SAMPLING AND ANALYSIS PLAN

PART II - QUALITY ASSURANCE PROJECT PLAN

Pennsylvania Department of Environmental Protection

April 3, 2013

Prepared for:
Pennsylvania Department of Environmental Protection

pennsylvania
DEPARTMENT OF ENVIRONMENTAL
PROTECTION

Prepared by:
Perma-Fix Environmental Services, Inc.
325 Beaver Street, Suite 3
Beaver, PA 15009

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Quality Assurance Project Plan (QAPP)
Pennsylvania Department of Environmental Protection

QAPP APPROVALS

By their specific signature, the undersigned certify that they prepared, reviewed or provided comments on this QAPP for sample and analyses activities on Exploration and Production sites.

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ABBREVIATIONS, ACRONYMS AND SYMBOLS

%R	Percent Recovery
CHP	Certified Health Physicist
CLP	Contract Laboratory Program
COI	Constituent of Interest
CWT	Centralized Waste Treatment
DQL	Data Quality Level
DQO	Data Quality Objective
O&G	Oil and Gas
ELAP	Environmental Laboratory Accreditation Program
EPA	U.S. Environmental Protection Agency
MDA	Minimum Detectable Activity
MS	Matrix Spike
MSD	Matrix Spike Duplicate
NBS	National Bureau of Standards
NELAC	National Environmental Laboratory Accreditation Conference
NIST	National Institute of Standards and Technology
NORM	Naturally Occurring Radioactive Material
PA DEP	Pennsylvania Department of Environmental Protection
PA	Pennsylvania
PESI	Perma-Fix Environmental Services Inc.
POTW	Publicly Owned Treatment Works
psi	pounds per square inch
QA	Quality Assurance
QAM	Quality Assurance Manual
QAPP	Quality Assurance Project Plan
QC	Quality Control
Ra-226	Radium-226
Ra-228	Radium-228
Rn-220	Radon-220
Rn-222	Radon-222
RAS	Routine Analytical Services
RPD	Relative Percent Difference
SAP	Sampling and Analysis Plan
TENORM	Technologically Enhanced Naturally Occurring Radioactive Material
Th-228	Thorium-228
Th-230	Thorium-230
Th-232	Thorium-232
U-234	Uranium-234
U-235	Uranium-235
U-238	Uranium-238
USEPA	US Environmental Protection Agency
ZLD	Zero Liquid Discharge

1.0 PURPOSE

This document is the Quality Assurance Project Plan (QAPP), which provides specific quality assurance/quality control (QA/QC) procedures to be executed and supported for the comprehensive study of Natural Occurring Radioactive Material (NORM) and Technologically Enhanced NORM (TENORM) related to the oil and gas exploration activities throughout the Commonwealth of Pennsylvania (PA).

Data generated for environmental purposes must be technically sound and legally defensible, and supported by defined and verified limits of confidence. Therefore, the objective of this QAPP is to ensure the generation of accurate, precise, representative and complete data. The QAPP sets forth the data collection procedures and data evaluation processes, which will ensure that appropriate levels of data quality are obtained.

Analyses must meet the QA/QC requirements associated with this QAPP and the following documents:

U.S. Environmental Protection Agency (EPA) "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods" (SW-846, Third Edition), as amended by the most current SW-846 update (January 2008);

U.S. EPA "Handbook for Analytical Quality Control in Water and Wastewater Laboratories" (EPA 600/4-79-019, June 1972); and

American Public Health Association, American Water Works Association, and Water Environment Federation publication Standard Methods for the Examination of Water and Wastewater, 22nd Edition (August 2012).

2.0 PROJECT DESCRIPTION

Perma-Fix Environmental Services, Inc. (PESI) has prepared a standard sampling and analysis protocol to be implemented in the course of preparing this comprehensive study of NORM and TENORM related to the oil and gas exploration activities including conventional and unconventional drilling through geological formation(s) and associated wastewater operations throughout PA.

NORM consists of uranium, thorium and progeny, including radium. Radionuclides in NORM include primordial radionuclides that are naturally present in the rocks and minerals of the earth's crust and cosmogenic radionuclides produced by interactions of cosmic nucleons with target atoms in the atmosphere and in the earth. TENORM is produced when radionuclides that occur naturally in ores, soils, water or other natural materials are concentrated or exposed to the environment by human activities. Throughout PA many companies perform oil and gas exploration and production activities by conventional and unconventional drilling through various subsurface layers of shale and rock to produce oil and natural gas. The Oil and Gas (O&G) industry produced water and flowback water, as well as drill cuttings and sources of off gassing, are potentially impacted with NORM and/or TENORM.

2.1 SCOPE OF WORK

The proposed comprehensive study will focus on the quantification of TENORM in rock cuttings (both vertical and horizontal); off gas from flaring; compressed gas; process and flowback water and waste water generated on O&G sites; and on waste water transported off site to public and privately owned wastewater treatment plants (POTWs), centralized waste treatment (CWT) facilities, zero liquid discharge (ZLD) facilities and solid waste facilities (landfill leachate). In addition, a literature search of relevant data on all geological formations and currently available data will be included and a sampling of applicable areas potentially impacted through beneficial reuse of brine and other impacted media will be performed.

Unconventional drilling process water sample results indicate significant concentrations of radium-226 (Ra-226), a common NORM radionuclide and the element associated with the natural decay series with the most mobility. Because NORM is most likely associated with various geologic units, the scope of work will focus on these units and the operations, equipment and features related to the exploration and production of natural gas from these geologic units and also in the transfer of water to POTWs and CWTs for processing. Landfill leachate will also be sampled to study whether radium has migrated from POTW, CWT and ZLD sludge to the landfill leachate. Any beneficial reuse of any of the oil and natural gas exploration and production media will also be surveyed and sampled as appropriate, including but not limited to:

- Vertical and horizontal drill cuttings;
- Onsite pits containing cuttings;
- Production water;
- Flowback water;
- Filter socks;
- Compressor stations and gas lines;
- Off gassing;
- Well pads;
- Centralized impoundments;
- Waste water facility sludge;
- Waste water facility influent and effluent water;
- Piping and casing scale;
- Vapor capture systems;
- Fresh proppant sand; and
- Drilling mud.

