SAMPLING AND ANALYSIS PLAN

PART I – FIELD SAMPLING 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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Field Sampling Plan (FSP)
Pennsylvania Department of Environmental Protection

FSP APPROVALS

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

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April 3, 2013
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ABBREVIATIONS, ACRONYMS, AND SYMBOLS

ANSI	American National Standards Institute
CHP	Certified Health Physicist
COC	Contaminant of Concern
CWT	Centralized Waste Treatment
DOT	(US) Department of Transportation
DQO	Data Quality Objective
O&G	Oil and Gas
FSP	Field Sampling Plan
HTRW	Hazardous Toxic or Radioactive Waste
keV	kilo-electron volt
MDA	Minimum Detectable Activity
MS	Matrix Spike
MSD	Matrix Spike Duplicate
NA	Not Applicable
NaI	Sodium Iodide
NELAC	National Environmental Laboratory Accreditation Conference
NIST	National Institute of Standards and Technology
NORM	Naturally Occurring Radioactive Material
NRC	(US) Nuclear Regulatory Commission
PA DEP	Pennsylvania Department of Environmental Protection
PA	Pennsylvania
pCi, pCi/g	picocurie(s), picocurie(s) per gram
POTW	Publicly-Owned Treatment Works
QA	Quality Assurance
QAPP	Quality Assurance Project Plan
QC	Quality Control
Ra-226	Radium-226
Ra-228	Radium-228
Rn-220	Radon-220
Rn-222	Radon-222
SAP	Sampling and Analysis Plan
TENORM	Technologically Enhanced Naturally Occurring Radioactive Material
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 INTRODUCTION

1.1 Purpose and Approach

Pennsylvania Department of Environmental Protection (PA DEP) selected Perma-Fix Environmental Services, Inc. (PESI) as the contractor for this project to perform a comprehensive study of the naturally occurring radioactive material (NORM) and technologically enhanced NORM (TENORM) related to the oil and gas exploration activities including conventional and unconventional drilling through geological formation(s) and associated waste water operations throughout the Commonwealth of Pennsylvania (PA). As part of this effort PESI has prepared a field sampling plan (FSP) to explain the details of the sampling activities to be carried out during this study.

The following proposed comprehensive study will focus on the quantification of TENORM in:

- Ambient air;
- Drill cuttings (vertical and horizontal);
- Natural gas;
- Natural gas processing pipes and equipment;
- Waste water generated on drilling sites;
- Sludge resulting from the processing of waste water from the well pad development process; and
- Landfill leachate.

Other potentially impacted areas may be surveyed and sampled as appropriate when identified, including but not limited to land surface beneficial reuse application areas.

Throughout Pennsylvania many companies perform oil & gas (O&G) activities by conventional and unconventional drilling through various subsurface layers of rock to produce oil and natural gas. The natural gas industry produced water and flowback water, as well as drill cuttings and sources of off gassing, are potentially impacted by NORM and/or TENORM. Unconventional O&G process water (e.g., flowback and produced 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 presented herein 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 publicly owned treatment works (POTWs), centralized waste treatment (CWT) facilities and zero liquid discharge (ZLD) facilities for processing. Landfill leachate will also be sampled to determine if radium has migrated from the waste water sludge and drill cuttings to the landfill leachate. Any beneficial reuse of any of the O&G exploration and production media will also be surveyed and sampled as appropriate. Sampling activities will include but are not limited to:

- Vertical and horizontal drill cuttings;
- Onsite pits containing cuttings;
- Production water;
- Flowback water;
- Filter socks;
- Filter presses;
- Compressed 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 sands; and
- Drilling muds.

The Commonwealth of Pennsylvania has not established occupational exposure regulations/standards for NORM or TENORM. The American National Standards Institute (ANSI) approved and published a standard addressing the control and release of NORM/TENORM titled Control and Release of TENORM (ANSI/HPS N13.53-2009). The standard applies to industries or activities that are not covered by existing federal or state regulations. The standard provides the following dose criteria (2.2.1.a.(i)):

"an annual dose limit of 1 mSv (100 mrem), above background, from all pathways and sources of radioactivity (except radon and its short-lived decay products) and practices associated with site and facility operations, ..."

Pennsylvania has established disposal criteria for solid waste impacted with TENORM. Specifically the Commonwealth limits the exposure of future residents, the hypothetical resident farmer, from a RCRA Subtitle D landfill to 25 mrem per year from all pathways including radon.

This *Field Sampling Plan* (FSP or "Plan"), which is Part I of the PA DEP *Sampling and Analysis Plan* (SAP), describes and presents procedures and protocols for field radiological surveys, sampling, including types, quantities, sample technique, and chain of custody, and on-site radiological analysis; and off-site physical, chemical, and radiological laboratory analyses. Part II of the SAP is a project-specific *Quality Assurance Project Plan* (QAPP).

1.2 Report Organization

This FSP consists of the following sections:

1. Introduction – purpose of the report and report organization;
2. Site Description – physical description of the site, site contaminants and site selection criteria;
3. Scope and Objectives –field screening techniques and sampling;
4. Field Screening – methods used to conduct field screening activities of soil, equipment and personnel, for radiological contamination;
5. Field Sampling – methods and procedures of collecting soil, water and air samples for on-site and off-site laboratory analysis;
6. Field Quality Control – processes and procedures for maintaining adequate quality control (QC) for field activities;
7. Laboratory Analysis – methods for analyzing soil and water samples collected; and
8. References – citations.

