the course of this study will go through a process of validation and usability determination prior to being analyzed for comparison to primary and secondary NAAQS for criteria pollutants or mean ambient concentration determination for cancer inhalation risk and non-cancer inhalation hazard analysis. This validation and usability process will ensure that conclusions reached by the study not only accomplish the study's goals but do so with a certain measure of confidence that can both inform future decisions of the Department and provide the public at large with information based on sound scientific principles.

1. Validation

Data validation consists of a systematic review of all data collected to ensure that each data point has been collected consistent with the MQO's set for the study and clearly identifying and/or excluding inconsistent data. In the case of continuous measurements this process is performed by the Division's Quality Assurance & Data Assessment Section both as the data is collected, and at automatic intervals consistent with the QAPP for each pollutant. Using equipment auditing and statistical analysis as specified in the QAPP, quality assurance staff will then review data sets to determine their validity for use in the study. For discreet PM_{25} samples, the Field Operations Staff will ensure that samples will be collected on schedule and in accordance with SOP's to ensure MQO's for PM_{25} collection are met. Quality assurance staff will ensure that required auditing of all analyzers and samplers is performed.

For discreet VOC and carbonyl sampling staff from the Quality Assurance & Data Assessment Section, in addition to confirming that MQOs have been met for each sample, will confirm that data sets meet data completeness objectives and that samples are analyzed within the maximum sample retention time windows established by the corresponding analysis method and that sampling flow rate and/or beginning and ending canister pressures are within the established method parameters. Deviations from MQO's will be recorded and reported.

Laboratory analysis procedures for quality assurance and validation for reporting will be consistent with the requirements for laboratories accredited under the National Environmental Laboratory Accreditation Program (NELAP). The Department's Bureau of Laboratories is NELAP accredited. Any results that may be released outside of the scope of NELAP accreditation will be noted by the lab to the project team and summarized in the final report.

2. Usability

During the course of the study, data may be collected that while valid and consistent with the pollutant DQO's and MQO's, may not be usable for final analysis. This condition could occur in the event of a local or regional pollution anomaly that might upwardly bias ambient air concentrations. An example of this might be an instance where the samplers/analyzers record emissions from a temporary air pollution source within the sampling domain that is not characteristic of "routine emissions" (e.g. house or forest fire, vehicular accident with large fuel spill). Unusual weather events such as exceptionally strong high or low pressure systems or long duration weather events could also influence sampled results either by damaging sampling equipment or inducing non-typical wind patterns that may inadequately represent typical weather conditions for the area.

Project data analysts will evaluate the pollutant data sets to look for these anomalies as data is collected. Identification is not always a straightforward process as the data alone does not always convey the source of emissions. Data analysts will rely on information provided by, but not limited to the following:

- Field monitoring staff observations during the course of their operating duties,

- Department regional inspection, compliance, and enforcement staff,

- Local, county and state Emergency Management Coordinators and Response Teams (including police, fire and ambulance services),

- National Oceanic and Atmospheric Administration (NOAA), including the National Weather Service, National Hurricane Center, etc.,

- Local and regional news media,

- Other local, state and federal agencies with activities in the study area,

- The public (residents, commercial, and industrial).

Another potential source of anomalous data is from the permanent shale gas sources that are within the study area. Infrequent operational upsets and non-routine events might be reflected in the monitored/sampled ambient air. Existence of these events alone will not render monitored data unusable however it is important the Department note and characterize these events if and when they are identified. The project team will coordinate with regional field office air quality enforcement and permitting staff to identify incidents reported by the industry and, where practicable, contact permanent shale gas facility owners/operators as to operating conditions at the time of possible events identified via monitoring results.

3. Analysis

Data analysis will generally consist of employing methods to compare mean ambient annual air pollutant concentrations estimations between sampling sites within the study and to statewide and national datasets. After mean pollutant concentrations are estimated and associated descriptive statistics, including confidence limits, are determined, the data will be analyzed where applicable using three general techniques:

1. Comparison of measured values to established health based standards (e.g. NAAQS).

2. Comparison to measured long-term average concentrations at study background sites, other comparable monitoring locations across the Commonwealth, and/or comparable national monitoring sites (e.g. NAATS)

3. Inhalation risk and hazard assessment using generally accepted methods and comparison of results to comparable sites across the Commonwealth.

a. Mean Pollutant Concentration Determination

Mean pollutant concentrations for criteria pollutants (Ozone, NO_2, CO, $PM_{2.5}$) will be estimated consistent with the procedures established for NAAQS compliance determination. However, due to the availability of only one year of data, the measured concentrations cannot be used specifically for Ozone, 1-hour NO_2, and $PM_{2.5}$ NAAQS compliance determination.

For toxic VOC/HAP and carbonyl measurements where 15% or less of the measurements are below the Method Detection Limit (MDL), mean concentrations will be estimated using an arithmetic mean with 1/2 the MDL substituted for those data points measured below the MDL. This substitution method will also be employed for analyte data sets where greater than 15% but less than 85% are non-detects, however the reported confidence in this estimate may be lower depending on the final percentage of non-detects. Lastly if 85% or more of the collected data is reported below the MDL, the data will be reported but the analyte will not be included for further comparative or risk / hazard analysis. Descriptive statistics, including but not limited do, standard deviation, variance, range, and results of goodness-of-fit tests will be included where practicable.

Methane and Non-Methane Hydrocarbon concentrations will be estimated using arithmetic averages of valid data collected every 10 minutes, 23 hours per day[29]. Daily, monthly and annual averages will be determined.

H_2S mean ambient concentrations will be estimated by arithmetic mean of valid data over both 1-hr and 24-hr periods.

Concentration estimates and descriptive statistics will be generated using Microsoft Excel and/or statistical packages such as VOCDat or ProUCL[30]. In instances where insufficient data exist to confidently use an arithmetic average or MDL substitution schema to estimate the mean concentration of a specific analyte, alternative mean estimation or distribution description methods may be used (e.g. 95% Upper Confidence Limit or Kaplan-Meier Method).

b. Comparison of measured values to established health based standards

Where there exists a health based ambient standard such as a NAAQS, both estimated mean ambient concentration values, and NAAQS comparable observed concentration estimates will be directly compared. Given that some NAAQS do not use a simple arithmetic mean of all values for concentration determination and that some NAAQS compliance evaluations use multiple years of data, a comparison of both an arithmetic average of valid concentration data (reflecting actual concentrations) and a concentration estimated using federally approved methods for NAAQS compliance determination will be used.

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[29] One hour per day is used for auto-calibration of the GC analyzer. An ambient sample is not collected during this period.

[30] VOCDat is a U.S. EPA approved program for analyzing ambient VOC and carbonyl data sets for the purpose of data preparation for upload to the national AQS data system. http://vocdat.sonomatech.com/ . ProUCL is an EPA approved and maintained statistical software package developed for analysis of environmental datasets with and without non-detect observations. It provides a wide range of descriptive statistical analysis tools and mean estimation methods that support environmental decision making. http://www.epa.gov/osp/hstl/tsc/software htm

Values for H_2S will be compared to both the 24-hr and 1-hr Pennsylvania ambient air quality standard contained in 25 Pa. Code Chapter 131, Section 131.3.

No health based standards exist for methane or non-methane hydrocarbons.

Observed VOC and carbonyl mean concentrations will be examined through the cancer inhalation risk and non-cancer inhalation hazard assessment as ambient health-based standards do not exist for these compounds.

The action criteria for pollutants with health based ambient standards will be the following:

- If the observed concentration is greater than the established standard, then the pollutant concentration is significant enough to <u>potentially</u> violate the national or Pennsylvania ambient air quality standard and thus posing a health concern to the exposed population. Monitoring for the pollutant observed to be potentially in excess of the standard will continue in order to determine actual compliance with the standard.

c. *Comparison of measured values to study background and Commonwealth comparison sites.*

Measured concentrations of pollutants will be compared to the study background and statewide criteria pollutant and toxics monitoring sites. Potential comparison sites are listed in Section II.2.e above. This comparison will be both a direct comparison of estimated mean concentrations of pollutants (i.e. is the study site higher or lower than a background/comparison site) and, where able, statistical comparison of contemporaneous data sets. Observed mean concentration estimates will also be compared to three-year average pollutant concentrations where possible. A two-sample statistical test(s) will be selected depending on the distribution attributes of the data and, in the case of VOC and carbonyl data, the proportion of non-detected to detected analytes. This hypothesis testing will be conducted in accordance with generally accepted statistical analysis methods and EPA approved methodology[31] and will be documented in the final report.

One-sample statistical tests will be conducted, where practicable, on observed criteria pollutant data versus the compared health based standard. This will be done to help determine if observed data is statistically different than the comparable pollutant standard.

There are no direct action criteria for this analysis. Statistically valid differences will be noted and will serve to inform the Department and the public as to the nature of observed ambient air downwind from permanent shale-gas facilities.

d. *Inhalation Risk Assessment*

Observed ambient concentrations of VOC and carbonyl analytes will be used to perform both an Extended Lifetime Cancer Risk (ELCR) and chronic non-cancer hazard human health inhalation risk assessment. This will be conducted in accordance with the Toxic Monitoring Section's procedure for data analysis, risk assessment and air toxics data reporting. This procedure is included as Appendix F. This

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[31] A listing of select statistical analytical references is provided in Appendix A.

procedure uses ambient air toxic risk assessment methods recommended by the U.S. Environmental Protection Agency[32].

Risk factors employed for the study will use latest unit risk factors (cancer) and inhalation reference concentration (non-cancer) values for detected analytes available from the Risk Assessment Information System (RAIS) maintained by the U.S. Department of Energy's Oak Ridge National Laboratory[33].

Action criteria for the risk assessment will be the following:

- For ELCR – An estimated *cumulative* excess cancer risk of 1 in 100,000 population or greater for detected analytes will trigger a review of data and risk assessment by the PA Department of Health. Otherwise no additional cancer risk will be reported.

- For non-cancer hazard – A *cumulative* detected analyte Hazard Quotient (cumulative ratio of observed mean concentrations to the inhalation reference concentrations) greater than 1 will trigger a review of data and risk assessment by the PA Department of Health. Otherwise no additional non-cancer hazard will be reported.

The PA Department of Health will review any results of the study, regardless if risk assessment is warranted based on observed data.

4. Results Reporting

A final report with supporting documentation will be published on the Department's website once all data has been validated and analysis concluded. In the event that ambient concentrations of a pollutant or pollutants would appear to be in excess of acceptable inhalation cancer risk or non-cancer hazard levels, data will be reviewed and independent risk assessment performed by the PA Department of Health prior to publication.