This Quality Assurance Project Plan (QAPP) provides details of the laboratory analytical methods, the quality control of both field instruments and laboratory equipment, and the quality control program including establishing reference background samples where appropriate, blank analyses, duplicate analyses and spike analyses where possible and applicable.

3.0 QUALITY ASSURANCE OBJECTIVES FOR MEASUREMENT DATA

Data Quality Objectives (DQOs) are qualitative and quantitative statements to ensure that data of known and appropriate quality are obtained during the characterization study (sampling and analysis).

The data objectives will address the quantification of TENORM in the following materials:

1) **Exploration and Production Sites Survey and Sampling** – The study will include survey and sample events on active and inactive drill sites, including:
   a) Open/Operating Cuttings Pits – Radiological characterization will include field screening (exposure rates/gross gamma activity) of the cutting pits areas using portable survey meters and the sampling and laboratory analysis of the drill cuttings stored in the open/operating pits. The sampling and analysis of the drill cuttings (solid material) will assist in determining radiological isotopes of concern and in evaluating their potential mobility in the environment.
   b) Closed/Reclaimed Cuttings Pits - Radiological characterization will consist of field screening (exposure rate/gross gamma activity) using portable survey meters to evaluate the potential for elevated radiological activity (above a background reading from a non-impacted site location) at the ground surface above the closed/reclaimed pits.
   c) Sample and analyze flowback and produced water on sites in accordance with the Sampling and Analysis Plan (SAP). Evaluate solid and aqueous phases separately as specified in this program.
   d) PESI will coordinate with PA DEP central and regional office staff, Radon Division and well operators to perform radiological surveys and radon sampling of gas as appropriate.
   e) Temporary Water Storage Vessels and Recycle Systems (Hydraulic Fracturing Water Storage Tanks, Produced Fluids Tanks, Filtration Equipment, Water Trucks)
      i) Exposure rate/gross gamma activity survey of temporary water storage vessels to identify potential areas of NORM/TENORM.
      ii) Collect and screen samples of solids accumulated in vessels for gross activity.
      iii) Collect swipe (smear) samples to determine removable surface contamination in units of disintegrations per minute per 100 centimeters squared (dpm/100cm^2). Removable surface activity is an indicator of potential airborne exposure through inhalation and/or ingestion of removable contamination.

f) Drilling Rigs and Associated Equipment
   i) Structural surface survey of drilling rigs and equipment to identify potential areas where NORM/TENORM may be present. The survey will consist of scanning with portable survey meters for gross gamma activity and/or total surface contamination (dpm/100cm^2) and collecting swipe (smear) samples to determine removable surface contamination (dpm/100cm^2). Total contamination is the sum of fixed and removable contamination. As mentioned above, removable surface activity is an indicator of potential airborne exposure through inhalation and/or ingestion of removable contamination.
   ii) Collect and screen samples of solids (scale) accumulated on rigs, pipes, used well casings and associated equipment.
   iii) PESI will coordinate with PA DEP Radon Division and well operators to perform radon sampling of gas as appropriate.

g) Offices, Office Trailers, Trucks, etc.
   i) Instrument surveys (exposure rate, gross gamma and/or total contamination) of offices, trailers, trucks, etc to identify the possible presence of NORM/TENORM.
   ii) Collect swipe (smear) samples to determine removable surface contamination.

h) Production Equipment (Separators, Heater/Treaters, Dehydration Units, Compressors)
   i) Instrument surveys (exposure rate, gross gamma and/or total contamination) of production equipment to identify potential areas of NORM/TENORM.
   ii) If possible, collect and screen samples of solids and/or liquids accumulated in/on production equipment.
   iii) If possible, collect swipe samples to determine removable surface contamination.
   iv) PESI will coordinate with PA DEP Radon Division and well operators to perform radon sampling of gas as appropriate.

2) **Waste Water Facilities Sampling and Analysis**
   a) Twenty-two (22) of the highest volume Marcellus shale waste water treatment facilities will be included. Sixteen (16) are located in the Western sector of Pennsylvania. The other six (6) are located in the Central sector. Facilities will include POTWs, CWTs, ZLDs and specialized Marcellus shale water treatment operations.
   b) Each of the 22 waste water treatment facilities will be sampled three (3) times to establish a trend.
   c) A total of three to four (3-4) media samples will be taken at each facility during each of the 3 sample events: influent Marcellus shale industry water, facility effluent

discharge water, sludge from the treatment of the water and sediments at the effluent discharge point where applicable.