2.0 SITE DESCRIPTION

2.1 Background

The sampling locations associated with O&G will vary from site to site throughout the Commonwealth of Pennsylvania. The study will include survey and sample events on active and inactive O&G sites, waste water facilities and landfills. Each site may have its own discrete water storage and residual waste storage location(s).

Various O&G and waste processing and disposal sites and facilities will be evaluated for TENORM generation and handling. The study's facility selection criteria are as follows:

Well Sites and Pad Selection Criteria:

- Select Marcellus shale formation well sites from the 'dry' gas areas predominantly in the northern and central parts of the state.
- Include at least one Marcellus shale formation well site from the 'wet' gas area found predominantly in the southwestern part of the state.
- Select a Utica formation well site and other non-Marcellus shale formations (e.g., Geneseo, Burket and Rhinestreet) that become available.
- Include 'conventional' shallow O&G well sites in the Oriskany sandstone formation.
- Sample, as applicable, during the five phases of development including: vertical drilling, horizontal drilling, fracturing, flowback and production.
- Sampling activities will include associated well development and production equipment and operational facilities at each above-referenced site.

Waste Water Treatment Facility Selection Criteria:

- Select a representative sample of the four types of waste water treatment plants (WWTPs) public including privately owned treatment works (POTWs), CWT facilities, ZLD facilities and onsite well pad treatment units that exist and that are known to, or have been known to, take waste water from natural gas well pads.
- Include waste water treatment facilities that accept waste water from conventional and unconventional types of drill pads.
- Examine waste water treatment facilities that accept waste material from unconventional well pads in the wet gas vs. dry gas production areas.
- Include facilities where historic positive radioactivity readings have been measured from the intake waste water, produced sludge, effluent discharge, or discharge point stream / river sediments, etc.

- Include facilities the PA DEP regional offices have indicated are of particular interest.

Landfill Facility Selection Criteria:

- Include and rank landfill facilities based on the amount of TENORM waste they have accepted during the past year.
- Examine large-volume TENORM disposal sites where onsite worker exposure measurements can be obtained and representative samples of solids can be collected.
- Collect leachate samples from all PA landfills.

Gas Distribution and End Use Operations / Facility Selection Criteria:

- Examine facilities that compress, carry and distribute gas from the 'wet gas' producing area of the state.
- Examine facilities that compress, carry and distribute gas from the 'dry gas' producing area of the state.
- Include facilities that handle gas produced in Pennsylvania as opposed to those which handle gas imported from out of state.
- Include any major gas user (e.g., electrical generator), processing and storage facilities.
- A representative selection of the types of facilities which come into contact with natural gas after it leaves production wells out to, and including, end users.
- Sample private residences.

Well Component Reconditioning Selection Criteria:

- Include any major well casing / pipe reconditioning or de-scaling facilities in the Commonwealth.

2.2 Site Characterization

Primary constituents of concern (COCs) for O&G production radiological characterization include uranium (U-238, U-235 and U-234), thorium-232, radium (Ra-226 and Ra-228), radon (Rn-220 and Rn-222) and any unsupported decay chain radionuclides. Radiological characterization will consist of field screening/surveys (gamma exposure rate/gross gamma activity) using portable survey meters, collection and screening samples of solids and/or liquids, collection of swipe (smear) samples to determine removable alpha and beta surface contamination, and radon sampling of gas as appropriate.

3.0 SCOPE AND OBJECTIVES

This study is to examine the generation of TENORM in the Pennsylvania O&G industry, as well as evaluate the potential pathways for public and non-radiation worker exposure. Information on waste volumes and levels of radioactivity will be informative to the management of these materials.

Radiological support surveys and sampling performed for this TENORM study may consist of: (a) field alpha/beta/gamma screening, and (b) sampling of various media for off-site radiological and laboratory analyses. This section summarizes the scope and objectives of these survey activities; a detailed description of field screening and sampling are presented in Sections 5.0 and 6.0, respectively.

3.1 Scope of Field Screening Activities

Field screening activities will consist of using field instruments and detectors to identify the possible presence and degree of NORM and/or TENORM in cutting pits (open and closed), flowback and produced water, temporary water storage vessels and recycle systems, drilling rigs and associated equipment, offices, trailers and trucks, etc., production equipment, waste water facilities, landfill leachate, and beneficial reuse areas. Screening of solid and aqueous samples and swipes (smears) samples will be performed.

Direct-read radiological instruments and detectors will be used throughout the field operations of the project for scanning and surveying of personnel, equipment, materials and areas. The instruments and detectors will be operated and maintained by the PA DEP staff, PESI technician(s) or subcontractors, and will be quality control (QC) checked as required by PESI's operating procedures. Additional equipment that may be used on-site will be maintained and operated by the operator's technician(s) or subcontractors. Proposed instruments, detectors, and equipment (or their equivalents) to be used on-site during field screening are listed in Table 3-1.