While the goal of the project is to collect usable data for one-year, the Department may extend sampling at one or more locations in order ensure that representative ambient pollutant concentration data is collected. The Department may also need to modify the protocol, sampling strategy and/or analysis methods during the course of the study if new information comes to light that might either adversely impact or improve the confidence in the overall study results. In cases where these changes may be warranted, the Department will defer to maintain the goal of providing confident results that provide useable information on ambient air concentrations of pollutants associated with permanent shale gas facilities over strict adherence to a predetermined protocol. Any deviations from the study protocol will be documented and reported in the final report.

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[32] http://www.epa.gov/risk/health-risk htm for Human Health Risk Assessment Guidance; Additional guidance can also be found at the EPA Region III Mid-Atlantic Risk Assessment webpage at   http://www.epa.gov/reg3hwmd/risk/human/index.htm
[33]Risk Assessment Information System (RAIS) - http://rais.ornl.gov/

Appendices

APPENDIX A – Select Study Technical References and Guidance by Subject

Study Planning and Design

40 CFR Part 58, Appendix D – Network Design Criteria for Ambient Air Quality Monitoring

40 CFR Part 58, Appendix E – Probe and Monitoring Path Siting Criteria for Ambient Air Quality Monitoring

PA DEP., 2010, *Southwestern Pennsylvania Marcellus Shale Short-Term Ambient Air Sampling Report*, PA Department of Environmental Protection, Bureau of Air Quality, Harrisburg, PA. November 2010. http://www.dep.state.pa.us/dep/deputate/airwaste/aq/aqm/docs/Marcellus_SW_11-01-10.pdf.

PA DEP. 2011a, *Northeastern Pennsylvania Marcellus Shale Short-Term Ambient Air Sampling Report*, PA Department of Environmental Protection, Bureau of Air Quality, Harrisburg, PA. January 2011. http://www.dep.state.pa.us/dep/deputate/airwaste/aq/aqm/docs/Marcellus_NE_01-12-11.pdf.

PA DEP. 2011b, *Northcentral Pennsylvania Marcellus Shale Short-Term Ambient Air Sampling Report*, PA Department of Environmental Protection, Bureau of Air Quality, Harrisburg, PA. May 2011. http://www.dep.state.pa.us/dep/deputate/airwaste/aq/aqm/docs/Marcellus_NC_05-06-11.pdf.

U.S. EPA., 1984. *Network Design and Site Exposure Criteria for Selected Noncriteria Air Pollutants*, U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, NC, September 1984. http://www.epa.gov/nscep/index.html.

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U.S. EPA. 2012a. *National Ambient Air Quality Standards (NAAQS)*, U.S. Environmental Protection Agency, Technology Transfer Network, Internet, http://www.epa.gov/ttn/naaqs/, 2012.

Operational Guidance & Methods

PA DEP, 2012a. *Determination of Carbonyls in Air by Liquid-Solid Extraction, Derivatization and High Performance Liquid Chromatography (HPLC) with Diode Array Detection, Revision 3,* PA Department of Environmental Protection, Bureau of Air Quality & Bureau of Laboratories, Harrisburg, PA. June, 2012

PA DEP, 2012b. *Determination of PM$_{2.5}$ Fine Particulate Matter in Ambient Air by Gravimetric Analysis EPA Title 40 CFR Appendix L to Part 50. Revision 000*, PA Department of Environmental Protection, Bureau of Air Quality & Bureau of Laboratories, Harrisburg, PA. June 2012.

PA DEP, 2000. *PM$_{2.5}$ Field Standard Operating Procedures for the Ambient Air Monitoring Program*, PA Department of Environmental Protection, Bureau of Air Quality, Harrisburg, PA. June 2000.

PA DEP, 2001a. *Carbon Monoxide (CO) Field Standard Operating Procedures for the Ambient Air Monitoring Program*, PA Department of Environmental Protection, Bureau of Air Quality, Harrisburg, PA. July 2001.

PA DEP, 2001b. *Nitric Oxide (NO), Nitrogen Dioxide (NO$_2$) and Oxides of Nitrogen (NO$_x$) Field Standard Operating Procedures For the Ambient Air Monitoring Program*, PA Department of Environmental Protection, Bureau of Air Quality, Harrisburg, PA. July 2001.

PA DEP, 2012c. *Carbonyl Standard Operating Procedures For the Ambient Air Monitoring Program*, PA Department of Environmental Protection, Bureau of Air Quality, Harrisburg, PA. October 2012.

PA DEP, 2001c. *Hydrogen Sulfide (H$_2$S) Field Standard Operating Procedures for the Ambient Air Monitoring Program*, PA Department of Environmental Protection, Bureau of Air Quality, Harrisburg, PA. August 2001.

PA DEP, 2008. *Ozone (O$_3$) Field Standard Operating Procedures for the Ambient Air Monitoring Program*, PA Department of Environmental Protection, Bureau of Air Quality, Harrisburg, PA. June 2008.

PA DEP, 2012c. *Volatiles in Air by EPA Method TO-15: Measurement of Volatile Organic Compounds (VOCs) in Air by Collection in Summa® Canisters and Analysis by Gas Chromatography with Mass Spectrometric Detection (GC/MS), Revision 007,* PA Department of Environmental Protection, Bureau of Laboratories, Harrisburg, PA. September 2012.

PA DEP, 2012d. *VOC Canister Standard Operating Procedures For the Ambient Air Monitoring Program*, PA Department of Environmental Protection, Bureau of Air Quality, Harrisburg, PA. November 2012.

U.S. EPA, 1999a. Compendium Method TO-11A, 2nd Ed., *Determination of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed by High Performance Liquid Chromatography (HPLC)*, EPA/625/R-96/010b, U.S. Environmental Protection Agency, Office of Research and Development, Center for Environmental Research Information, Cincinnati, OH, January 1999.

U.S. EPA, 1999b. Compendium Method TO-15, *Determination of Volatile Organic Compounds (VOCs) In Air Collected In Specially-Prepared Canisters And Analyzed By Gas Chromatography/Mass Spectrometry (GC/MS)*, U.S. Environmental Protection Agency, Office of Research and Development, Center for Environmental Research Information, Cincinnati, OH, January 1999.

U.S. EPA. 2012b. *List of Designated Reference and Equivalent Methods*, U.S. Environmental Protection Agency, Office of Research and Development, National Exposure Research Laboratory, Human Exposure & Atmospheric Science Division, Research Triangle Park, NC. June 6, 2012.
http://www.epa.gov/ttn/amtic/files/ambient/criteria/reference-equivalent-methods-list.pdf

Quality Assurance and Quality Control

40 CFR Part 58, Appendix A – Quality Assurance Requirements for SLAMS, SPMs and PSD Air Monitoring

PA DEP, 2012e. *Quality Assurance Manual for the PA Department of Environmental Protection Bureau of Laboratories, Revision 005.* PA Department of Environmental Protection, Bureau of Laboratories, Harrisburg, PA, January 2012.

PA DEP, 2007. *Quality Assurance Project Plan for the Air Toxics Monitoring Program*, PA Department of Environmental Protection, Bureau of Air Quality, Harrisburg, PA, Sept 2007.

PA DEP, 2012f. *Quality Assurance Project Plan for the PM$_{2.5}$ Ambient Air Monitoring Program*, PA Department of Environmental Protection, Bureau of Air Quality, Harrisburg, PA, January 2012.

PA DEP, 2012g. *Quality Assurance Project Plan for Nitrogen Dioxide, Sulfur Dioxide and Carbon Monoxide Ambient Air Monitoring Program (Draft)*, PA Department of Environmental Protection, Bureau of Air Quality, Harrisburg, PA, July 2012.

PA DEP, 2012h. *Quality Assurance Project Plan for the Ground-Level Ozone Ambient Air Monitoring Program*, PA Department of Environmental Protection, Bureau of Air Quality, Harrisburg, PA, May 2012.

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A. Singh, 2006, *On the Computation of a 95% Upper Confidence Limit of the Unknown Population Mean Based Upon Data Sets with Below Detection Limit Observations*, J.M. Nocerino, editor. March, 2006. **EPA/600/R-06/022**

ATSDR, 2012. *ATSDR Toxics Substances Portal*, Agency for Toxics Substances and Disease Registry, Atlanta, GA. 2012. http://www.atsdr.cdc.gov/substances/index.asp.

Gilbert, Richard O.,1987. Statistical Methods for Environmental Pollution Monitoring, Van Nostrand Reinhold Company, New York, NY, 1987, 320 pp.

Ott, Wayne R.,1995. Environmental Statistics and Data Analysis, CRC Press, Boca Raton, FL, 1995. 313 pp.

U.S. EPA. 1992. *Guidelines for Exposure Assessment*, U.S. Environmental Protection Agency, Risk Assessment Forum, Washington, DC, EPA/600/Z-92/001, May 1992.

U.S. EPA. 2000. *Science Policy Council Handbook: Risk Characterization*, U.S. Environmental Protection Agency, Office of Science Policy, Office of Research and Development, Washington, DC, EPA 100-B-00-002, December 2000.

U.S. EPA. 2003. *Framework for Cumulative Risk Assessment*. U.S. Environmental Protection Agency, Office of Research and Development, National Center for Environmental Assessment, Washington Office, Washington, DC, EPA/600/P-02/001F, May 2003.

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APPENDIX B – Development of Unconventional Shale Gas Resources in Pennsylvania

Pennsylvania is famous as the birthplace of the commercial petroleum industry with the completion of "Colonel" Edwin Drake's oil well on Oil Creek near Titusville in August of 1859. Pennsylvania has also had a long history of natural gas extraction and use. While early oil drillers would capture natural gas produced from their oil wells and use it to power engines (and in some cases provide light to the boom towns), it can be argued it wasn't until 1883 when John Newton Pew and Edward O. Emerson (cousin of Ralph Waldo Emerson) founded the Penn Fuel Gas Company, took gas from their wells in Murraysville, PA and provided gas to the Strip District in Pittsburgh did commercially produced natural gas serve as a legitimate commercial source of energy Pennsylvania[34]. J.N. Pew is also credited with the installation of the country's first natural gas compressor station in 1890, in addition to being one of the founders, with Emerson, of Sun Oil Company…later known as Sunoco.

In the 1920's and 30's natural gas production increased throughout the western and northcentral portions of Pennsylvania with the advancements in drilling that allowed producers to explore and tap formations of Pennsylvania's diverse geology that served as reservoirs for natural gas. Combined with the continued drilling to the shallow deposits, the shallow and deep drilling to these largely sandstone, siltstone and limestone strata have constituted all "conventional" natural gas drilling in Pennsylvania. At the close of the 20th century, thousands of producing conventional wells were, and still are, producing marketable amounts of natural gas. (see Figures B-1, B-2). It wasn't until early in the 21st century, however, that a combination of old and new technologies would open huge heretofore only speculated reserves of natural gas from an unconventional source…the dark, organically rich shales.