d) PESI will perform a gamma exposure rate survey at the facility each time a sample event occurs. Gross gamma radiation will be measured on the outside of sludge tanks as access allows, at the effluent discharge point and around the incoming waste water truck if available.
e) PESI will record any other pertinent data during each sample event, e.g., influent volume from Marcellus shale, total influent flow, effluent flow. To the extent possible PESI will coordinate the sampling of the influent water, the sludge and the effluent water with the facilities such that the samples are all related to the processing of the influent Marcellus shale industry water.
f) Each of the samples will be analyzed for gross alpha and beta and by gamma spectroscopy to identify TENORM radionuclides.
g) 10% of the samples, based on the gross alpha and beta, and gamma spectroscopy results, will also be analyzed by alpha spectroscopy for uranium (U-238, U-235 and U-234), thorium-232, radium (Ra-226 and Ra-228) and for any unsupported decay chain radionuclides; and for radon (Rn-220 and Rn-222)
h) Sampling and analysis will be coordinated and performed by PESI, through the Beaver, PA office, in accordance with the SAP developed by PESI and approved by PA DEP prior to implementation.
i) Facilities located in the Western sector of PA will be surveyed and sampled per the schedule jointly developed by PA DEP and PESI. Two PESI field technicians will travel to each facility with up to two PA DEP field staff. Day trips will be utilized when cost effective.
j) For facilities located in the Central sector of PA, the two field technicians will travel to each facility and require overnight trips.
k) Each sample will be surveyed for gross gamma radiation and loose alpha and beta surface contamination. The sludge within the facility will also be surveyed for gross gamma activity at the time the sample is taken.
l) In addition to the media sampling, indoor working level measurements for radon gas exposure will also be performed within any buildings, trailers or enclosures where personnel occupancy is required.
m) Samples will be packaged and delivered to either an appropriate radiochemistry laboratory for the analyses or the PA DEP Laboratory.
n) Survey and analytical data will be reviewed and validated by a radiological engineer. The data will be compiled in tables and trended as appropriate.

o) A final report specific to waste water treatment facilities will be prepared and submitted to PA DEP for review and comments. The report will include the sampling protocol, the data presentation, the data review and assessment and recommendations.

3) **Landfills**

a) Landfill Leachate – Landfill leachate will be sampled at each of the 54 active landfills and analyzed for gross alpha/beta and Ra-226/Ra-228 by gamma spectroscopy to evaluate the effects of NORM/TENORM disposal on leachate quality.

b) TENORM Disposal – PESI will conduct field sampling at nine (9) landfills to include ambient measurements, solid samples and sweeps of facilities and equipment at entry points to the facilities, the working faces and other areas potentially affected during disposal activities.

4) **Beneficial Reuse**

a) Areas adjacent to road beds where brine has been used will be surveyed for residual NORM/TENORM and sampled as appropriate.

5) **Gas Processing and Distribution**

a) Natural gas samples will be taken and tested for radon at compressor stations, storage facilities, processing facilities and end users such as natural gas fueled power plants.

b) Ambient gamma radiation will be measured within these facilities.

c) Ambient radon sampling will also be conducted in these facilities due to the possible presence of radon in the gas.

3.1 DATA QUALITY LEVELS

There are typically five analytical levels of data quality, or Data Quality Levels (DQL), available to accomplish the objectives of investigations of this type. These levels are typically designated as follows:

Level I: field screening or analysis using portable instruments, calibrated to non-compound specific standards;

Level II: field analysis using portable instruments, calibrated to specific compounds;

Level III: non-Contract Laboratory Program (non-CLP) laboratory methods;

Level IV: CLP Routine Analytical Services (RAS) methods; and

Level V: non-standard analytical methods.

DQO Levels I and III will be used in this investigation. The following sections describe the use of the analytical procedural levels for the project.

Field Screening Methods - Level I

The following field screening sampling will be conducted by PESI technicians:

- Exposure rate surveys in units of micro-Roentgen per hour (μR/hr) around and above sampling areas when possible, around and on contact with water tanks/trucks full or partially full of water/sludge prior to sampling when possible, at effluent discharge points when possible, and around and on contact with equipment and/or structures prior to sampling when possible; and on contact with sample container; and/or
- Gross gamma surveys in units of counts per minute (cpm) to be correlated with activity concentration (pCi/g); and/or
- Total surface contamination in units of disintegrations per minute per 100 centimeters squared (dpm/100 cm^2); and
- Removable contamination (smear) in units of dpm/100 cm^2, as required; and
- Background exposure rate and/or gross gamma count rates measured outside the influence of sampling areas.

These analytical methods are typically designated as Level I data quality.

Non-CLP Laboratory Methods - Level III

Level III analytical procedures provide precise, accurate and defensible data for the intended data uses, with a less formal documentation and reporting nomenclature at reduced analytical costs over Level IV data quality procedures. Data Quality Level III will be used for all characterization studies. Table 6-1 summarizes analyses that will be conducted to characterize and quantify constituent concentrations.

3.2 QUALITY CONTROL PARAMETERS

The exact quantitative criteria used to evaluate data quality from the laboratory's precision and accuracy perspective for the aqueous and solid sampling media will be presented in the selected laboratory Quality Assurance Manual(s) (QAM, Appendix QAPP-1 and following). The following is a description of terms that appear in the QAM.

Reference: The reference of the U.S. EPA standard analytical methodology used for each procedure.

Precision: A measure of the mutual agreement among individual measurements of the same property under prescribed similar conditions. Precision is evaluated based on the relative percent difference (RPD) between duplicate matrix spike (MS) results or duplicate sample results, as appropriate. The matrix spike duplicate (MSD) RPD limits are parameter- and method-specific; MS/MSD RPD QC limits will be presented in the laboratory QAMs. Laboratory duplicate sample RPD limits are typically 20 percent for aqueous media and 35 percent for solid media (exceptions may apply for solid media whose samples may be nonhomogeneous). Field duplicates are also evaluated by calculating the RPDs between field duplicate sample results. However, evaluations of field duplicate RPDs are used as advisory determinations since numerous factors in sampling and analysis may cause variances between field duplicate results.

Accuracy: The degree of agreement of a measurement with an accepted reference or true value. Accuracy is evaluated based on the percent recovery of spiked samples. The matrix spike recoveries for organic analyses are method- and parameter-specific and are typically used as an advisory QA/QC measure due to the difficulty associated with recovering spiked organic parameters. Organic parameter percent recovery QC limits will be presented in the laboratory's QAM. The matrix spike recoveries for inorganic and most conventional parameters are typically a range of ±25 percent.