Table 3-1. Field Screening Equipment

Instrument	Detector	Parameters/Usage
Ludlum Model 2224, or equivalent	e.g., Ludlum Model 43-89, 100 cm^2 Scintillator	Portable scaler/ratemeter (alpha/beta)
Ludlum Model 2221, or equivalent	e.g., Ludlum Model 44-10, 2x2 NaI Scintillator	Portable scaler/ratemeter (high energy gamma)
Ludlum Model 2929, or equivalent	Ludlum Model 43-10-1	Smear/air sample filter counter (alpha/beta)
Bicron Microrem , or equivalent	--	Portable low-level dose rate meter (gamma)
Ludlum Model 3, or equivalent	Ludlum Model 44-9 Pancake Frisker	General purpose survey meter (beta/gamma)
Ludlum Model 19 Micro-R Meter	1x1 NaI Scintillator	Exposure rate survey meter (high energy gamma)

3.2 Scope of Field Sampling Activities

Field sampling will consist of collecting samples of environmental media from sources for either on-site evaluation or off-site laboratory analysis. The following types of field samples will be collected for the purposes identified:

- Drill cuttings, accumulated solids, scale, treatment water sludge, discharge sediment, soil samples and crystalline salts from brine water evaporation as appropriate for off-site radiological laboratory analyses for characterization and evaluation of potential mobility in the environment.
- Flowback and produced water, waste water treatment influent and effluent, and landfill leachate samples for off-site radiological laboratory analysis for characterization purposes. Solid and aqueous phases to be evaluated separately.
- Radon sampling of gas as appropriate to monitor occupant/worker/public exposure.
- Swipe (smear) samples to determine removable alpha and beta surface contamination as an indicator of potential airborne exposure.

Off-site analyses of solid and aqueous samples may include the following parameters as specified in Section 6.0:

- Gross alpha and beta
- Gamma spectroscopy to identify radionuclides
- Alpha spectroscopy for uranium (U-238, U-235, and U-234), radium (Ra-226), thorium (Th-232, Th-230 and Th-228), and for any unsupported decay chain radionuclides, and for radon (Rn-220 + Rn222)
- Beta analysis for Ra-228

Sampling and laboratory analysis requirements are summarized in Table 7-2; minimum sample quantities, containers, preservation and holding times are summarized in Tables 7-3 and 7-4 (see Section 7.0).

4.0 FIELD SCREENING AND TESTING ACTIVITIES

Procedures and activities for radiological field surveys (screening) of solid and aqueous samples and sampling areas are described below.

4.1 Radiological Surveys of Solid Sample Areas

Radiological surveys will be performed on solid sample areas, including:

- Gamma exposure rate surveys in units of micro-Roentgen per hour (μR/hr) around and above sampling areas when possible; and/or
- Gross gamma surveys in units of counts per minute (cpm); and
- Background exposure rate and/or gross gamma count rates measured outside the influence of sampling areas.

4.2 Radiological Surveys of Aqueous Sample Areas

Radiological surveys will be performed on containerized water and/or sludge, and effluent discharge points including:

- Gamma exposure rate surveys in units of μR/hr around and on contact with water tanks/trucks full or partially full of water/sludge prior to sampling when possible, and/or at effluent discharge points; and
- Background exposure rate and/or gross gamma count rates measured outside the influence of sampling areas.

Water tanks screened at greater than two times natural background μR/hr levels may be sampled and analyzed in accordance with Section 5.

4.3 Radiological Surveys of Equipment and Structures

Radiological surveys will be performed on drilling rigs and well development equipment (e.g., platforms, pipes, tanks, etc.), including:

- Gamma exposure rate surveys in units of μR/hr around and on contact with equipment and/or structures prior to sampling when possible; and/or
- Gross gamma surveys in units of cpm; and/or
- Total alpha and beta surface contamination in units of disintegrations per minute per 100 centimeters squared (dpm/100 cm^2); and
- Removable alpha and beta surface contamination (smear) in units of dpm/100 cm^2; and
- Background exposure rate and/or gross gamma count rates measured outside the influence of sampling areas.

4.4 Radiological Surveys of Samples

Radiological surveys will be performed on all samples, including:

- Gamma exposure rate surveys in units of μR/hr on contact with sample container; and/or
- Gross gamma surveys in units of cpm on contact with sample container (correlated to pCi/g); and
- Total alpha and beta surface contamination in units of dpm/100 cm^2; and
- Removable alpha and beta contamination (smear) in units of dpm/100 cm^2; and
- Background exposure rate and/or gross gamma count rates measured outside the influence of samples and sampling areas.

5.0 FIELD SAMPLING ACTIVITES

This section of the FSP describes sampling and analyses to be performed by off-site laboratories. The quantitative analytical data that are generated as a result of these activities will be sufficient in type, quantity, and quality such that data quality objectives (DQOs)discussed in the QAPP, are met, radiation exposure to on-site workers is minimized, and to avoid migration or dispersion of radioactive materials as a result of the field activities. Field sampling will be performed for solid, aqueous, and gas samples as described below.

Specific sampling parameters, laboratory analytical methods and numbers of samples are discussed further in Section 7.0 and summarized in Table 7-2, while analysis methods and sample volume, preservation, and holding times are summarized in Tables 7-3 and 7-4.