Geologists and drillers have known since the early days of gas drilling that dark, organically rich shale formations held natural gas. These deposits however were generally not commercially viable as the amounts of gas produced were small compared to the gas rich conventional formations that had been historically tapped. The shales were known to be long duration producers though. In fact many of the earliest gas wells drilled in Pennsylvania were to shale formations and some of them continue to produce small quantities of gas to this day.

In the 1970's after the oil price hikes resulting from the OPEC oil embargo, the U.S. Department of Energy funded the Eastern Gas Shales Project (EGSP) that's purpose was to extensively map organic rich shales and to research and develop new techniques to recover this gas. The Pennsylvania Geologic Survey took a large role in this project as five wells were drilled in western Pennsylvania Devonian[35] shales that provided critical technical information on the geology of the Devonian system and associated formations.

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[34] While earlier natural gas companies were established in Pennsylvania to provide gas in competition to the widely used gas created from coal ("manufactured" or "town" gas), Pew and Emerson's company was the first company in Pennsylvania chartered as a natural gas *utility* under then newly established gas utility laws.

[35] The Devonian is a geologic period and system that began at the end of the Silurian period (approximately 420 million years ago) to the beginning of the Carboniferous period (approximately 359 million years ago). It is divided into three series: upper, middle and lower. Upper Devonian strata are the youngest in the Devonian system while the lower are the oldest.

It was during these studies that correlations between high natural gas quantities and high organic richness of shales were made.

Figure B-1: Distribution of Pennsylvania Conventional Gas Wells and Oil/Gas Wells in 2011 – Light colored dots represent gas only producing wells (greater than 1000 cubic feet annually). Purple dots are wells that produce more than 1000 c.f. of gas in addition to more than 1 barrel of oil annually. Due to scale and the close proximity of most gas wells across a developed field, concentrations of white and/or purple dots may appear to be black. Figure B-2 shows a typical well density in a developed conventional gas field.
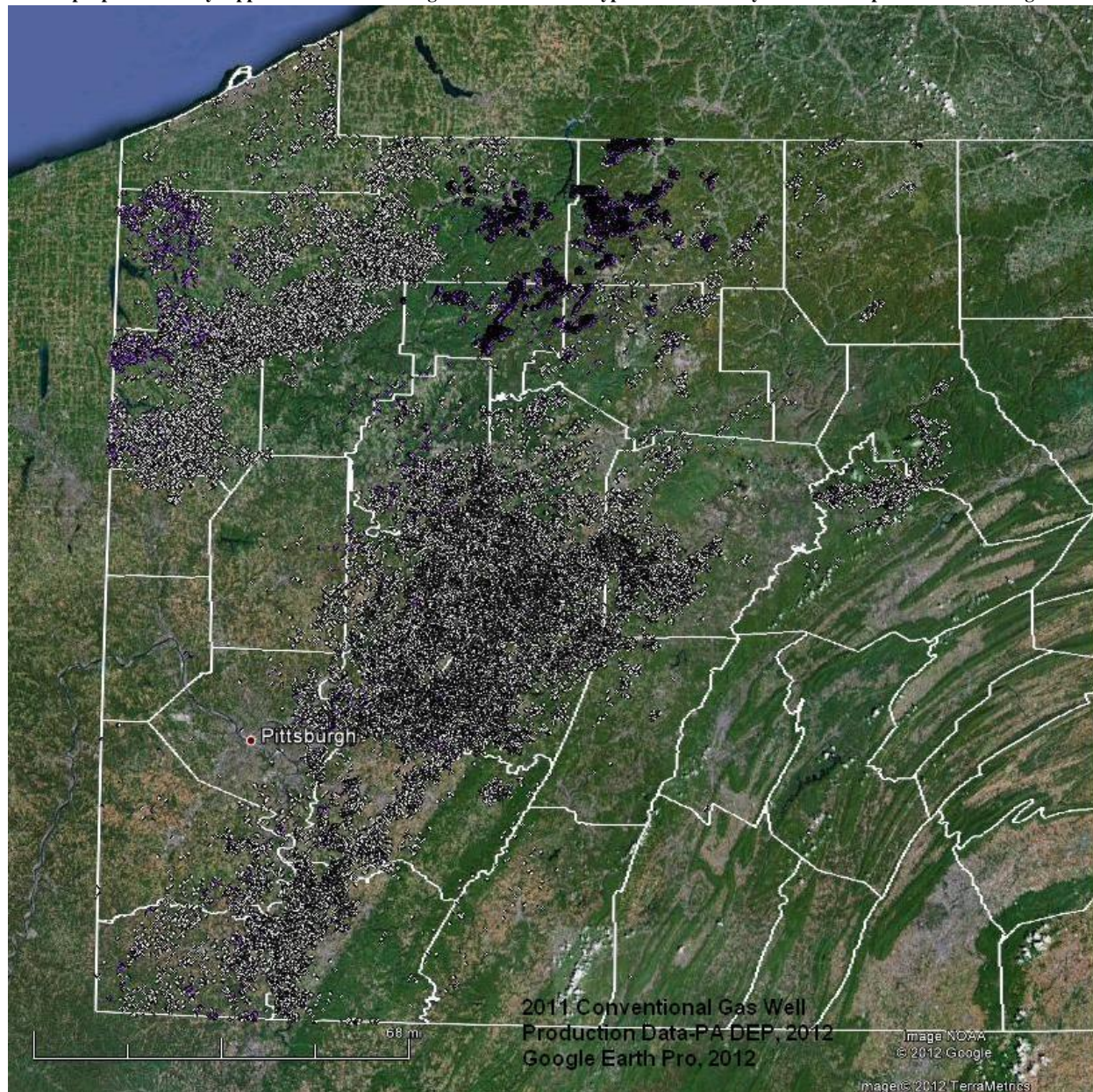
Part of the research of the EGSP was to experiment with extraction techniques to release the gas held in the shales. Different hydraulic fracturing[36] methods were employed using variations of fluid, proppant and

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[36] Hydraulic fracturing has been used for decades in Pennsylvania as a means to allow more gas to be released from a formation. At its simplest, the process historically involved pumping millions of gallons of water, or sometimes kerosene, mixed with sand,

Figure B-2: Central Indiana County, PA Conventional Well Distribution – In order to fully tap the gas reservoir underlying , historical conventional vertical drilling required placement of single wells usually no more than one quarter to one half mile from the next. Of the almost 9700 gas and oil/gas producing wells in Indiana County, over 83% now produce less than 5 million cubic feet of gas each annually. Wells shown below extract gas from the shallow Upper Devonian formations and are typical "Conventional" wells. It is important to note that these wells are mature and long past their prime production. Their current production is not indicative of gas flows when first drilled.

pressures to see the variation in production. This research was ultimately carried on into production in the 1990's as a combination of these methods was found to be particularly effective in the Barnett Shale in

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and other substances, under very high pressure into a drilled section of a well. The liquid fractured the rock and the sand, or other "proppant", propped open the fractures vertically thus allowing the gas to escape and be recovered. Shale formations, though, because of their density and low permeability, were difficult to fracture using these traditional methods.

Texas. Most notable of the new hydraulic fracturing method for shale was the introduction of a friction reducing gel that enhanced the ability of the fracture to penetrate the tight shale. This method became known as "slick-water" hydraulic fracturing.

Another new "old" technology that allowed for gas recovery from shales was the use of "directional" or "horizontal" drilling. While conventional wells were drilled vertically from the surface to the target formation, advances in drilling technology widely adopted in the 1980's would now allow wells to be bored away from the vertical and drill laterally along the shale bed instead of just through it. This increased the exposed shale from tens of feet to potentially thousands thus increasing the amount of recoverable gas. Additionally the technology allowed for multiple vertical well bores to be drilled from a single pad and access far more gas producing shale than by using vertical wells alone. This not only reduced overall costs but reduced the surface footprint of the drilling activity substantially over the conventional methods.

These technologies combined now allow drillers to access and commercially produce natural gas from the organic rich shale formations that previously were regarded as unproductive and more often than not a nuisance. Unconventional drilling became defined as the processes used to extract natural gas from the "unconventional" organic rich shale formations throughout the U.S.

As these technologies were shown to be effective in the Texas Barnett shale, producers explored other shale basins in the U.S. for what they hoped would be similar results. Plays in the Haynesville shale in Louisiana and the Fayetteville shale in Arkansas soon were producing similar commercial quantities as the Barnett. However it wasn't long before producers would soon set their sights on what was likely the largest known shale gas resource in the country…the Appalachian Basin and the Marcellus shale.

Figure B-3 depicts the extent of currently known shale gas plays, in their appropriate geologic basins, for the U.S. as of 2011.

The Marcellus Shale is but one of three major organically rich shale formations contained within the Appalachian Basin: the Devonian (Ohio), Marcellus and the deeper Ordovician[37] Utica.

Activity in the Marcellus play began in Pennsylvania with single well drilled in Mount Pleasant Township, Washington County in 2003 by Great Lakes Energy Partners, LLC (now Range Resources Appalachia LLC). Originally the drillers were targeting a lower formation of dolomite (Lower Silurian Lockport). After this formation was unproductive they drilled deeper to the Salina Group. With still no production the drillers looked to the higher Marcellus coupled with the "slickwater" hydraulic fracturing method used in the Barnett shale. This produced sizeable quantities of gas. The Renz #1 well went into production in 2005 and produced over 44 million cubic feet of natural gas in its first full year of production. A second well at the same site (Renz #2) produced over 52 million cubic feet in its first 11 months of production concurrently with Renz #1. This was quickly followed by others in the County as the sustained production appeared to be viable. In addition to natural gas, wells in Washington County also produced commercial amounts of natural gas liquids that could be fractionated and sold as high value petroleum liquids (e.g. propane, butane and mixed liquids).

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[37] The Ordovician period and system is comprised of formations that were formed between approximately 485 to 443 million years ago. The Utica shale formation of this system is older and generally deeper than both the Marcellus and Ohio formations.