Completeness: A measure of the amount of valid data obtained from a measurement system compared to the amount expected to be obtained under normal conditions. The method of calculation for percent completeness is defined in Section 12.3. Completeness can be evaluated in two ways: 1) by comparing the number of samples actually collected to the expected number of samples to be collected; and 2) by comparing the number of valid analyses received from the laboratory to the number of actual samples collected. The results of any Level III analyses to be

performed are typically used for characterization studies and as such will have a minimum completeness of 95 percent for both evaluations of completeness.

Exact QA/QC criteria the laboratory will use to evaluate its data's precision and accuracy will be provided following selection of the analytical laboratory, if the criteria are not method-specific.

Table 6-1 summarizes the individual parameters and associated reporting limits.

There are also qualitative criteria that are followed to ensure that data of known and appropriate quality are obtained during investigation activities. These criteria include representativeness and comparability.

The sampling and analysis programs are designed to ensure that analytical data obtained during the characterization study represent current conditions found at the site and produce data of comparable quality. The sampling frequency was selected to ensure data are suitable for their intended use and to adequately characterize the drill cuttings and produced water. Additionally, standard recognized analytical methodologies will be utilized to ensure comparability. These designs are instituted to ensure appropriate sample representativeness and data comparability.

4.0 SAMPLING PROCEDURES

This section outlines the procedures to be used for the preparation of sampling equipment and containers and for sample preservation. It also provides some of the quality control and operating procedures to be followed for sampling. Detailed field sampling procedures, including the number of samples to be collected, the rationale for sampling, and QC requirements, are described in the Field Sampling Plan.

4.1 SAMPLE IDENTIFICATION

Each sample collected for this characterization study will be assigned a unique sample tracking number generated by the collector. Sample identification will be a unique system to include the collector identification, sequence number and date.

Solid Samples

Eight types of solid samples may be collected:

1) Cuttings as produced on a drill rig including cuttings stored temporarily on site in lined pits or containers;
2) Solid phase from flowback and produced water;
3) Solids accumulated in vessels or on equipment;
4) Scale from drill rigs and associated equipment;
5) Wastewater treatment facility sludge;
6) Wastewater treatment facility discharge sediments;
7) Soil/salt samples from beneficial reuse areas; and
8) Fresh proppant sands.

Grab sample(s) will be collected from site as appropriate.

Aqueous Samples

Six types of aqueous samples may be collected:

1) Flowback and produced waters;
2) Accumulated liquids from production equipment;
3) Influent Marcellus shale industry water;
4) Wastewater treatment facility effluent discharge water;
5) Various receiving water body samples; and
6) Landfill leachate.

Gas Samples

Radon gas sampling occurs with one of two methods. The first is to sample occupied spaces with standard passive charcoal canisters. The canisters will be placed in areas occupied by site personnel. The canisters are opened and allowed to adsorb ambient air for a period of 2-5 days. The canisters are then sealed and sent to the laboratory. Gamma spectroscopy will be performed by an off-site laboratory. Radon is also found in natural gas in combination with methane. A method is currently being developed to capture natural gas from a source in an industry standard sample bottle capable of holding the high pressure off gas (approximately 800 psi). The sample container will be regulated down to an acceptable pressure to utilize a laboratory radon capture device. The device typically used for capturing gas to perform radon emanation is a Lucas cell. An appropriate method will be determined and used.

Labeling

Each sample container will be marked with a label identifying the specific parameters of interest. The label will record the date of sample collection, alphanumeric identification, parameters to be analyzed and preservatives, if applicable. The specific information for each sample will be documented in the field logbook and on a chain-of-custody form. The sample identification will be correlated in the logbook and chain-of-custody by sample designation, sampling date, time and location. The analytical parameters for which the sample is to be analyzed and the respective number of sample bottles will be provided on the chain-of-custody sheet.

Further details of labeling and documentation may be found in the Field Sampling Plan, Sections 6.1 and 6.2.

4.2 SAMPLE CONTAINERS

All new pre-cleaned 500 mL sample containers with screw-type Teflon®-lined lids will be used for holding and shipping soil samples. Collapsible cube style 4 L containers will be utilized for produced fluid samples. Industry specific gas collection containers will be utilized for collection of methane. The containers will arrive under negative pressure ready to collect natural gas. Other containers may be used when the analysis or media require it. Generally sample bottles will be supplied by the analytical laboratory without preservative.

4.3 DOCUMENTATION

Chain-of-Custody Forms

The field chain-of-custody form is used to record the custody of all samples collected. This chain-of-custody form documents the transfer of the custody from the sampling personnel to another person, to the laboratory, or another party, such as a courier delivery service.

When the field team sends samples to an analytical laboratory, each shipping cooler containing samples, which are sent under one shipping document, must be accompanied by a chain-of-custody form. These forms document information regarding the origination of samples and those parties having subsequent possession of samples. They also contain information pertaining to these samples, such as project name, name of the individuals collecting the samples, sample identification number, the date and time of collection, the number of sample containers for each parameter of interest for each sample, remarks or observations of samples, if appropriate, the signature of the person relinquishing control of the samples and the person receiving the samples, and the name of the overnight carrier shipping the samples to the laboratory. The original chain-of-custody sheet is sent with the samples. The remaining copy is stored in the field team files.

Further details pertaining to chain-of-custody may be found in the Field Sampling Plan, Section 6.2.4.

5.0 SAMPLE CUSTODY

The primary objective of sample custody is to create an accurate written verified record, which can be used to trace the possession and handling of the samples from the moment of collection through data analysis and reporting.