5.1 Objectives

It is important to understand the movement and exposure pathways of TENORM through the entire O&G process in the Commonwealth of Pennsylvania. In this regard the purpose of this comprehensive study is to have a more complete understanding of TENORM in O&G industry and waste disposal operations, and to document and evaluate potential radiation exposure to workers and the public, as well as to ensure protection of the environment. The sampling and analysis will assist in determining radiological isotopes of concern and in evaluating their potential mobility in the environment.

5.2 Solid Samples

Various types of solid samples may be collected:

1. Rock 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;
8. Fresh proppant sands; and
9. Drilling muds.

5.2.1 Sample Type and Location

Sample(s) will be collected as outlined below:

1. Exploration and Production Site Sampling – This study will include sample events on active and inactive sites, including:
    a. Open/Operating Cuttings Pits – Sampling and laboratory analysis of the drill cuttings (solid material) stored in the open/operating pits. Cuttings from both the vertical and horizontal drilling phases will be sampled. Vertical cuttings will be selected based on well bore gamma logs if available.
    b. Flowback and produced water on sites, evaluate solid and aqueous phases separately.
    c. Temporary Water Storage Vessels and Recycle Systems (Hydraulic Fracturing Water Storage Tanks, Produced Fluids Tanks, Filtration Equipment, Water Trucks) – Collect and screen samples of solids accumulated in vessels for gross activity.
    d. Drilling Rigs and Associated Equipment – Collect and screen samples of solids (scale) accumulated on rigs, pipes used well casings and associated equipment.
    e. Production Equipment (Separators, Heater/Treaters, Dehydration Units, Compressors) – If possible, collect and screen samples of solids accumulated in/on production equipment.

2. Waste Water Facilities Sampling
    a. Twenty-two (22) of the highest volume Marcellus shale waste water treatment facilities will be included in this study. Sixteen (16) are located in the Western sector of Pennsylvania. The other six (6) are located in the Central or Eastern sector. Facilities will include normal POTWs, specialized CWT facilities used for Marcellus shale hydraulic fracturing water treatment operations and ZLDs.
    b. Each of the 22 waste water treatment facilities will be sampled three (3) times to establish a trend.
    c. A total of two (2) solid samples will be taken at each facility during each of the 3 sample events: sludge from the treatment of the water and sediments at the effluent discharge point.
    d. 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 sludge with the facilities such that the samples are all related to the processing of the influent Marcellus shale industry water.

3. Landfills
    a. TENORM Disposal – Soil samples and rock cutting samples.

4. Beneficial Reuse – areas adjacent to road beds where beneficial reuse brine has been used will be surveyed for residual NORM/TENORM and sampled as appropriate. Similarly other areas where rock cuttings have been used will be surveyed.

5.2.2 Sampling Methods

Solid samples will be collected using decontaminated reusable or disposable sampling tools (e.g., stainless steel trowels or tubes). Sampling tools may be decontaminated prior to first use on-site, between sampling locations, and following last use on-site (i.e., before demobilizing that equipment) as appropriate based on survey data. The samples selected for analysis will be placed into laboratory approved containers immediately following collection and labels promptly affixed to the sample containers. The samples will be transported via delivery service under chain-of-custody control to the off-site subcontract laboratory for analysis. Table 7-3 identifies container types that will be used for collection of these samples. Minimum sample quantities required for laboratory analysis are also identified in Table 7-3.

Subsurface sampling, e.g. by auger will be considered when a gradient in the media sampled is suspected and the volume of material represented is not homogeneous. For example, for drill cuttings, in order to access cuttings from the horizontal zone, subsurface sampling of a cuttings pile maybe necessary. Samples will be collected in 15 cm intervals either using an auger or other appropriate sampling tool. Each segment will be field screened for gross gamma activity and/or exposure rate to determine if materials above ambient background are present in the sample. If materials are present in multiple contiguous intervals, all of the materials in those intervals will be homogenized in a stainless steel bowl or disposable aluminum pan to the best that the material will allow. A sample will be collected from the homogenized material and sent for the appropriate analysis. If conditions allow, an attempt may be made to down-hole log the auger hole to confirm the depth of activity encountered within the sample location.

Additional sample preparation as specified by the laboratory for specific analyses may be required. For gamma spectroscopy usually no field prep is necessary. However, for gross alpha and beta analyses additional sample preparation may be necessary in the laboratory.

5.2.3 Laboratory Analysis

Solid samples will be analyzed by gamma spectroscopy to identify TENORM radionuclides. Approximately 10% of the samples, based on the gamma spectroscopy results, will also be analyzed by alpha spectroscopy for uranium (U-238, U-235 and U-234), thorium (Th-232, Th-230 and Th-228) radium (Ra-226) and isotopic analysis for Ra-228 (a beta emitter) and for any unsupported decay chain radionuclides; and for radon (Rn-220 and Rn-222)

5.3 Aqueous Samples

Various types of aqueous samples may be collected:

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

5.3.1 Sample Type and Location

Grab samples will be collected as outlined below:

1. Exploration and Production Site Sampling – The study will include survey and sample events on active and inactive drill sites, including:
    a. Flowback and produced water on sites, evaluate solid and aqueous phases separately.
    b. Temporary Water Storage Vessels and Recycle Systems (Hydraulic Fracturing Water Storage Tanks, Produced Fluids Tanks, Filtration Equipment, Water Trucks) – Water tanks screened at greater than five (5) times background should be sampled and analyzed in accordance with Section 5.
    c. Production Equipment (Separators, Heater/Treaters, Dehydration Units, Compressors) – If possible, collect and screen samples of liquids accumulated in/on production equipment.

