GWERD QUALITY ASSURANCE PROJECT PLAN

Title: Hydraulic Fracturing Retrospective Case Study, Bradford-Susquehanna Counties, PA

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TABLE OF CONTENTS

1.0 Project Management

1.1 Project/Task Organization

Described below are the roles and primary responsibilities of personnel associated with the Hydraulic Fracturing Retrospective Case Study located in the Marcellus Shale, Bradford-Susquehanna Counties, PA. An organizational chart for the project is presented in Figure 1.

Dr. Ralph Ludwig, U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Robert S. Kerr Environmental Research Center, Ada, OK. Dr. Ludwig is the principal investigator (PI) for this project and is responsible for preparing and maintaining the QAPP and ensuring completion of all aspects of this QAPP, including overall responsibility for QA. He will lead all aspects of the study, including collection, analysis, and interpretation of ground water and surface water samples. He is the Health and Safety Officer for ground water and surface water sampling activities carried out by NRMRL-Ada. His HAZWOPER certification is current.

Dr. Robert Puls, U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Robert S. Kerr Environmental Research Center, Ada, OK. Dr. Puls is the Technical Research Lead for case studies and is responsible for approval of this QAPP.

Mr. Steve Vandegrift, U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Robert S. Kerr Environmental Research Center (RSKERC), Ada, OK. Mr. Vandegrift is responsible for quality assurance review/approval of the Quality Assurance Project Plan (QAPP), conducting audits, and QA review/approval of the final report. His HAZWOPER certification is current.

Ms. Alexandra Kirkpatrick, Student Contractor, Ada, OK. Ms. Kirkpatrick is responsible for assisting in ground water and surface water sampling. Her HAZWOPER certification is current.

Dr. Carl Miller, U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Robert S. Kerr Environmental Research Center, Ada, OK. Dr. Miller is a co-PI for the study and will work with Dr. Ludwig in ensuring completion of all aspects of this QAPP including collection, analysis, and interpretation of ground water and surface water samples as well as geophysical characterization of the study area, as applicable. His HAZWOPER certification is current.

Dr. Randall Ross, U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Robert S. Kerr Environmental Research Center, Ada, OK. Dr. Ross is responsible for assisting Dr. Ludwig in understanding ground water flow directions. His HAZWOPER certification is current.

Dr. Doug Beak, U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Robert S. Kerr Environmental Research Center, Ada, OK. Dr. Beak is a co-PI for the study and will work with Dr. Ludwig in ensuring completion of all aspects of this QAPP including collection, analysis, and interpretation of ground water and surface water samples with particular emphasis on the geochemical characterization of samples. His HAZWOPER certification is current.

Mr. Steven Acree, U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Robert S. Kerr Environmental Research Center, Ada, OK. Mr. Acree is responsible for assisting Dr. Ludwig in understanding ground water flow directions. His HAZWOPER certifications are current.

Mr. Russell Neill, U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Rohert S. Kerr Environmental Research Center (RSKERC), Ada, OK. Mr. Neill is responsible for assisting in ground water and surface water sampling. His HAZWOPER certification is current.

Mr. Mark White, U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Rohert S. Kerr Environmental Research Center (RSKERC), Ada, OK. Mr. White is responsible for overseeing sample analysis in the General Parameters Laboratory (anions, nutrients, organic and inorganic carbon).

Ms. Cherri Adair, U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Robert S. Kerr Environmental Research Center (RSKERC), Ada, OK. Ms. Adair is responsible for assisting Dr. Ludwig with health and safety issues related to the study. Her HAZWOPER certification is current.

Dr. Sujith Kumar, Shaw Environmental, Ada, OK. Dr. Kumar is responsible for overseeing the analytical work performed under GWERD's on site analytical contract (stable isotopes, organic analysis, dissolved gases, and metals).

Ms. Shauna Bennett, Shaw Environmental, Ada, OK. Dr. Ms. Bennett is the QC Coordinator for Shaw Environmental and will coordinate QC for Shaw Environmental portion of this study.

Ms. Cynthia Caporale, USEPA Region 3 Analytical Laboratory, Laboratory Branch Chief/Technical Director. Ms. Caporale will act as a liason between the Region 3 Lab and RSKERC.

Dr. Jennifer Gundersen, U.S. Environmental Protection Agency – Region III, Ft. Meade, MD. Dr. Gundersen will analyze samples for glycols.

Dr. Mark Burkhardt, U.S. Environmental Protection Agency – Region VIII, Golden, CO. Dr. Burkhardt will be responsible for overseeing analysis of organic compounds in the Region VIII laboratory.

Mr. Ronald Furlan, Pennsylvania Department of Environmental Protection, Mr. Furlan is the point of contact for the state of Pennsylvania.

Mr. Dave Rectenwald, U.S. Environmental Protection Agency – Region III. Mr. Rectenwald is the point of contact for the Region 3 office.

Mr. Steve Pelphrey, Isotech Laboratories, Inc. Champaign, IL. Mr. Pelphrey is responsible for overseeing the laboratory analysis of ground water samples for carbon isotope ratio analysis.

Dr. Zell Peterman, U.S. Geological Survey, Denver, CO. Dr. Peterman is responsible for the analysis of strontium isotope ratios.

Mr. Gregory Oberley, U.S. Environmental Protection Agency – Region VIII. Mr. Oberley is the point of contact for the Region 8 office.

Mr. Justin Groves, U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Robert S. Kerr Environmental Research Center (RSKERC), Ada, OK. Mr. Groves is responsible for assisting in ground water and surface water sampling. His HAZWOPER certification is current.