The field sampler will be personally responsible for the care and custody of the samples collected until they are properly transferred. Samples will be accompanied by a chain-of-custody form. Upon arrival at the laboratory, samples will be checked in using laboratory custody procedures outlined in the laboratory QAM and the cooler receipt checklist will be completed. The laboratory is required to verify that all samples were received and in good condition. The laboratory should assign laboratory-specific sample identification. This unique identification guarantees sample anonymity to the analyst of the sample's site.

Once samples have been logged-in and transferred to the proper storage areas, the laboratory department manager is responsible for their proper storage and condition. Copies of the completed chain-of-custody form and an analysis narrative presenting laboratory sample identifications and their correlating field-assigned sample identifications should be included in the data package for delivery to the data user.

Further details pertaining to sample custody may be found in the Field Sampling Plan, Section 6.2.4.

6.0 ANALYTICAL PROCEDURES

Table 6-1 summarizes the list of constituents of interest (COIs) associated with the investigation. The analytical method selection for water samples is based upon anticipated concentrations of dissolved solids. Historically, groundwater methodologies for radiochemistry have failed due to high dissolved solids and high barium concentrations. Alternate EPA methods are amenable to samples with high levels of total dissolved solids.

Table 6-1 Summary of Sampling/Laboratory Analysis

Sample Type	Media/ Sample Type	Analytical Parameters	Analysis[c] Methods	Frequency[a]
Vertical and Horizontal Phase Drill Cuttings Cuttings as produced on a drill rig including cuttings stored temporarily on site in lined pits or containers Solid phase from flowback and produced water Solids accumulated in vessels or on equipment Scale from drill rigs and associated equipment Soil/salt samples from beneficial reuse areas (Off-site Lab)	Soil/soil-like	Gamma spectroscopy to identify TENORM radionuclides Alpha spectroscopy to identify isotopic uranium (233/234, 235 and 238) and isotopic thorium (228, 230 and 232)	USEPA 901.1 Modified HASL 300	Once per site
Wastewater treatment facility sludge Wastewater treatment facility discharge sediments (Off-site Lab)	Soil/soil-like	Gamma spectroscopy to identify TENORM radionuclides Alpha spectroscopy to identify isotopic uranium (233/234, 235 and 238) and isotopic thorium (228, 230 and 232)	USEPA 901.1 Modified HASL 300	Three times per facility.

Sample Type	Media/ Sample Type	Analytical Parameters	Analysis[c] Methods	Frequency[a]
Flowback and produced waters Accumulated liquids from production equipment (Off-site Lab)	Aqueous (Grab)	Gross alpha and beta Gamma spectroscopy to identify TENORM radionuclides Alpha spectroscopy to identify isotopic uranium (233/234, 235 and 238) and isotopic thorium (228, 230 and 232)	USEPA 900.0 USEPA 901.1 Modified HASL 300	Once per site
Influent Marcellus shale industry water (as is and filtered) Wasterwater treatment facility effluent discharge water (as is and filtered) (Off-site Lab)	Aqueous (Grab)	Gross alpha and beta Gamma spectroscopy to identify TENORM radionuclides Alpha spectroscopy to identify isotopic uranium (233/234, 235 and 238) and isotopic thorium (228, 230 and 232)	USEPA 900.0 USEPA 901.1 Modified HASL 300	Quarterly x3
Landfill Leachate	Aqueous (Grab)	Gross alpha and beta Gamma spectrosopy analysis	USEPA 900.0 USEPA 901.1 Modified	Once per landfill (54)
Gas sampling as necessary (Off-site Lab) Ambient Radon	Gaseous (Grab) Charcoal canister	Radon Radon		As determined by PADEP

Notes for Table 6-1:

(a) Quality Control samples will be collected as follows:
- Solid Samples – 5% (field replicate/split) QC samples (one every 20 samples collected to verify results of off-site laboratory per total samples in a calendar year).
- Aqueous Samples - 5% (field replicate/split) QC samples (i.e., one every 20 samples collected to verify results of on-site laboratory per total samples in a calendar year).

(b) 10% of the samples, based on the gross alpha and beta, and gamma spectroscopy results, will also be analyzed by alpha spectroscopy for uranium (U-238, U-235 and U-234), thorium-232, radium (Ra-226 and Ra-228), for any unsupported decay chain radionuclides, and for radon (Rn-220 and Rn-222).

(c) Analysis method as specified or an equivalent method where appropriate.

All procedures for environmental sample handling, storage and documentation while in the laboratory's custody, and deliverable requirements upon delivery of the data to the user, are stated in the laboratory's quality assurance manual.

7.0 CALIBRATION PROCEDURES AND FREQUENCY

All field and laboratory equipment must be calibrated before use to ensure proper operating capability. Laboratory instrument calibration procedures are presented in the laboratory QAMs. Field calibration procedures and frequencies should be followed in accordance with the manufacture's specifications. Field operational checks must be completed each day at a minimum.

7.1 PREPARATION OF STANDARDS

A calibration standard is prepared by the appropriate dilution of a pure substance, the purity of which is traceable to National Bureau of Standards (NBS)/National Institute of Standards (NIST) or U.S. EPA standards. Because of the high sensitivity of many analytical instruments, the calibration standard is an extremely dilute version of the pure compound. Because of the high dilution required to be within the linear range of the instrument, the preparation of the calibration standard is frequently made by serial dilution rather than in a single step. In order to provide standard solutions at sufficiently low concentrations, a minuscule amount of the pure substance will be required, the measurement of which is subject to extreme error. Thus, it is preferable to deal with potential dilution errors, rather than with the large error associated with the measurement of a very small amount of the pure substance.