2. Waste Water Facilities Sample and Analysis
    a. Twenty-two (22) of the highest volume Marcellus shale waste water treatment facilities will be included in this study. Sixteen (16) are located in the Western sector of Pennsylvania. The other six (6) are located in the Central or Eastern sector. Facilities will include normal POTWs, specialized CWT facilities used for Marcellus shale hydraulic fracturing water treatment operations and ZLDs.
    b. Each of the 22 waste water treatment facilities will be sampled three (3) times to establish a trend.
    c. A total of two (2) aqueous samples will be taken at each facility during each of the 3 sample events: influent Marcellus shale industry water and facility effluent discharge water. An additional solid sample will be collected from the waste-water sludge generated at the facility and a sediment sample will be collected at the effluent discharge point where applicable.
    d. 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 and the effluent water with the facilities such that the samples are all related to the processing of the influent Marcellus shale industry water.

3. Sampling of Landfill Leachate – a sample of landfill leachate will be taken at each of the 54 active landfills in PA and analyzed for gross alpha/beta and Ra-226/Ra-228 by gamma spectroscopy.

5.3.2 Sampling Methods

A representative grab sample will be collected from the appropriate tank/outlet using a disposable Teflon® bailer or a reusable stainless steel thief sampler; contents of the selected sampling implement will be added directly to sample containers. Samples will be placed into laboratory-prepared containers immediately following collection and caps and labels promptly affixed to the sample containers. In cases where sample valves are available, samples may be collected directly into approved sample containers. The samples will be transported via overnight delivery service under chain-of-custody control to the off-site subcontract laboratory for analysis or transported to the on-site lab. Table 7-4 identifies container types to be used for collection of

these samples. Once the sample is received by the off-site analytical laboratory the laboratory personnel will immediately filter the sample using a 0.45 micron filter. The filtered sample will placed into a new pre-cleaned container and properly preserved.

If a stainless steel thief sampler is used, it will be decontaminated prior to first use, between sampling locations, and following last use (i.e., before demobilization). Sampling equipment decontamination procedures are described in Section 5.5.

5.3.3 Laboratory Analysis

Each of the samples will be split in two so that one sample is analyzed "as is" and the other sample is preserved, filtered (by the off-site laboratory), then analyzed (both the liquid and the filter medium). Each of the samples will be analyzed for gross alpha and beta and by gamma spectroscopy to identify radionuclides. Approximately 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 (Th-232, Th-230 and Th-228) radium (Ra-226) and isotopic analysis for Ra-228 (a beta emitter) and for any unsupported decay chain radionuclides; and for radon (Rn-220 and Rn-222)

Laboratory analysis methods for these parameters are identified in Table 7-3 and discussed in the QAPP.

5.4 Gas Samples

Radon gas sampling occurs via several methods. The specific method chosen will depend on the characteristics of the sampling location, such as indoor or outdoor locations, relative humidity considerations and length of time of samples. The sampling methods available are activated charcoal analysis, electret ion chambers (both short- and long-term), alpha track detectors, continuous radon monitors and grab sampling. On occasion, it will be necessary to determine the amount of radon that is contained within the product side mixed with methane. Since both are gases, methane and radon are comingled in natural gas. This is particularly relevant to the downstream processors and distributers of natural gas. Natural gas samples will be collected in an industry-approved sample container capable of direct sampling from the high pressure 800 to 1000 psi distribution lines. These sample containers will be delivered to the laboratory by the sample collector or some other ground transport method. Regulators will be applied to the sample container so the laboratory can collect a specific volume of methane. The methane will be captured inside a device typically used for capturing radon during radon emanation analysis. Standard radon emanation counting via gamma spectroscopy, lucas cell, or equivalent as appropriate will be utilized to determine the concentration of radon.

5.5 Equipment Decontamination Procedures

Disposable sampling equipment will be used wherever possible to minimize decontamination requirements. When reusable equipment is used, such equipment will be decontaminated both prior to sampling in the field and between uses, as appropriate. The following decontamination steps will be performed for reusable equipment, in the following order as necessary:

1) Potable water rinse;
2) Wash with laboratory-grade detergent (Alconox®, Liquinox® or equivalent);
3) Distilled water rinse;
4) Acetone, Isopropanol or Methanol rinse;
5) Distilled water rinse; and
6) Air drying.