Drilling also began in 2005 and 2006 in northeastern Pennsylvania in both Bradford and Susquehanna Counties. Unlike the southwestern portion of PA, natural gas from the northeast and northcentral counties largely lacked the high value gas liquids but however proved to be of exceptional quality. It had few impurities and needed very little post extraction treatment (e.g. dehydration). Anecdotally the gas from

Source: Energy Information Administration
Updated: May 9, 2011

Figure B-3 - Major Shale Plays in Continental U.S. - Shale gas is available in many basins across the United States. The Marcellus Shale Formation, which extends from New York into Pennsylvania, Maryland, Ohio, Virginia, and West Virginia, and covers approximately 95,000 square miles, is the most expansive shale gas "play" in the United States. An organically rich, black shale at the base of the Middle Devonian Hamilton Group, the Marcellus Shale is now one of the most active shale plays in terms of drilling, with Pennsylvania operations primarily in the southwest, northcentral and northeast portions of the state.

 this region has been called "Gucci Gas" because from many wells the gas is nearly pipeline grade commercial quality right out of the ground.

Across most of the Marcellus play in Pennsylvania, drilling and production increased significantly every year from 2006 onward. While 186 permits to drill and operate a new unconventional well or drill an existing well deeper were issued in 2007, 3,561 permits were issued in 2011. For the same years, unconventional gas wellhead production increased from 1.9 billion cubic feet to just over 1 trillion cubic feet annually.   In order to accommodate the increasing supply, placement of a more permanent gathering,

processing and transmission infrastructure also increased. Pennsylvania's proximity to major northeast markets and an already existing network of interstate gas transmission pipelines and underground storage fields (repurposed formerly producing gas fields first) stimulated further unconventional development in Pennsylvania.

As more wells came into production and were placed "in-line" (connected to a gathering and transmission network), it became apparent that shale gas production from the Marcellus was not an isolated occurrence but indicative of a general trend of productivity across the play.

Figure B-4 – Unconventional Gas Well Distribution in Pennsylvania June 2012 - Light blue dots represent wells that reported natural gas production in the first 6 month of 2012. Dark blue squares represent wells that have been "spud" (drilled) but are not yet producing because they are awaiting hydraulic fracturing, completion or have been "shut-in" and are awaiting collection infrastructure. Each dot or square may represent multiple wells due to the scale of the image and the existence of multiple wells on one drilling pad. Red dots indicate natural gas compression, dehydration and/or processing facilities (constructed or planned) that had received either air quality plan approvals, general air quality permits (GP5) or air quality operating permits as of September 2012. These facilities include conventional gas facilities. Data Source: PA DEP, Jan-Jun 2012 Statewide Oil & Gas Production Reports.
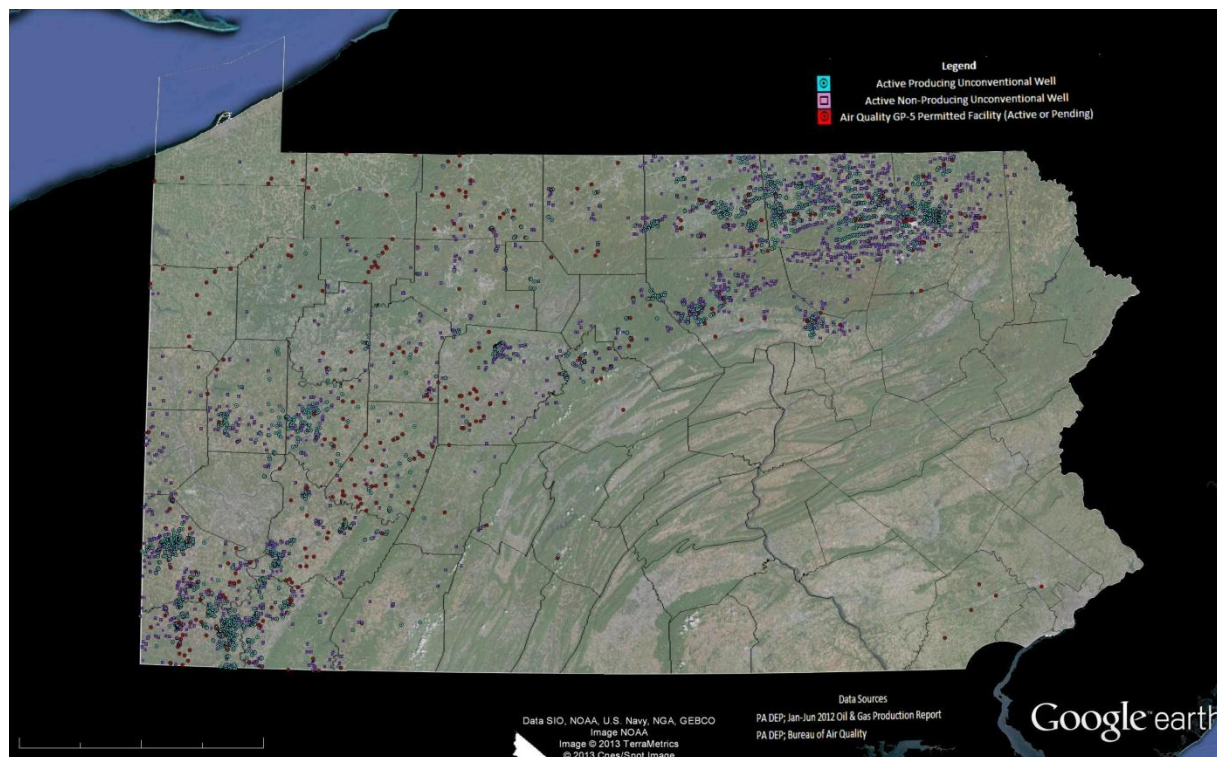
Further examination of the northeast / northcentral region of the state with active unconventional production (figure B-5), shows that while the activity is widespread across those counties, the well pattern is unlike that seen in the historical Pennsylvania conventionally drilled fields shown in Figure B-2. This is due largely to the use of horizontal drilling that allows greater access to more of the subsurface area of the target formation with comparatively less surface land disturbance.

Figure B-5 – Unconventional Gas Well Pad Locations in Central Bradford County–Each location usually represents multiple wells on a single pad. However the counties are clearly not being developed in the grid configuration as evidenced in the conventionally drilled areas of Pennsylvania. The active non-producing wells (dark blue squares) are those that are either ready to be drilled, fractured, completed or have been completed and are shut-in awaiting connection to gathering infrastructure. GP-5 facilities are either proposed, in construction, or operating. For comparison purposes, the scale of Figures B-2 and B-5 are similar. Data Source: PA DEP, Jan-Jun 2012 Statewide Oil & Gas Production Reports.

References

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Harper, John A. and Kostelnik, Jamie. *The Marcellus Shale Play in Pennsylvania: Parts 1-4* (Online Presentations), PA Dept. of Conservation and Natural Resources / Pennsylvania Geologic Survey. Accessed 12/4/2012. http://www.dcnr.state.pa.us/topogeo/econresource/oilandgas/marcellus/index.htm

APPENDIX C – Study Toxic Volatile Organic and Carbonyl Analyte List with Method Detection Limits (MDLs)

Target Pollutant List

CAS#	Analyte	MDL (ppbv)	CAS#	Analyte	MDL (ppbv)	CAS#	Analyte	MDL (ppbv)
74-82-8(Methane)	**Methane/Non-Methane Compounds**	0.1 ppm / 5 ppb	622-96-8	1-Ethyl-4-methylbenzene	0 043	1634-04-4	2-Methoxy-2-methylpropane (MTBE)	0 030
10028-15-6	Ozone	<0 6 ppb	591-78-6	2-Hexanone	0 030	75-09-2	Methylene chloride	0 078
10102-44-0	**Nitrogen Oxides**	0.4 ppb	67-64-1	**Acetone (2-Propanone)**	0 076	108-10-1	4-Methyl-2-pentanone (MBK)	0 040
630-08-0	**Carbon Monoxide**	<0 05 ppm	107-02-8	Acrolein*	0 057	142-82-5	**n-Heptane**	0 040
6/4/7783	Hydrogen Sulfide (API / Jerome)	0.4 ppb / 3 ppb	71-43-2	**Benzene**	0 030	110-54-3	**n-Hexane**	0 038
n/a	Particulate Matter (<2 5 microns)	n/a	75-27-4	Bromodichloromethane	0 017	95-47-6	**o-Xylene**	0 043
71-55-6	1,1,1-Trichloroethane	0.017	75-25-2	Bromoform	0 019	115-07-1	**Propene**	0 030
79-34-5	1,1,2,2-Tetrachloroethane	0.019	74-83-9	Bromomethane	0 046	100-42-5	Styrene	0 041
79-00-5	1,1,2-Trichloroethane	0.018	75-15-0	Carbon disulfide	0 064	127-18-4	Tetrachloroethene (PERC)	0 030
76-13-1	1,1,2-Trichloro-1,2,2-trifluoroethane	0.061	56-23-5	Carbon tetrachloride	0 015	109-99-9	Tetrahydrofuran (THF)	0 027
75-34-3	1,1-Dichloroethane	0.021	108-90-7	Chlorobenzene	0 029	108-88-3	**Toluene**	0 028
75-35-4	1,1-Dichloroethene	0.059	75-00-3	Chloroethane	0 056	156-60-5	trans-1,2-Dichloroethene	0 025
120-82-1	1,2,4-Trichlorobenzene	0.048	75-01-4	Chloroethene	0 072	10061-02-6	trans-1,3-Dichloro-1-propene	0 021
95-63-6	1,2,4-Trimethylbenzene	0.043	67-66-3	Chloroform	0 019	79-01-6	Trichloroethylene (TCE)	0 025
106-93-4	1,2-Dibromoethane	0.025	74-87-3	Chloromethane	0 055	75-69-4	Trichlorofluoromethane	0 064
95-50-1	**1,2-Dichlorobenzene**	0.035	156-59-2	cis-1,2-Dichloroethene	0 028	75-07-0	**Acetaldehyde (Ethanal)**	0 035
107-06-2	1,2-Dichloroethane	0.026	10061-01-5	cis-1,3-Dichloro-1-propene	0 026	67-64-1	**Acetone (2-Propanone)**	0 054
78-87-5	1,2-Dichloropropane	0.021	110-82-7	Cyclohexane	0 027	100-52-7	Benzaldehyde	0 017
76-14-2	1,2-Dichloro-1,1,2,2-tetrafluoroethane	0.034	124-48-1	Dibromochloromethane	0 024	123-72-8	Butyraldehyde (Butanal)	0 024
108-67-8	1,3,5-Trimethylbenzene	0.045	75-71-8	Dichlorodifluoromethane	0 021	50-00-0	**Formaldehyde**	0 060
106-99-0	1,3-Butadiene	0.065	100-41-4	**Ethylbenzene**	0 040	590-86-3	Isovaleraldehyde (3-methyl-Butanal)	0 039
541-73-1	**1,3-Dichlorobenzene**	0.033	87-68-3	Hexachloro-1,3-butadiene	0 027	123-38-6	Propionaldehyde (Propanal)	0 026
106-46-7	**1,4-Dichlorobenzene**	0.030	108-38-3	**m&p-Xylene**	0 087	123-73-9	Crotonaldehyde (trans-2-Butenal)	0 029
106-94-5	1-Bromopropane	0.028	78-93-3	2-Butanone (Methyl Ethyl Ketone)	0 032			

MDL	Minimum Detection Limit (by unit) for continuous monitors; Method Detection Limit (by unit-volume) for Canister/Carbonyl	
	Continuous Measurement Compounds	
	TO-11A Compound (Carbonyl) - DNPH Cartridge	
	TO-15 Compound - Canister	

Compounds in **bold** are analytes potentially associated with permanent shale gas facilities through natural gas combustion, or direct/fugitive emissions of "wet" gas.