The initial standard is typically obtained either as a pure material or as a prepared certified solution of a given concentration of the pure compound or compounds. In preparing the stock solution of the calibration standard, great care must be exercised in measuring weights and volumes as accurately as possible, since all of the analyses following the calibration will be based on the accuracy of the calibration, and the accuracy of the analytical data is dependent on the calibration curve. It is the analyst's responsibility to assure that all standards used are within the standard solution holding time, and to prepare fresh standard solutions whenever necessary. In preparing working solutions, or using working solutions, the analyst must check for signs of deterioration of the standard, such as cloudiness, precipitation or discoloration. The standard must also be periodically compared with previous runs of standards, and with independently prepared standards to assure that response factors fall within a historically accepted range.

8.0 DATA EVALUATION/VALIDATION

Data are typically validated by the laboratory and field personnel. First, during the field operations, field measures will be validated at the time of collection by the field sampler by verifying the use of standard operating procedures for the sampling effort and using field QC checks. Second, laboratory analytical results will be validated by the Laboratory Department Manager or the analyst who is the specific analytical task leader.

8.1 FIELD DATA VALIDATION

Validation of field obtained data, as well as ongoing QA/QC checks of environmental samples being taken, is performed on field data. All field data are reviewed during the time of collection and second, all data are reviewed by secondary field personnel if multiple personnel are present. Errors in the field logbooks will be corrected by placing a single line through the entry, initialing and dating the correction. If information is added without a correction being necessary, that entry will be initialed and dated to indicate that it was not entered at the original time of data entry. Entries should never be "whited out" or made in pencil.

8.2 LABORATORY DATA VALIDATION

The individual Laboratory Department Managers shall validate all laboratory data prior to reporting. The following typical QA/QC reviews and/or procedures shall be used:

- Standard calibration curves are prepared prior to sample analysis;
- The standard regression coefficient is within the acceptable range;
- Standard reference materials are analyzed at the proper frequencies and acceptable results are obtained;
- The reagent blanks are analyzed at the proper frequency;
- Precision requirements of this plan are met;
- Accuracy requirements of this plan are met;
- Completeness requirements of this plan are met;
- Samples are analyzed within the proper sample holding times;
- All calculations are verified as correct;
- Proper units are reported; and
- The proper methodologies were used.

In addition to this review of analytical results and project specific precision, accuracy, and completeness requirements, the Laboratory Department Manager should perform unannounced audits of report forms and other data sheets as well as regular reviews of instrument logs, performance test results, and analysts' performance. In the event that any review of analytical results or internal QA/QC checks indicate problems, immediate corrective actions must be taken and all data collected because the previous approved QC audits must be reviewed for validity.

Specific laboratory procedures for validation of the analytical data generated are described in the laboratory QAMs.

8.3 INDEPENDENT DATA VALIDATION

The laboratory will provide DQO Level III (i.e., CLP Like) data packages. However, the data packages will not be validated at this time. Data validation procedures following the applicable guidance from the current U.S. EPA's "Contract Laboratory Program, National Functional Guidelines for Inorganic SUPERFUND Data Review (OSWER 9240.1-51, EPA 540-R-10-011, January 2010) will be performed, if required.

8.4 DATA REPORTING

Analytical Laboratory

After the data have been validated internally by the laboratory, all of the results are electronically or automatically entered into the laboratory's data management system where they are stored prior to reporting. When all analyses are completed, the Laboratory Director (or his/her designee) will issue a final data report including a descriptive case narrative. He or she will then issue the report to the data user.

The data reports generated for this project should contain all pertinent information for the data user to determine the applicability and usability of the data for its intended purposes. For this reason, a specified and uniform data reporting format should be implemented. For this project, DQO levels III data packages will be reported as a Level IV (CLP-like) deliverable to facilitate data validation, if needed. The following criteria and information should be supplied, at a minimum, for data reports generated for this project:

1. A descriptive case narrative identifying any problems encountered during internal data validation (as described above);

2. Completed and legible chains-of-custody for all analyses contained within each submitted data package;

3. A lab sample chronicle indicating which analyses were requested and performed for the samples contained in the data package;

4. A summary of the laboratory sample identifications and the correlating field sample identifications;

5. A summary of all applicable analytical results, errors, MDCs reported in the correct number of significant figures, reporting units; and

6. Included in the individual sample reporting results should be the complete sample identifications, the sample dilutions (if necessary), and the individual sample analysis dates.

8.4.1 Level I Reporting

Summary reporting only will be provided. Bulleted items above are required under this DQL.

8.4.2 Level II Reporting

Summary reporting only will be provided. The data package reporting requirements are the same as Level I except legible and calculated QA/QC summaries for laboratory blanks, surrogate recoveries (if applicable), laboratory control sample recoveries, and matrix spike/matrix spike duplicate recoveries (or matrix spike recovery and laboratory duplicate results) must also be supplied under this DQL.

8.4.3 Level III Reporting

The following summary forms and raw data deliverable requirements will apply for Data Quality Level III.

The following forms are required to be made available (upon request) for all analyses using Gamma Spectroscopy, isotopic Uranium and Thorium, and Alpha Spectroscopy methods:

- Narrative and sample identification cross reference;
- Copies of Chain-of-Custody documentation;
- Laboratory chronicle;
- Method summaries and references;
- Matrix spike/Matrix spike duplicate summary or any lab duplicate;
- QC Check Sample summary;
- Method blank summary and results;
- Instrument performance check summary;
- Instrument set up and calibration summary;
- Continuing calibration check summary for all constituents of interest.

9.0 QUALITY CONTROL PROCEDURES

Quality control (QC) procedures and checks are used to verify the accuracy of investigation data. Field QC checks are used to identify potential problems with sampling procedures such as the inconsistent use of sampling standard operating procedures or field introduced sample or water supply contamination and/or problems with sample homogeneity or representativeness. Laboratory QC checks are used to identify potential problems with analytical procedures such as the misapplication of required analytical methodologies or other laboratory-related problems which could result in inaccurate or imprecise data reported. The laboratory QC checks and procedures presented in this section are required for most of the applicable methods, but the frequency of the QC checks should follow procedures outlined in the laboratory QAMs.