6.0 DOCUMENTATION

6.1 Field Documentation

6.1.1 Log Books and Field Data Sheets

Information pertinent to field activities will be recorded on field logbooks. The logbooks will be bound and the pages will be consecutively numbered. Sufficient information will be recorded in the logbooks to permit reconstruction of site sampling activities. Information recorded on official project documents (e.g., survey forms, chains-of-custody, etc.) will not be repeated in the log books except in summary form or cross-reference notation where determined necessary. Field log books will be kept in the possession of the appropriate field personnel, or in a secure place when not being utilized during field work. Logbooks will become part of the final project file upon completion of the field activities. Entries recorded in log books will be made in blue or black, waterproof ink and may include, but not be limited to, the following information:

- Surveyor/sampler, date, and times of arrival at and departure from the site;
- Description of the field activity and summary of daily tasks;
- Names and responsibilities of field crew members;
- Sample collection method and number/volume of sample(s) collected;
- Information regarding activity changes and scheduling modifications;
- Field observations and weather conditions;
- Types of field instruments used and purpose of use, including calibration methods and results;
- Field measurements made and quantities/volumes of material sampled;
- Scanning/surveying of equipment and materials;
- Global Positioning System (GPS) coordinates as appropriate; and
- Days elapsed since flowback as applicable.

Additionally, the sampler 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.

Field data sheets and Radiological Survey forms may be used to record field information in addition to the use of log books.

6.2 Sample Documentation

6.2.1 Sample Numbering System

A unique sample numbering scheme will be used to identify each sample collected and designated for on-site and off-site laboratory analysis. The purpose of this numbering scheme is to provide a tracking system for the retrieval of analytical and field data on each sample. Sample identification numbers will be recorded on sample labels or tags, field data sheets and/or logbooks, chain-of-custody records and all other applicable documentation used during the project.

6.2.2 Sample Labels

Labels will be affixed to all sample containers during sampling activities. Information will be recorded on each sample container label at the time of sample collection. The information to be recorded on the labels will be as follows:

- Sample identification number;
- Sample type (discrete or composite);
- Site name and area/location number;
- Analysis to be performed;
- Type of chemical preservative present in container;
- Date and time of sample collection; and
- Sample collector's name and initials.

6.2.3 Cooler Receipt Checklist

The condition of shipping coolers and enclosed sample containers will be documented upon receipt at the analytical laboratory. This documentation will be accomplished using a cooler receipt checklist utilized by the contract laboratory.

6.2.4 Chain-of-Custody Records

Chain-of-custody procedures implemented for the project will provide documentation of the handling of each sample from the time of collection until completion of laboratory analysis. The chain-of-custody form serves as a legal record of possession of the sample. A sample is considered to be under custody if one or more of the following criteria are met:

- The sample is in the sampler's possession;
- The sample is in the sampler's view after being in possession;
- The sample was in the sampler's possession and then was placed into a locked area to prevent tampering; and/or
- The sample is in a designated secure area.

Custody will be documented throughout the project field sampling activities by a chain-of-custody form initiated each day during which samples are collected. The chain-of-custody will accompany the samples from the site to the laboratory and will be returned to the laboratory coordinator with the final analytical report. Personnel with sample custody responsibilities will

be required to sign, date and note the time on a chain-of-custody form when relinquishing samples from their immediate custody (except in the case where samples are placed into designated secure areas for temporary storage prior to shipment). Bills of lading or air bills will be used as custody documentation during times when the samples are being shipped from the site to the laboratory, and will be retained as part of the permanent sample custody documentation.

Chain-of-custody forms will be used to document the integrity of all samples collected. To maintain a record of sample collection, transfer between personnel, shipment, and receipt by the laboratory, chain-of-custody forms will be filled out for sample sets as determined appropriate during the course of fieldwork.

The individual responsible for shipping the samples from the field to the laboratory will be responsible for completing the chain-of-custody form and noting the date and time of shipment. This individual will also inspect the form for completeness and accuracy. After the form has been inspected and determined to be satisfactorily completed, the responsible individual will sign, date, and note the time of transfer on the form. The chain-of-custody form will be placed in a sealable plastic bag and placed inside the cooler used for sample transport after the field copy of the form has been detached. The field copy of the form will be appropriately filed and kept at the site for the duration of the site O&G activities.

Chain-of-custody seals may also be placed on each cooler used for sample transport. These seals will consist of a tamper-proof adhesive material placed across the lid and body of the coolers. The chain-of-custody seals will be used to ensure that no sample tampering occurs between the time the samples are placed into the coolers and the time the coolers are opened for analysis at the laboratory. Cooler custody seals will be signed and dated by the individual responsible for completing the chain-of-custody form contained within the cooler.

6.2.5 Receipt of Sample Forms

The subcontract laboratory will document the receipt of samples by accepting custody of the samples from the approved shipping company. In addition, the subcontract laboratory will document the condition of the environmental samples upon receipt.

6.2.6 Documentation Procedures

The tracking procedure to be utilized for documentation of all samples collected during the project will involve the following steps:

- Collect and place samples into laboratory sample containers;
- Complete sample container label information;
- Complete sample documentation information in the field logbook;
- Complete project and sampling information sections of the chain-of-custody form(s);
- Complete the air bill for the cooler to be shipped to off-site laboratory, if applicable;
- Perform a completeness and accuracy check of the chain-of-custody form(s);
- Complete sample relinquishment section of form(s) and place the form(s) into cooler;
- Pack cooler with ice, as needed, for samples requiring preservation to 4^{o} Celsius (C);
- Place chain-of-custody seals on the exterior of the cooler; and
- Package and ship the cooler to the laboratory.