* While Acrolein (propenal) is being sampled, there exist high uncertainty in reported results due to sampling and analytical limitations. Because of this uncertainty, results for Acrolein may not be used for final risk analysis.

APPENDIX D – Example Sampling Site Agreement

THIS AGREEMENT, made this XX day of *Month*, 2012, by and between *resident*, hereinafter called **OWNER** and the Commonwealth of Pennsylvania, Department of Environmental Protection, Harrisburg, Pennsylvania, hereinafter called **LICENSEE**.

   WHEREAS, LICENSEE is authorized under Section 4(8) of the Air Pollution Control Act (35 P.S. 4001 et seq.) to conduct atmospheric sampling programs; and

   WHEREAS, pursuant to such authority, **LICENSEE** seeks to erect an Air Monitoring Station to monitor air quality;

   NOW, THEREFORE, the parties hereto, intending to be legally bound hereby, agree as follows:

   1. The **OWNER** grants to **LICENSEE** a license to use certain premises to access, erect, maintain, operate and remove an Air Sampler. The said Air Sampler and its associated equipment shall be located on *Street* in *Town*, PA in Washington County, a site designated as a blue dot on the map attached hereto, made part hereof, and marked Exhibit "A", hereinafter called the "premises".

   2. This **AGREEMENT** shall be for a term of eighteen (18) months commencing on the date of this agreement, or until either party gives the other party ninety (90) day notice in writing of its intention to terminate the **AGREEMENT**, whichever occurs first. At the end of the term, the **LICENSEE** shall remove all materials placed on the premises and shall restore the premises to the same condition as it was found, to the reasonable satisfaction of the **OWNER**, provided that the **OWNER** may waive this requirement if it wishes to have the benefit of any of the improvements made by the **LICENSEE**.

   3. **LICENSEE** shall pay to **OWNER** a monthly fee of $X, payable by the first day of each month. Checks shall be made payable to: *Property Owner*.

   4.   After the original installation of said equipment has been completed, **LICENSEE**, at its own expense, shall maintain the same in good order and repair. No substantial changes, additions or alterations shall be made without obtaining prior written approval of **OWNER**.

   5. **OWNER** agrees to allow road access to and parking for one (1) vehicle on the premises.

   6. **LICENSEE** agrees that in the event **OWNER** sells the property where **LICENSEE** has been permitted to enter on the premises, the **PURCHASER** of **OWNER'S** property shall have at their option the right to continue the license agreement, or terminate the agreement.

   OWNER and/or **PURCHASER** will notify **LICENSEE** in writing, and sent by mail with both **OWNER'S** and **PURCHASER'S** signatures, of the intention to terminate the license, within five (5) business days of the closing on the sale of property.

   Upon such notice, the **LICENSEE** shall within ninety (90) days of written notification, remove all materials placed on the premises and shall restore the premises to the same condition as it was found, provided that the **PURCHASER** may waive this requirement if it wishes to have the benefit of any of the improvements made by **LICENSEE**.

   If **LICENSEE** is not so notified, this **AGREEMENT** shall remain in full force and effect.

  7. In the event of any personal injury or property damage, liability will fall where it does by law against the responsible party. In any event, **LICENSEE** shall maintain comprehensive general liability insurance to protect **LICENSEE** and **OWNER** from claims arising out of the Department's performance of this **AGREEMENT**. The amounts of said insurance shall be for personal injury and property damage, a combined single limit of $250,000 per person and $1,000,000 per occurrence.

  8. All notices under this **AGREEMENT** must be in writing, and shall be validly given when sent to the address set forth below (or any other address that the party may have designated to the sender by like notice):

   To **OWNER**: *Property Owner*
          Street
          Town, PA *Zip Code*

   To **LICENSEE**: Commonwealth of Pennsylvania
          Department of Environmental Protection
          Bureau of Office Services
          15th Floor, Rachel Carson State Office Building
          P.O. Box 8473
          Harrisburg, Pennsylvania 17105-8473

  9. The **OWNER** shall comply with the terms and conditions of the following attached hereto and made a part hereof:

   Exhibit "B" - Provisions for Commonwealth Contracts
   Exhibit "C" - Nondiscrimination Clause

  10. All rights, duties and responsibilities under this **AGREEMENT** shall extend to and be binding upon the heirs, legal representatives, successors and assigns of the parties hereto.

        IN WITNESS WHEREOF, the parties have duly executed this **AGREEMENT** the day and year first above written.

ATTEST: **OWNER:**

_____   _____

                                            Property Owner
                                            SSN# or EIN:

ATTEST: **LICENSEE:**

_____   _____

                                            Executive Deputy Secretary of
                                            Administration and Management Services
                                            Department of Environmental Protection

Approved as to Legality and Form:

_____   _____
Office of Attorney General   **Chief/Assistant Counsel**
                                            Department of Environmental Protection

Approved:

_____
Comptroller

APPENDIX E – Toxic VOC, Carbonyl Sampler and Meteorological Equipment Minimum Specifications

Design and performance specifications for the VOC sampler.

Equipment	Acceptance Criteria	Reference
Canister Design Specifications		
Size	6 liters	TO-15[1], Sec 8.2.2.1
Medium	Passivated electro-polished stainless steel	TO-15, Sec 2.1
Max Pressure	30 psig	TO-15, Sec 8.2.2.1
Collection efficiency	> 99%	Vendor Specified
Method Detection Limit	Compound specific, usually >0.1 ppbv	TO-15, Sec 11.2
Sampler Performance Specifications		
Sample Flow Rate	3 to 10 cc/min	TO-15, Sec 8.2.3.1
Flow Regulation	1.0 cc/min	Vendor Specified
Flow Rate Precision	$\pm$10%	TO-15, Sec 7.1.1.4
Flow Rate Accuracy	$\pm$10%	TO-15, Sec 7.1.1.4
External Leakage	None	
Internal Leakage	None	
Clock/Timer	24 hour $\pm$ 5 min accuracy	TO-15, Sec 8.2.3.2

1 U.S. EPA, Compendium Method TO-15, *Determination of Volatile Organic Compounds (VOCs) In Air Collected In Specially-Prepared Canisters And Analyzed By Gas Chromatography/Mass Spectrometry (GC/MS)*, U.S. Environmental Protection Agency, Office of Research and Development, Center for Environmental Research Information, Cincinnati, OH, January 1999.

Design and performance specifications for the carbonyl sampler.

Equipment	Acceptance Criteria	Reference
Filter Design Specifications		
Type	Silica Gel cartridge	TO-11A[1], Sec 4.4.1
Size	350 mg	Vendor Specified
Medium	2,4-Dinitro-phenyl hydrazine coating	
Pressure Drop	< 3.5 in H20 @ 200 cc/min	Vendor Specified
Sampler Performance Specifications		
Sample Flow Rate	150 ml/min	TO-11A, Sec 7.3
Flow Regulation	$\pm$5 ml/min	
Flow Rate Precision	$\pm$5%	
Flow Rate Accuracy	$\pm$5%	
External/Internal Leakage	None	
Clock/Timer	24 hour $\pm$ 2 min accuracy	

Equipment	Acceptance Criteria	Reference
Ozone Denuder Specifications		
Size	1/4" x 24" coiled tube	
Material	Etched glass	
Coating	Potassium Iodide, ACS cert. Reagent	TO-11A, Sec 6.7
Temperature	60 °C	

1 U.S. EPA, Compendium Method TO-11A, 2nd Ed., *Determination of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed by High Performance Liquid Chromatography (HPLC)*, EPA/625/R-96/010b, U.S. Environmental Protection Agency, Office of Research and Development, Center for Environmental Research Information, Cincinnati, OH, January 1999.

Minimum design and performance specifications for meteorological measurement equipment

Measurement	Method	Reporting Units	Operating Range	Resolution	Min. Sample Frequency	Raw Data Collection Frequency
Ambient Temperature	Thermistor	ºC	-30 – 50	0.5	Hourly	1 minute
Wind Speed	Cup, prop or sonic anemometer	m/s	0.5 – 50.0	0.2	Hourly	1 minute
Wind Direction	Vane or sonic anemometer	Degrees	0-360 (540)	1.0	Hourly	1 minute

APPENDIX F – Toxic Monitoring Section Data Analysis, Risk Assessment and Data Reporting Protocol

This protocol should be used for the development of cancer risk and non-cancer hazard inhalation assessments using ambient toxic monitoring network data. The protocol may also be adapted for use in special air monitoring studies as needed.

Data Analysis & Risk Assessment

1. For short-term screening studies (less than 10 samples), if there is at least one valid sample above the non-detect concentration, substitute ½ the Method Detection Limit (MDL) or Reporting Limit (RL) for all non-detects. If all sample concentrations are non-detects, do not use the compound in data or risk analysis. Refer to Tables 1 and 2.

2. For both long-term studies (10 samples or more) and toxics network stations, if 15% or less of the samples are non-detects, substitute ½ the MDL or RL for all non-detects, calculate risk values and bold in the risk table. If greater than 15%, but 85% or less, of the samples are non-detects, substitute ½ the MDL or RL for all non-detect data, calculate risk values and show in risk table in normal font. If greater than 85% of the samples are non-detects, do not show risk values in risk table. Refer to Table 3.

3. For datasets where there exist fewer than 10 measurements (including ½ MDL/RL substitutions), instead of using the arithmetic mean of the samples, calculate risk based on the 95th percentile upper confidence limit average of the samples. This will insure that the risk assessment will give us a probability of being correct in our analysis 95% of the time. Refer to Tables 1 and 2.

4. For long-term studies, use the arithmetic mean of the samples for calculating risk since we have a more representative data set and we assume near normal or lognormal distribution.