9.1 FIELD QC CHECKS

To check the quality of data from field sampling efforts, field duplicate samples will be collected for analysis. These samples will be treated as separate samples for identification, logging and shipping. Analytical results on duplicates will be reported with the appropriate field sample data. The number of these samples, when required, and their use is described in Table 6-1.

9.2 INTERNAL LABORATORY QC CHECKS

The QC check frequencies and requirements specified in the following sections is a general description only. The laboratory will follow the internal QC checks specified in its QAM for each analysis type employed. However, these QC checks must meet, at a minimum, the requirements specified in the respective U.S. EPA analytical methods.

The following internal laboratory QC checks are performed for most analyses, whenever applicable, to ensure the measurement systems are under control:

- Initial and continuing calibrations;
- Preparation/method blanks; and
- Matrix spike and matrix spike duplicate or matrix spike and laboratory duplicate analysis, as appropriate.

Additional internal laboratory QC checks are typically performed for most analyses, as required by the associated analytical method. Only the most common QC checks are generally described below.

9.2.1 Initial and Continuing Calibration

Each measurement system may be calibrated immediately prior to use and be shown to maintain the calibration throughout the course of the analysis, as appropriate. An initial calibration will be performed and/or confirmed prior to the sample analyses. Continuing calibrations will be typically analyzed at a minimum frequency as recommended by manufacturer. For radiological analysis, calibration checks are only required once every 24 hours of analysis.

9.2.2 Preparation/Method Blanks

A preparation or method blank is analyzed with each batch of samples received for analysis. Analyte responses observed in the blank at levels above the reportable detection limit are reviewed for possible laboratory contamination. If high blank values are observed, laboratory glassware and reagents may need to be checked for contamination and the analysis of future samples halted until the system can be brought under control. A high blank value is typically defined as a value greater than the method detection limit. A preparation and/or method blank will be prepared at a frequency of one per 20 samples or one per day, whichever is greater.

9.2.3 Matrix Spike and Duplicate (Matrix Spike Duplicate) Analysis

For all analyses where matrix spiking is possible, 1 in 20 samples is analyzed as matrix spikes and matrix spike duplicates. Field personnel must provide additional sample volume for the laboratory to complete an MS/MSD. The percent recovery for spiked samples is calculated using the equations provided in Section 12.0 and compared to the accuracy criteria specified in the QAM for the associated analytical method. The relative percent difference of replicate spikes or replicate analytical results is calculated using the equations given in Section 12.0 and compared to the precision criteria specified in the laboratory QAMs for the associated analytical method.

9.2.4 Calibration Check Compounds and Reagent Blanks

Calibration check compounds and reagent blanks are analyzed periodically throughout the course of the analysis, depending upon the required analysis. The exact frequencies and methods of use are presented in the laboratory QAM.

10.0 PERFORMANCE AND SYSTEM AUDITS

Two types of audit procedures may be conducted during any environmental investigation: performance audits and system audits. These audits may be performed on the laboratory as well as field activities. A description of the laboratory's specific guidance for Performance and System Audits will be presented in the laboratory QAM. General procedures for laboratory performance and system audits are presented below.

10.1 PERFORMANCE AUDITS

10.1.1 Laboratory Performance Audits

Laboratory performance audits are typically conducted by the Laboratory QA Officer on a routine basis. Each laboratory analyst is provided a performance evaluation sample containing analytes for the parameters which he/she performs. These audit samples are used to identify problems in sample preparation or analytical techniques or methodologies which could lead to future analytical problems.

Additionally, the laboratory performance audits include verification of each analyst's record keeping, proper use and understanding of procedures, and performance documentation. Corrective action will be taken for any deficiencies noted during the audit.

10.2 SYSTEM AUDITS

10.2.1 Laboratory System Audits

Laboratory system audits are typically conducted by the Laboratory QA Officer. These audits are used to ensure that all aspects of the Laboratory's QAM are operative. This involves a thorough review of all laboratory methods performed and documentation to confirm that work is performed according to project specifications.

In some cases, outside certification agencies conduct performance and system audits to verify contract compliance or the laboratories' ability to meet certification requirements on methods of analysis and documentation. Results of these outside certification audits may be reviewed at any time as a check on the laboratory's internal auditing procedures.

11.0 ASSESSMENT PROCEDURES FOR DATA ACCEPTABILITY

The following discussion describes the procedures that will be employed to evaluate the precision, accuracy and completeness of the generated data.

11.1 PRECISION

Precision is a measure of agreement among individual measurements of the same property under prescribed similar conditions. Precision is assessed by calculating the relative percent difference (RPD) of replicate spike samples or replicate sample analyses according to the following equation:

Relative Percent Difference: $RPD = \frac{R_1 - R_2}{(R_1 + R_2)/2} \times 100$

Where: R_1 = result 1
R_2 = result 2

11.2 ACCURACY

Accuracy is a measure of the closeness of an individual measurement to the true value. Accuracy is measured by calculating the percent recovery (%R) of known levels of spike compounds as follows:

Percent Recovery:

$$\%R = \frac{[spike\ sample] - [unspiked\ sample]}{[spike\ added]} \times 100$$

Where: [*s*] denotes concentration

11.3 COMPLETENESS

Completeness is a measure of the amount of valid data obtained from a measurement system, expressed as a percentage of the number of valid measurements that should have been collected. As is specified in Section 4.2, more than one completeness check can be evaluated. It is calculated as follows:

$$Completeness\ (\%) = \frac{number\ of\ valid\ samples\ reported}{total\ number\ of\ samples\ analyzed} \times 100$$