The following steps will be made upon receipt of the cooler at the subcontract laboratory:

- Inspection of contents;
- Complete requested analyses; and
- Transmit original chain-of-custody form(s) with final analytical results from laboratory.

6.2.7 Corrections to Documentation

Original information and data in field logbooks, on sample labels, on chain-of-custody forms, and on any other project-related documentation will be recorded in blue or black waterproof ink and in a completely legible manner. Errors made on any accountable document will be corrected by crossing out the error and entering the correct information or data. An error discovered on a document will be corrected by the individual responsible for the entry, as possible. Erroneous information or data will be corrected in a manner that will not obliterate the original entry, and corrections will be initialed and dated by the individual responsible for the entry.

6.3 Sample Packaging and Shipping

Sample containers destined for off-site laboratory analysis will be packaged in thermally insulated rigid-body coolers, and will be stored in a secure area during the time period between collection and shipment to the off-site subcontract laboratory. These samples will be packaged, classified, labeled, stored, shipped and tracked in accordance with current US Department of Transportation (DOT) regulations (e.g., 49 CFR 173 et. seq.).

6.4 Management and Retention of Records

Original copies of field data, field records, analytical data, training records, and other project-specific documentation will be retained by PESI.

7.0 LABORATORY ANALYSIS

The PA DEP laboratory shall perform radiological analysis of solid and aqueous samples for characterization. The PA DEP radiochemistry laboratory has prior experience capable of providing the analytical services required to meet the project objectives.

Table 7-2 summarizes sampling and analysis requirements for the project. Table 7-3 (solid samples), Table 7-4 (aqueous and gas samples) summarize sample collection, preservative, and holding time requirements for each applicable media on this project. Laboratory analysis of matrix spike/matrix spike duplicate (MS/MSD), field duplicate, and QA split samples will be performed in accordance with the project QAPP.

Solid samples will be transported to off-site laboratories for analyses in accordance with documented laboratory-specific standard methods listed in the Analysis Methods column of Table 7-2. Specific sample and laboratory requirements are provided in the project QAPP.

7.1 Spectroscopic Energy Lines

Radiological COCs for these samples may be quantified for activity concentrations directly via gamma decays, or inferred via gamma-emitting progeny, assuming a secular equilibrium state. Table 7-1 lists gamma and X-ray emissions from site radiological COCs that may be used for determining soil activity concentrations. The list is broken down into direct emissions from the radiological COC itself or from its decay progeny, which can be used to infer the parent's activity.

Table 7-1. Spectroscopic Gamma Energy Lines for Site Radiological COCs

Radiological COC	Direct / Inferred	Inferred Nuclide	Photon Emission (keV), *primary	Yield (%)	Sample HPGe MDA (pCi/g)(a)
Th-232 and Ra-228	Inferred	Pb-212	238.6	43.3	
		Ac-228	*911.2	25.8	0.25
Th-230	Direct	Not Applicable	12.3 (X-ray) *67.6 (X-ray)	8.6 0.38	~20
Ra-226	Direct	Not Applicable	*186.2	3.59	0.5 – 2.5
	Inferred	Bi-214	609.3	46.3,	0.05
		Pb-214	1,764.5	15.8	0.04
			295.2, 351.9	19.2, 37.2	
U-238[b]	Inferred	Th-234	*63.3	4.8	1.9 - 3.5
		Pa-234m	1,001.0	0.84	

Notes for Table 7-1:

(a) The nuclide minimum detection activity (MDA) values stated in the table are from pre-remediation samples analyzed by the HPGe in a 1 liter Marinelli beaker counted for 15 minutes inside a lead shield.
(b) XRF may be used for solid matrix uranium determination and ICP-MS used for liquid samples.

Table 7-2. Summary of Sampling/Laboratory Analysis

Sample Type	Media/ Sample Type	Analytical Parameters	Analysis Methods	Frequency[a]
Vertical and Horizontal Phase Drill Cuttings Vertical and horizontal drilling-phase cuttings 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	USEPA 901.1 Modified	Once per site
Wastewater treatment facility sludge Wastewater treatment facility discharge sediments (Off-site Lab)	Soil/soil-like	Gamma spectroscopy to identify TENORM radionuclides (b)	USEPA 901.1 Modified	Quarterly x3
Flowback and produced waters Accumulated liquids from production equipment (Off-site Lab)	Aqueous (Grab)	Gross alpha and beta Gamma spectroscopy to identify TENORM radionuclides	USEPA 900.0 USEPA 901.1 Modified	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 (b)	USEPA 900.0 USEPA 901.1 Modified	Quarterly x3
Landfill Leachate	Aqueous (Grab)	Gross alpha and beta Tritium Gamma spectroscopy analysis	USEPA 900.0 EPA 906.0 USEPA 901.1 Modified	Once per landfill (54)
Gas sampling as necessary (Off-site Lab)	Gaseous (Grab)	Radon		As determined by PADEP

Notes for Table 7-2:

(a) Quality Control samples will be collected as follows:
Solid Samples – 5% (field replicate/split) QC samples collected to verify results of off-site laboratory per total samples in a calendar quarter.