5. Alternative mean estimation methods for datasets containing high percentages of non-detect observations may be used in addition to the above methods. These alternative methods, however, must be clearly documented and used for comparative purposes only. These methods and their effectiveness at mean estimation are summarized by EPA at their Site Characterization and Monitoring Technical Support Center website at http://www.epa.gov/osp/hstl/tsc/issue.htm#singh06. Most of these methods have also been incorporated into a shareware statistical software suite supported by EPA: ProUCL. This software can be found for download at http://www.epa.gov/osp/hstl/tsc/software.htm.

6. For hexavalent chromium (Cr^{+6}) continue to use the assumption that this compound is $1/7^{th}$ of the total chromium concentration in the absence of a true Cr^{+6} measurement.

7. Because MDL's are based on the performance of the analytical equipment at the time the MDL is determined (generally annually), there can exist variability between years. Large variations in MDLs between two years can have a pronounced, artificially induced effect on risk estimates for analytes with a high percentage of substituted data. In order to "smooth" this inevitable variation, MDLs used for any given year will be a rolling average of the five (5) preceding years. For example the substituted MDLs value used for non-detect observations for risk assessment in 2013, will be the arithmetic mean of the MDL's for 2009 through 2013.

8. Use up-to-date cancer Unit Risk Factor (URF) and non-cancer Reference Concentration (RfC) values at the time of the report writing, using an EPA-based hierarchy of sources:
    a. EPA – Integrated Risk Information System
    b. Provisional Peer-Reviewed Toxicity Values (PPRTV)
    c. Other peer-reviewed values such as (and in no order)
        i.   California EPA (CalEPA)
        ii. Agency for Toxic Substances & Disease Registry (ATSDR)
        iii. National Center for Environmental Assessment (NCEA)

    DEP will utilize the Dept. of Energy's Risk Assessment Information System (RAIS) to automate the process of updating risk factors since it also follows the same hierarchy of sources. DEP may make adjustments to the risk factors based on the project and DEP experience.

9. If a study report contains data over multiple years, the latest risk factors will be applied to the estimated mean concentration of the multi-year dataset. Additionally if two or more time periods are compared for relative change in risk, the latest risk factors will be used for both/all time periods to reflect the best known past and present risk given current knowledge.

10. Use the appropriate risk factors based on sampling duration. For example, 1-hour canister samples should only be compared with 1-hour risk values (such as EPA's Acute Exposure Guideline Levels (AEGL-1)).

11. Calculate an Excess Lifetime Cancer Risk (ELCR) for each compound by multiplying the estimated mean concentration by the respective URL. A minimum of 6-months sampling (on a 1-in-6-day schedule) is required with a minimum of 1 year desired.

12. Use the EPA-recommended minimum acceptable excess lifetime cancer risk limit of 1-in-10,000 (i.e. any risk less than 1 would be acceptable). For excess lifetime cancer risks greater than 1, the information may be forwarded to the PA Department of Health for further analysis. Other risk limits may be used at the discretion of the

Bureau of Air Quality. For example, a specific study may have a minimum allowable risk of 1-in-1,000,000 to reflect a higher threshold of acceptable risk.

13. Calculate a Hazard Quotient for each compound by dividing the average by the respective RfC. A minimum of 6-months sampling (on a 1-in-6-day schedule) is required with a minimum of 1 year desired.

14. Use the EPA-recommended acceptable hazard quotient/index limit of 1.0 (i.e. for any quotient/index less than 1.0, a non-cancer health effect is not expected). For a hazard quotient/index greater than 1.0, the information may be forwarded to the PA Department of Health for further analysis.

Data Presentation

1. All excess lifetime cancer risk results will be normalized to a population size of 10,000. Alternatively, cancer risk results may be normalized to a different population size based on what is appropriate for the study. For example, in a large population area, all excess lifetime cancer risk assessment will be presented for a risk per 100,000 population size.

2. Raw sample data should be listed in the Appendix of the report separate from the risk assessment results (Table 1 and 2). For toxic VOC data, both ppbv and ug/m^3 units will be presented. Toxic metal data will be presented in ug/m^3 to be consistent with VOC units.

3. Present URF risk factors (for both VOC's and metals) in decimal notation (as opposed to scientific) in m^3/ug units. Similarly, present RfC values in decimal notation in ug/m^3 units.

4. Compound names will be names in most common use or using latest International Union of Pure and Applied Chemistry (IUPAC) nomenclature and presented in the tables sorted alphabetically. Chemical Abstract Service (CAS) numbers will be included with each compound to ensure proper compound identification.

5. A clarification should accompany all risk data in a report. The clarification should address the fact that the "risk results are for the target set of compounds only, that is, the sampled set of pollutants most likely to be a factor in, or are relevant to, the study".

Table 1. Example of DEP Reported Toxic Metal Estimated Risk/Hazard Assessment at Air Toxic Study Site using a TSP Sampler[38].

Air Toxics Study Site

Metals - TSP

Metal	Average µg/m³	95% UC µg/m³	Chronic Excess Lifetime Cancer Risk in 10,000	2007 PA Exces Lifetime Cancer Risk in 10,000	Chronic Hazard Quotient[d]
Arsenic	0 00202	0 00257	0.110	0 036	0.17
Beryllium	<RL	<RL			
Cadmium	0 00026	0 00032	0.006	0 005	0 02
Chromium (Total)	0 00539	0 00701			
Chromium VI (Assumed)[e]	0 00077	0 00100	0.120	0 050	0 01
Lead[f]	0 01099	0 01410	0.002	0 001	
Manganese	0 03852	0 05008			0 56
Nickel[g]	0 03237	0 04944	0.120	0 006	0 99
Zinc	0 07673	0.10675			
			0.358	0 098	1.8

[b] 1 in 10,000 risk due to inhalation is based on the average of samples (ELCR =95%UC x URF). Risk is not calculated for compounds that were not detected in all samples.

[c] Calculated by averaging data collected in 2007 at the Chester, Erie, Lancaster, Lewisburg, Marcus Hook, Reading and Swarthmore toxic monitoring sites.

[d] A Hazard Quotient < 1 indicates no expected non-cancer health effects (HQ = 95%UC / RfC). The HQ is not calculated for compounds that were not detected in all four samples.

[e] Chromium VI concentration assumed to be 1/7th the Total Chromium concentration by DEP for study purposes.

[f] The NAAQS standard for lead is 0.15 ug/m³ (rolling 3-month average).

[g] The URF for Nickel is the IRIS value for Nickel (Refinery Dust).

<RL - Compound not detected, or less than the Lab Reporting Limit (RL), in all DEP Samples

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[38] Data in Tables 1, 2 and 3 are not representative of actual data but are for demonstration purposes only.

Table 2. Example of DEP Reported Estimated VOC Inhalation Risk/Hazard Assessment at the Air Toxics Study Site.

Air Toxics Study Site

Volatile Organic Compounds (VOCs)

A. High Degree of Certainty in Estimated Risks (85% of Data Above Minimum Detect Limit)

CAS #	Compound	Average ug/m³	Excess Lifetime Cancer Risk[b] in 10,000	2007 PA Excess Lifetime Cancer Risk[c]	Hazard Quotient[d]
76-13-1	1,1,2-Trichloro-1,2,2-trifluoroethane	0.548			0.00
95-63-6	1,2,4-Trimethylbenzene	0.747			0.11
106-46-7	1,4-Dichlorobenzene	0.450	0.0500		0.00
622-96-8	1-Ethyl-4-methylbenzene	0.600			
78-93-3	2-Butanone (MEK)	3.808			0.00
71-43-2	Benzene	1.421	0.1100	0.0620	0.05
56-23-5	Carbon tetrachloride	0.702	0.1100	0.0800	0.02
67-66-3	Chloroform	0.117	0.0270	0.0340	0.00
74-87-3	Chloromethane	1.022	0.0180	0.0180	0.01
75-71-8	Dichlorodifluoromethane	2.480			0.01
100-41-4	Ethylbenzene	0.406	0.0100	0.0047	0.00
108-38-3	m&p-Xylene	1.218			0.01
75-09-2	Methylene chloride	0.689	0.0032	0.0012	0.00
142-82-5	n-Heptane	1.406			
110-54-3	n-Hexane	0.454			0.00
95-47-6	o-Xylene	0.556			0.01
115-07-1	Propene	1.297			0.00
100-42-5	Styrene	0.281			0.00
108-88-3	Toluene	3.842			0.00
75-69-4	Trichlorofluoromethane	1.311			0.00
			0.3282	0.1999	0.2

B. Low Degree of Certainty in Estimated Risks (Less Than 85% of Data Above Minimum Detect Limit)

CAS #	Compound	Average ug/m³	Excess Lifetime Cancer Risk[b] in 10,000	2007 PA Excess Lifetime Cancer Risk[c]	Hazard Quotient[d]
107-06-2	1,2-Dichloroethane	0.060	0.0160	0.0320	
108-67-8	1,3,5-Trimethylbenzene	0.369			0.06
591-78-6	2-Hexanone	0.880			
108-10-1	4-Methyl-2-pentanone (MIBK)	0.541			0.00
108-90-7	Chlorobenzene	0.108			0.00
110-82-7	Cyclohexane	0.082			0.00
127-18-4	Tetrachloroethene (PERC)	0.197	0.0120	0.0120	0.00
109-99-9	Tetrahydrofuran (THF)	0.157			
79-01-6	Trichloroethylene (TCE)	0.083	0.0950	0.2300	0.00
			0.1230	0.2740	0.1

C. No Estimated Risk (No Data Above Minimum Detect Limit)

CAS #	Compound	Average ug/m³	Excess Lifetime Cancer Risk[b] in 10,000	2007 PA Excess Lifetime Cancer Risk[c]	Hazard Quotient[d]
71-55-6	1,1,1-Trichloroethane				
79-34-5	1,1,2,2-Tetrachloroethane				
79-00-5	1,1,2-Trichloroethane				
75-34-3	1,1-Dichloroethane				
75-35-4	1,1-Dichloroethene				
106-93-4	1,2-Dibromoethane				
76-14-2	1,2-Dichloro-1,1,2,2,tetrafluoroethane				
95-50-1	1,2-Dichlorobenzene				
78-87-5	1,2-Dichloropropane				
106-99-0	1,3-Butadiene				
541-73-1	1,3-Dichlorobenzene				
106-94-5	1-Bromopropane				
1634-04-4	2-Methoxy-2-methylpropane (MTBE)			0.0002	
75-27-4	Bromodichloromethane				
75-25-2	Bromoform				
74-83-9	Bromomethane				
75-15-0	Carbon disulfide				
75-00-3	Chloroethane				
75-01-4	Chloroethene			0.0034	
156-59-2	cis-1,2-Dichloroethene				
10061-01-5	cis-1,3-Dichloro-1-propene				
124-48-1	Dibromochloromethane				
87-68-3	Hexachloro-1,3-butadiene				
156-60-5	trans-1,2-Dichloroethene				
10061-02-6	trans-1,3-Dichloro-1-propene				

[b] Risk based on the sample average (ELCR = Avg x URF). Risk is not calculated for compounds that were not detected in all samples.