11.4 QUALITY CONTROL CHARTS

Quality control charts can be prepared after the initial 20 analytical determinations to graphically evaluate precision and accuracy criteria. The charts are prepared by calculating the mean value of the determinations and setting control limits at ± 3 standard deviations from that mean. The following equations are used:

$$mean = \bar{x} = \sum_{i-1}^{n} \chi_i/\eta$$

Mean:

$$\bar{X} = \frac{1}{N}\sum_{i=1}^{N} x_i$$

Where: N = number of samples
X_i = sample value

Standard Deviation:

$$\sigma = \sqrt{\frac{\sum_{i=1}^{N}(x_i - \bar{X})^2}{N-1}}$$

The control limits should be within acceptance limits or ranges presented in the as-yet-unselected laboratory's QAM. If the values are found to be outside these limits or ranges, the measurement system is examined to determine if possible problems exist.

12.0 PREVENTIVE MAINTENANCE

Periodic preventive maintenance is required for equipment whose performance can affect results. Instrument manuals are kept on file for reference if equipment needs repair. Troubleshooting sections of manuals are often useful in assisting personnel in performing maintenance tasks.

12.1 FIELD EQUIPMENT

Field sampling personnel will be responsible for preventive maintenance of all field instruments. The field sampling personnel will protect the instruments by placing them in portable boxes and/or protective cases.

All field equipment will be subject to a routine maintenance program, prior to and after each use. The routine maintenance program for each piece of equipment will be in accordance with the manufacturer's operations and maintenance manual. All equipment will be cleaned and checked for integrity before and after each use. Necessary repairs will be performed immediately after any defects are observed, and before the equipment is used again.

Equipment parts with a limited life (such as batteries, membranes and some electronic components) will be periodically checked and replaced or recharged as necessary according to the manufacturer's specifications.

Preventive maintenance provides for a longer useful life of the equipment and helps to ensure a successful field sampling and testing program. Each piece of field equipment will have its own log sheet which contains the equipment identification and the type of maintenance performed. Since most equipment is used on an irregular basis, all equipment will be properly stored when not in use.

12.2 LABORATORY INSTRUMENTS

All major laboratory instruments should normally be under service contract so that trained professionals are available on call to minimize instrument downtime. Other preventive maintenance schedules and/or procedures for laboratory equipment are presented in the laboratory QAM.

13.0 CORRECTIVE ACTION

There are many laboratory functions that may require corrective action. The decision to undertake corrective action and the ensuing action must be documented so that traceability can be maintained. Corrective action procedures are divided into two subgroups: methods corrective action and systems corrective action. These corrective actions are implemented whenever system or performance audits note deficiencies or when QC procedures indicate a potential analytical problem. The point of originating the corrective action varies, depending upon the mode of detection that such action is necessary. It is generally the role of either the Laboratory QA Officer or the Laboratory Department Manager to initiate such action. Those actions that affect the quality of the data will be recorded and the record maintained by the Laboratory QA Officer. The general procedures for appropriate laboratory corrective actions and identification of potential problems are presented in the analytical laboratory QAM.

14.0 QA REPORTS TO MANAGEMENT

This QAPP provides methods and documentation for the assurance of quality work performed for the characterization study. Audit reports will be provided by the Laboratory Director (or his/her designee) as a means of tracking program performance, as applicable, or if needed. Additionally, periodic assessments of measurement data accuracy, precision, completeness and significant QA/QC problems will be performed and reported to laboratory and/or project management, if needed.

Field QA reports will not be necessary considering the expected size and length of any individual sample collection activity. Any problems noted during sampling will be immediately communicated to the project Certified Health Physicist (CHP).

Upon completion of the project-specific Work Plans, a final QA/QC report will be issued, assessing the overall degree of project conformance to specifications and the impact of any non-conformances that may affect management decisions.

The final storage location of the files will be maintained by each operator. The files will be maintained for a period of at least three years.

15.0 REFERENCES

USEPA. January 2008. "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods" (SW-846, Third Edition).

USEPA. June 1972. "Handbook for Analytical Quality Control in Water and Wastewater Laboratories" (EPA 600/4-79-019).

American Public Health Association, American Water Works Association, and Water Environment Federation. August 2012. Standard Methods for the Examination of Water and Wastewater, 22nd Edition.

USEPA. January 2010. "Contract Laboratory Program National Functional Guidelines for Inorganic SUPERFUND Data Review" (OSWER 9240.1-51, EPA 540-R-10-011).

APPENDIX QAPP-1

LABORATORY QUALITY ASSURANCE

DEP Quality Assurance and Quality Control Parameters

All samples will be received and analyzed in accordance with BOL#1000 "Quality Assurance Manual for the PA Department of Environmental Protection Bureau of Laboratories," Revision 6. The radiological staff will follow procedures outlined in BOL8509, "Radiation Sample Receiving and Login," Revision 6, for sample receipt and any additional items outlined in this document. Each analysis consists of daily instrument quality control checks and batch quality control samples. The quality control parameters for each analysis can be found in the following documents:

BOL8000, Gross Alpha and Gross Beta Radioactivity in Water by EPA Method 900.0, Revision 8
BOL8003, Gamma Emitting Isotopes by EPA Method 901.1 and DOE 4.5.2.3, Revision 5
BOL8006, Radium 226 by EPA 903.1 and by DOE Ra-04, Revision 12
BOL8007, Radium-228 in Water by Brooks and Blanchard, Revision 11
BOL8008, Thorium, Plutonium, and Uranium Isotopes in Water and Solid Samples by Standard Methods 7500-U C, Revision 7
BOL8009, Gross Alpha and Gross Beta Radioactivity in Air Filters, Revision 4