Aqueous Samples - 5% (field replicate/split) QC samples collected to verify results of off-site laboratory per total samples in a calendar quarter.

(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 (Th-232, Th-230 and Th-228) isotopic radium (Ra-226 and Ra-228), for any unsupported decay chain radionuclides, and for radon (Rn-220 and Rn-222).

(c) The Commonwealth of Pennsylvania has not established effluent discharge standards for Ra-226. However, the U.S. Nuclear Regulatory Commission (NRC) has developed discharge standards for Ra-226 in Table II of Appendix B to 10 CFR Part 20, Standards for Protection Against Radiation. The discharge standard established by the NRC for Ra226 is 60 pico-Curies per liter (pCi/l). The effluent discharge limit is based on 50 mrem/year of exposure to a member of public drinking the discharged water. Therefore, this standard may be appropriate for comparison of monitoring data from Waste Water Treatment Facility effluent. Requested minimum detectable concentrations should be less than this value for Ra-226 analyses.

Ra-226 may be measured directly by detection of its 186.2 kilo-electron volt (keV) energy line for high activity waste-sludge samples. However, the presence of U-235 can cause interference with direct Ra-226 detection since it has a gamma line of similar energy (185.7 keV). The short-lived equilibrium daughters of radium may be used to determine Ra-226 concentrations in the soil when background levels of Ra-226 are encountered, for example 1 pCi/g. Unfortunately, once the soil is disturbed, these short-lived daughters must be allowed to grow back in. The parent of these daughters, radon-222 (Rn-222), has a moderate half-life of 3.8 days, therefore requiring at least two to three weeks of progeny in growth to reestablish equilibrium. Gamma spectroscopy will also identify other gamma emitting radionuclides that may be present in samples.

7.2 Laboratory Quality Control

Initial and daily calibrations of the off-site laboratory gamma spectroscopy system will be performed using a mixed-gamma National Institute of Standards and Technology (NIST)-traceable source. System QC will be ensured by tracking peak energy, peak resolution and net peak area for a high and low energy peak, based on daily source counts. These QC checks will be performed in accordance with applicable QC procedures.

Gamma spectroscopy system QC will be ensured by tracking peak energy, peak resolution and net peak area for a high and low energy peak, based on daily counts of a designated source.

Table 7-3. Sample Quantity, Preservation and Holding Time Requirements – Solid Samples

Parameter	Extraction/ Preparation Method(s)	Analysis Method	Sample Quantity/ Volume	Container Type	Preservative	Holding Time
RADIOLOGICAL PARAMETERS:						
Gross alpha/gross beta	NA	USEPA 900.0	100 g	Plastic	None	None
Ra-226 and Ra-228 by radon emanation or by gamma spec	NA	USEPA 903.1M USEPA 901.1 Modified (gamma spec)	4 oz 1 liter for gamma spec	Glass or Plastic	None	None
Thorium - Isotopic (228, 230, 232)	NA	ASTM D3972-90M or XRF	100 g	Plastic	None	None
Uranium - Isotopic (234, 235, 238)	NA	ASTM D3972-90M or XRF	100 g	Plastic	None	None
The majority of the above thorium and uranium isotopes can be inferred via gamma spectroscopy.	NA	USEPA Method 901.1 Modified	1 liter is requested for gamma spec.	Plastic	None	None

Notes for Table 7-3:

NA denotes not applicable

Table 7-4. Sample Quantity, Preservation and Holding Time Requirements – Aqueous and Gas Samples

Parameter	Extraction/ Preparation Method(s)	Analysis Method	Sample Quantity/ Volume	Container Type	Preservative	Holding Time
RADIOLOGICAL PARAMETERS:						
Gross alpha/gross beta	NA	USEPA 900.0	1 gallon	Plastic	None	6 months
Ra -226 (GFP - Total Radium Alpha)	NA		1 gallon	Glass or Plastic	None	6 months
Ra -228 (GFP)	NA	USEPA 904.0	1 gallon	Plastic	None	6 months
Ra-226 by Alpha-Scintillation (Rn-Emanation)	NA	USEPA 903.1	1 gallon	Glass or Plastic	None	6 months
Radon	NA	ASTM D5072 – 09, lucas cell	1 gallon	Plastic or metal canister	None	6 months
Thorium - Isotopic (232)	NA	ASTM D3972-90M or ICP-MS	1 gallon	Plastic	None	6 months
Uranium - Isotopic (234, 235, 238)	NA	ASTM D3972-90M or ICP-MS	1 gallon	Plastic	None	6 months

Notes for Table 7-4:

NA denotes not applicable

8.0 REFERENCES

Title 10 Code of Federal Regulations 20. 1995. U.S. Nuclear Regulatory Commission. "Standards for Protection Against Radiation."

ANSI/HPS N13.53-2009. August 31, 2009. American National Standards Institute. "Control and Release of Technologically Enhanced Naturally Occurring Radioactive Material (TENORM)."

Title 49 Code of Federal Regulations 173, Subpart I. 1996. US Department of Transportation. "Class 7 (Radioactive) Materials."