[c] Calculated by averaging data collected in 2007 at the Arendtsville, Chester, Erie, Lancaster, Lewisburg, Marcus Hook, Reading and Swarthmore toxic monitoring sites.

Table 3. Example of Reported DEP Toxic Metal Sampling Results at the Air Toxics Study Site using a TSP Sampler.

TSP/Metals

Date	Arsenic	Beryllium	Cadmium	Total Chromium	Lead	Manganese	Nickel	Zinc
			DEP Samples (ug/m^3)					
2/20/09	0.00087	<RL	0.00016	0.00170	0.00357	0.01817	0.00311	0.02583
2/24/09	0.00450	<RL	0.00033	0.00615	0.01601	0.05963	0.05001	0.17233
3/4/09	0.00709	<RL	0.00054	0.01647	0.02767	0.06745	0.18032	0.31740
4/19/09	0.00226	<RL	0.00019	0.00237	0.01634	0.02512	0.00634	0.05189
4/25/09	0.00256	<RL	0.00048	0.00577	0.02498	0.06069	0.01710	0.04389
5/1/09	0.00147	<RL	0.00024	0.00225	0.00615	0.00932	0.01066	0.03566
5/7/09	0.00154	<RL	0.00026	0.00327	0.00697	0.02884	0.01786	0.04655
5/13/09	0.00126	<RL	0.00020	0.00283	0.00706	0.04752	0.00544	0.06204
5/19/09	0.00261	<RL	0.00038	0.00618	0.01506	0.06562	0.04993	0.10667
5/25/09	0.00108	<RL	0.00018	0.00209	0.00582	0.02192	0.00522	0.04003
5/31/09	0.00112	<RL	0.00020	0.00360	0.00936	0.03767	0.00852	0.05417
6/6/09	0.00166	<RL	0.00020	0.00285	0.00775	0.02211	0.00994	0.04291
6/12/09	0.00086	<RL	0.00014	0.00175	0.00605	0.01647	0.00513	0.03310
6/18/09	0.00146	<RL	0.00011	0.00269	0.00440	0.02628	0.00598	0.03757
6/24/09	0.00165	<RL	0.00024	0.00417	0.01056	0.04573	0.03948	0.07548
6/30/09	0.00141	<RL	0.00020	0.00383	0.00883	0.03808	0.01562	0.07246
7/6/09	0.00242	<RL	0.00035	0.00809	0.01717	0.07906	0.12528	0.14618
7/12/09[a]	0.00400	<RL	0.00071	0.01434	0.03339	0.13355	0.10748	0.28300
7/18/09	0.00179	<RL	0.00030	0.00482	0.01226	0.02819	0.01456	0.06127
7/24/09	0.00167	<RL	0.00015	0.00598	0.00535	0.02940	0.02160	0.03855
7/30/09	0.00161	<RL	0.00023	0.00442	0.00773	0.03091	0.02372	0.04419
8/5/09	VOID							
8/11/09	VOID							
8/17/09	VOID							
8/23/09	0.00236	<RL	0.00034	0.01490	0.01099	0.06404	0.04628	0.05670
8/29/09	0.00112	<RL	0.00013	0.00735	0.00523	0.00005	0.01817	0.02613
9/4/09	0.00177	<RL	0.00016	0.00510	0.00347	0.00005	0.01982	0.03095
9/10/09	0.00036	<RL	0.00007	0.00177	0.00268	0.00708	0.00170	0.01336
9/16/09	VOID							
9/22/09	VOID							
9/28/09	VOID							
10/4/09	VOID							
10/10/09	VOID							
10/16/09	VOID							
10/22/09	VOID							
Average	0.00202		0.00026	0.00539	0.01099	0.03852	0.03237	0.07673

Table 4. Example of Reported Toxic Air Metals Risk Comparison Values

Consolidated Table of Risk Assessment Health Values (Inhalation) - Metals

CAS #	Metal	Chronic Unit Risk Factor				Chronic Reference Air Concentration			Acute Health Risks Minimal Risk Levels (MRL)		
		(URF) m³/µg	1 in 10,000 Risk Concentration µg/m³	Source of URF	Date Last Revised	(RfC) µg/m³	Source RfC	Date Last Revised	Concentration µg/m³	Source	Last Revised
7440-38-2	Arsenic	4.3E-03	0.020	IRIS	4/10/1998	0.015	CalEPA	12/18/2008	0.200	CalEPA	12/18/2008
7440-41-7	Beryllium	2.4E-03	0.040	IRIS	4/3/1998	0.007	CalEPA	12/18/2008			
7440-43-9	Cadmium	1.8E-03	0.060	IRIS	6/1/1992	0.020	CalEPA	12/18/2008	0.030	ATSDR	9/1/2008
7440-47-3	Chromium (Total)										
18540-29-9	Chromium VI (Assumed)[e]	1.2E-02	0.008	IRIS	9/3/1998	0.100	IRIS	9/3/1998			
7439-92-1	Lead[f]	1.2E-05	0.085	CalEPA	1/1/1997		IRIS	7/8/2004			
7439-96-5	Manganese			IRIS	12/1/1996	0.090	CalEPA	12/18/2008			
	Nickel[g]	2.4E-04	0.400	IRIS	1/1/1991	0.050	CalEPA	12/18/2008			
7440-66-6	Zinc			IRIS	8/3/2005						

[e] Chromium VI concentration assumed to be 1/7th the Total Chromium concentration by DEP for study purposes.

[f] The NAAQS standard for lead is 0.15 ug/m³ (rolling 3-month average).

[g] The URF for Nickel is the IRIS value for Nickel (Refinery Dust).

APPENDIX G – General Design and Methodology for using Methane/Non-Methane Hydrocarbon Optical Imaging Equipment for Source Investigation.

Advances in digital imaging technology allow for real-time investigation of methane/non-methane hydrocarbon (M/NMHC) sources that may be unknown and/or unreported using traditional detection methods (e.g. gas "sniffers"). This enhanced imaging technology was employed in the Department's Short-Term Monitoring studies to detect, but not quantify, fugitive emissions from well pad and natural gas compressor station sources. Those studies concluded that these sources did emit fugitive volatile organic compounds (VOC) during their routine operations and that this technology would be useful for further source characterization in future studies. This general protocol outlines how this technology will be used for this study to enhance the Department's understanding of the nature of M/NMHC and VOC sources and potentially be used to help the Department quantify emissions rates from select sources.

Background

Infrared Thermal and Gas Imaging Technology

Infrared thermal imaging, or thermography, has been used in various commercial, military, industrial and research applications for over 50 years. As the technology has advanced, thermal imaging equipment has become more powerful, smaller and less costly. The thermal imaging technology is similar to conventional digital imaging and looks and acts much like a typical camcorder with both still and motion video recording capability. A typical camcorder has a lens and a detector in addition to electronic processing circuits and some form of digital viewfinder. However unlike a conventional light detecting camera, the detector in an infrared camera detects and precisely measures energy in the infrared spectrum. This range is commonly known as heat and is invisible to the human eye. The greater amount of infrared energy emitted, the higher that object's temperature. As the detector translates detected heat into a digital signal, this signal is converted to a visual display with variations of the infrared wavelength expressed in color. The camera at its simplest allows humans to "see" the heat of objects that would normally be invisible. It also allows for precise temperature measurement. Figure 1 is an example of a typical thermal image.
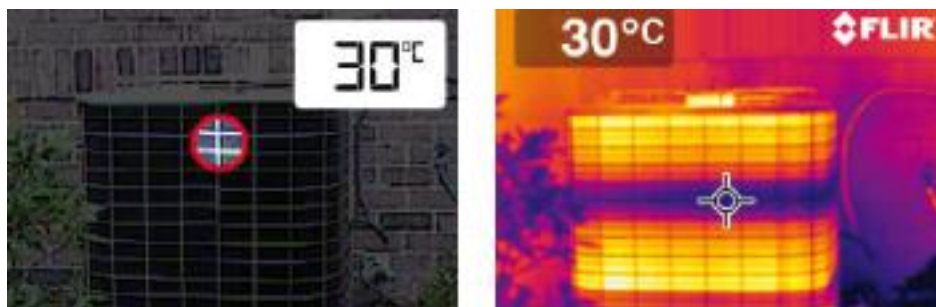
Figure 1 - Normal and Thermal Image Comparison – The left image is a traditional light image compared to the thermal image of the same air conditioning unit on the right. Typically thermographers use yellows, oranges and reds to visually denote gradations in hotter temperatures with blues, greens and violets to denote cooler temperatures. Image courtesy of FLIR Systems, Inc.

Gas detection cameras are similar to thermal imaging cameras in that they possess a lens, detector, processing electronics, a viewfinder and still/motion video recording capability. With gas detecting cameras though, the detector is a cryogenically cooled quantum detector that can measure the targets ability to absorb infrared radiation.

Different gasses have varying infrared absorption properties. This ability to absorb infrared radiation varies depending on the wavelength of the infrared radiation absorbed. This translates to a gases' transparency or opacity to infrared wavelengths. This is a measurable property and is known as a gases' infrared absorption spectrum. By knowing the spectrum of a known gas, a calibrated gas detector can "see" gases much like the infrared imager can "see" heat. Using cooled filters that can limit the camera to only using wavelengths where a gas highly absorbs infrared radiation, thus making the gas opaque for that wavelength, a calibrated detector can easily detect, and visually image, even trace quantities of previously invisible gasses. This is shown in Figure 2 below.

Figure 2 - Image of Natural Gas Condensate/Brine Tanks using Infrared Gas Detection – The left image shows the emissions of gas from the tank vents (denoted by the three arrows) using the gas detection camera. The right image was taken at about the same time with the same camera in normal photography mode, although from a slightly different angle for lighting purposes. Source: PA DEP

Unlike thermal imaging alone that can measure temperature in addition to providing a visual image of temperature gradients, gas detection imaging cameras can neither quantify concentrations nor provide visual gradients to distinguish different gasses that could be present from an emissions source. Relative intensity can be observed by the size and movement of a plume but the imagery cannot be used to support estimations of mass emission rates or concentrations. Simply put a small quantity of highly infrared absorptive gas may appear as a very large plume compared to one consisting of large quantities of lesser absorptive gas. For that reason, emissions rate and concentration conclusions should not be drawn from infrared gas detection images.

Infrared gas detection imagery has been used extensively in the chemical, petroleum and natural gas industries as a means to detect leaks and enhance health, environment, safety and maintenance programs across the world. The Department employed such imaging equipment for its short term study of Marcellus Shale activity in the Northeast region of Pennsylvania as a means to document the existence of gas emissions from well pads and compressor stations to support quantitative measurement of ambient air using known sampling methods and analytical techniques.

Use of Gas Imaging for the Long-Term Study

Washington County is now one of the Commonwealth's largest producers of natural gas from the Marcellus Shale play. This level of natural gas production is not new for the County, however, as natural gas has been extracted there since the late 1800's and played an important role in the early history of the natural gas industry in the Appalachian Basin and the U.S. Even before the unconventional shale gas "revolution" in the basin, Washington County had a large number of active, producing conventional natural gas wells. Even as of 2011, the number of active producing conventional gas wells, by the numbers, exceed their unconventional equivalents by more than two to one.

Given this long history of Countywide gas drilling, coupled with the past practice of not-plugging and then abandoning wells once their production declined to unprofitable amounts, there remains a legacy of an unknown number of abandoned wells of various condition throughout the County and Commonwealth[39]. Some early wells were plugged by operators, others were just left as open well casings to depth. Some open wells may have collapsed upon themselves as their casings corroded over time. Previous inadequately plugged wells may have unsealed with time. Of this universe of abandoned wells, some may have been "dry holes" that never produced gas or maybe a former "gasser" that, after abandonment, continued to emit gas, albeit intermittently or at an uneconomically recoverable level.

The Department's Office of Oil and Gas Management, Abandoned & Orphan Well Program tries to identify and physically locate these wells across the Commonwealth. They also implement a program to plug abandoned or orphaned wells where no operator or responsible party can be identified[40]. Abandoned wells can present both an environmental hazard due to both legacy gas and oil issues and a physical hazard to recreation, development and general public safety. Unfortunately, due to a lack of required recordkeeping at the time, locations of most of the wells drilled from the early years of the oil and gas industry are unknown.[41]

For the purpose of this study, abandoned/orphaned wells represent potentially undocumented sources of M/NMHC that could influence results of ambient air monitoring for M/NMHC and VOC. Infrared gas imaging technology represents a method of both potentially verifying the existence of M/NMHC emissions from these wells and/or discovering previously undocumented wells.

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[39] DEP estimates that some 300,000 oil and gas wells have been drilled in the Commonwealth since 1859.

[40] As defined by an amendment to the Oil and Gas Act of 1984, an "Orphan" well is a well that was abandoned prior to April 1985. The Department, through the Orphan Well Plugging Program, has the authority to plug orphaned wells if landowners, leaseholders and oil and gas operators have received no economic benefit from the well after April 19, 1979.

[41] Permitting for new wells was not required by Pennsylvania until 1956 and old wells were not required to be registered by operators until 1985. Current regulations prohibit operators from abandoning inactive wells without plugging. All oil and gas well permits require the exact location of the wellhead.

Goals and Protocol

For the purposes of the Long-Term Marcellus Ambient Air Monitoring Study, Bureau of Air Quality Staff from the Divisions of Air Quality Monitoring and Source Testing and Monitoring will use a FLIR GF320 Gas Imaging Camera to achieve the following goals:

1. Characterize potential M/NMHC emissions emanating from known historical abandoned/orphaned natural gas wells within the vicinity of the primary sampling site housing the M/NMHC continuous analyzer.

2. Identify potential, previously undocumented abandoned gas wells in the immediate vicinity of the sampling sites with a focus on the primary sampling site.

3. If M/NMHC emissions are detected from an abandoned/orphaned well, perform preliminary air flow and humidity measurements to ascertain if future quantitative sampling of the emitted gas can be performed and tested analytically or portable analyzers can be employed to determine M/NMHC concentrations. Only wells with exposed, measurable casings where a well bore diameter can be determined will ultimately be sampled.

4. If gas sampling conditions warrant, estimate M/NMHC emissions rates from concentration results obtained by either portable M/NMHC analyzers or through volumetric flow sampling and laboratory analytical analysis.

5. Laboratory analysis of M/NMHC samples will be performed by a laboratory that has received accreditation through the National Environmental Laboratory Accreditation Program (NELAP), using accepted, reproducible methods and that adheres to rigorous Quality Assurance and Quality Control protocols.

6. Using qualitative results of the gas detector imaging and, if available, quantitative results of analytical sampling and source concentration data, determine if potential M/NMHC emissions from abandoned/orphaned wells might influence both M/NMHC and VOC concentrations observed at the primary monitoring site or VOC concentrations observed at other sampling sites.

Source Survey Protocol

The FLIR GF320 will be employed by an operator that has been certified in gas imaging by the unit manufacturer (FLIR Systems, Inc.). The survey team will consist of at least one gas imaging camera operator and one assistant to record field conditions and use a Global Positioning System (GPS) to help locate the known abandoned/orphaned wells. Additional individuals may be used to assist in well location and documentation. Ideally weather conditions will consist of calm winds, low relative humidity, and temperatures within the GF320 unit operating range. The survey will be performed in late winter or early spring when the lack of tree foliage will enhance the ability of the camera to detect potential emissions plumes from a distance. Table G-1 summarizes the performance specifications and operating limits of the GF320.

If a previously unknown source is identified from a distance, local property tax assessment maps (plat maps) will be consulted to help determine ownership of the parcel upon which the suspected source may exist. That owner will then be contacted for permission to enter upon the property and further document the source. Property owners surrounding the sampling sites may be contacted prior to the survey to inform them of the survey and to secure their permission for entry. Landowners will be encouraged to accompany the survey team if entry to their property is warranted.

If a visually significant source is observed, a portable Lower Explosive Limit (LEL) gas monitor will be used by a trained assistant[42] while approaching the source location. This will help ensure that the survey team does not enter a dangerous or potentially explosive atmosphere. If such an atmosphere is detected, the survey team will evaluate the hazard of continued survey of the source. Future work at the location would only continue if measurements and sampling could occur without the risk of injury to the survey team members. Measurement and sampling equipment ultimately used at the well will be intrinsically safe and thus greatly reduce explosion potential. While the GF320 in of itself is not intrinsically safe, the operator can take care to avoid any detected plumes and guide survey team members away from entering plumes. Additionally, the GF320 is equipped with an optional long-distance lens that would eliminate the need for the camera and operator to be near the well if measurements and sampling at the well are required.

In the event that a previously undocumented abandoned well is discovered using the GF320, a team member will first document its condition, obtain location coordinates using a Global Positioning System (GPS), and measure the diameter of the well bore casing if present. A flow meter (rotary vane or hot wire anemometer) will be used to measure air flow from the well if measurable flow exists. Relative humidity and temperature of the flow will also be recorded. Lastly the FID will record the concentration of both methane and total hydrocarbon over a 5 minute period. If there appears to be significant variability in the readings using the FID, a sample of the gas of known volume will be taken over a 30 minute period for laboratory analysis and concentration determination. The GPS location, well condition and landowner information will also be forwarded to the Department's Abandoned & Orphaned Well program for follow-up.

Some discovered sources may not lend themselves to the measurement and sampling described above. Emissions that could emanate from a wider area, such as a seep or buried or subsided abandoned well casing, would prove more difficult to estimate. If discovered, these areas will be documented with GPS locations and a general estimation of surface area. Future quantitative sampling will be considered if warranted and if a general area sampling method can be developed.

Table G-1 - Select Technical Specifications of FLIR GF320[43]

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[42] At a minimum the LEL/FID operator will have completed EPA's course 165.4 Air Monitoring for Hazardous Materials or OSHA 40-Hr Hazardous Waste Operations and Emergency Response (HAZWOPR) course to ensure the operator's and survey team's safety.

[43] Source: FLIR Systems, Inc. http://www.flir.com/cs/emea/en/view/?id=55757

Imaging and Optical Data	
Field of view (FOV) / Minimum focus distance	24° x 18° / 0.3 m
F-number	1.5
Thermal sensitivity/NETD	<25 mK @ +30°C
Zoom	1–8× continuous, digital zoom
Digital image enhancement	Noise reduction filter, scene based NUC, High Sensitivity Mode (HSM)
Focal Plane Array (FPA) / Spectral range	Cooled InSb / 3–5 µm
IR resolution	320 × 240 pixels
Detector pitch	30 µm
Sensor cooling	Stirling Microcooler (FLIR MC-3)
Measurement	
Temperature Measurement Range	–40 to +350°C
Temperature Measurement Accuracy	±1°C for temperature range (0°C to +100°C)
	or ±2% of reading for temperature range (Above +100°C)
Measurement Analysis	
Spotmeter	10
Area	5 boxes (with max./min./average)
Profile	1 live line (horizontal or vertical)
Difference temperature	Delta temperature between measurement functions
	or reference temperature
Reference temperature	Manually set or captured from any measurement function
Emissivity correction	Variable from 0.01 to 1.0 or selected from editable materials list
Reflected apparent temperature correction	Automatic, based on input of reflected temperature
Measurement corrections	Reflected temperature, distance, atmospheric transmission,
	humidity, external optics

Gases Detected				
• Benzene	• Isoprene	• Pentane	• Ethane	
• Ethanol	• Methanol	• 1-Pentene	• Methane	
• Ethylbenzene	• MEK	• Toluene	• Propane	
• Heptane	• MIBK	• Xylene	• Ethylene	
• Hexane	• Octane	• Butane	• Propylene	

Results Analysis

With flow rate estimates, well casing diameter and by either using the recorded concentrations from the FID or the analytically determined concentrations, an estimate of the well's M/NMHC emissions rate can be grossly estimated. Assuming a constant flow of gas, emissions rates for varying time periods can be estimated. This can help inform the Department of relative M/NMHC emissions contribution from the undocumented sources. It can also serve as preliminary data for determination if additional, more precise measurements are required.

Coupling known sources and emissions rates with both measured M/NMHC concentrations and wind speed/direction data from the primary site, a clearer picture of observed M/NMHC can be made. Theoretically, the presence of a large number of previously undocumented, emitting abandoned gas wells or area seeps could be reflected in localized ambient air M/NMHC concentrations. If no or few such sources of significance are present in the sampling area, then observed M/NMHC concentrations could be viewed as being more representative of ambient M/NMHC emissions for the study area.