Chris Ruybal, Student Contractor, Ada, OK. Mr. Ruybal is responsible for assisting in ground water and surface water sampling. His HAZWOPER certification is current.

Dr. Ludwig is responsible for initiating contact with appropriate project participants when necessary. Other project participants will keep the PI informed whenever significant developments or changes occur. Lines of communication among project participants may be conducted via in-person conversations, electronic mail, phone conversations, conference calls, and/or periodic meetings.

1.2 Problem Definition/Background

The retrospective case study in northeast Pennsylvania will investigate the potential impacts of hydraulic fracturing and processes related to hydraulic fracturing on drinking water resources in selected areas of Bradford and Susquehanna Counties, PA. The location of this case study was based on homeowner complaints regarding appearance, odors, and possible health impacts associated with water from domestic wells. Several phases of investigation for this case study are anticipated. The initial phase of the investigation will be a screening phase involving sampling of domestic wells, surface water bodies, etc. at locations where concerns have been

raised by local residents. Depending on the results of the initial screening, several different possibilities could arise. It is possible that no anomalous chemical signatures will be detected. If this were to occur, a follow-up sampling event would likely be conducted using identical methods to confirm the results. On the other hand, if anomalies are found, confirmation sampling would be planned, but also additional studies and methods might be adopted to track the source of the anomalies, whatever they might be. This iterative approach is being adopted to meet the primary objective of the study which is to determine if ground-water resources in Bradford-Susquehanna Counties, PA have been impacted by hydraulic fracturing processes and the related secondary objective which is to determine the likely pathway(s) of contaminant migration, if applicable.

In Phase I, selected domestic wells and surface water bodies will be sampled with subsequent analyses to determine the nature of water contamination, if it exists. The wells selected for sampling are based on a site scoping trip conducted in August 2011 that included interviews with local residents and homeowners. If evidence of ground water or surface water contamination is indicated in Phase I sampling, Phase II activities will be targeted to confirm the initial result and to identify the source or sources of contamination. If no contamination is detected in the first Phase I screening event, it is anticipated that a limited follow-up sampling would take place to confirm the result. Phase II activities will likely involve additional surface water and ground-water sampling, monitoring well sampling, and may involve installation of temporary or permanent wells for hydrogeologic and geochemical characterization, core collection and analysis, and geophysical surveys (self potential and/or resistivity). Phase I sampling is expected to begin in late October 2011. Version 0 of this QAPP describes quality assurance and quality control procedures associated with Phase I studies. Subsequent revision of the QAPP, if appropriate, will occur following evaluation of Phase I results or whenever revisions are necessary.

In August 2011, a visit to the study area by the PI (Dr. Ralph Ludwig), the Technical Research Lead (Dr. Bob Puls), and co-PI (Dr. Carl Miller) was conducted and potential sites for sampling were identified following discussions with homeowners. On August 16, 2011, a meeting was held with representatives from the Pennsylvania Department of Environmental Protection and EPA Region 3 to provide background on the overall HF Study Plan and specifics about the case study in Bradford-Susquehanna Counties. This study will be conducted in conjunction with the Pennsylvania Department of Environmental Protection; U.S. Environmental Protection Agency, Region III (EPA R3); and U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Ground Water and Ecosystems Restoration Division (GWERD). GWERD will be the lead organization for this case study.

Site Background - Bradford and Susquehanna Counties are located in the northeast corner of Pennsylvania. The study area is underlain by nearly flat-lying sedimentary bedrock and unconsolidated deposits of glacial and post-glacial origin. The bedrock consists primarily of shale, siltstone, and sandstone of Devonian to Pennsylvanian age. The glacial and post-glacial unconsolidated deposits consist of till, stratified drift, alluvium, and swamp deposits. Bradford

and Susquehanna Counties are currently experiencing oil and natural gas exploration targeting the Marcellus Shale located more than 4000 ft beneath the study area. The exploration and development uses horizontal drilling technology and hydraulic fracturing to stimulate gas production. Data provided by the Pennsylvania Department of Environmental Protection indicates the number of drilled wells in the Marcellus Shale has increased rapidly over the past 4 years. In 2007, 27 Marcellus Shale wells were drilled in the state; however, by 2010 the number of wells drilled had increased to 1386.

The Marcellus Shale, also referred to as the Marcellus Formation, is a Middle Devonian-age (about 390 million years), black, low density, organic-carbon rich shale that occurs in the subsurface beneath much of Ohio, West Virginia, Pennsylvania and New York. Smaller areas of Maryland, Kentucky, Tennessee, and Virginia are also underlain by the Marcellus Shale. The Marcellus is part of a transgressive sedimentary package, underlain by sandstones and siltstones (Onondago Formation), and overlain by carbonate rocks (Mahantango Formation). These sediments were deposited under a sea that covered the Appalachian Basin. It is believed that during the deposition of the Marcellus Shale very little oxygen was present at the bottom of the ocean. Thus, organic detritus was preserved in the deposited sediments. Subsequent burial of the carbon-rich sediments ultimately led to the formation of gas that became trapped in the rock. Natural gas occurs within the Marcellus Shale in three ways: 1) within the pore spaces of the shale; 2) within vertical fractures (joints) that break through the shale; and, 3) adsorbed on mineral grains and organic material. An assessment conducted by the U.S. Geological Survey (2003) suggested that the Marcellus Shale contained an estimated 1.9 trillion cubic feet of recoverable natural gas. Estimated volumes have increased significantly in more recent assessments of gas reserves (U.S. Geological Survey, 2006).

1.3 Project/Task Description

Data collection in Phase I will involve sampling water from domestic wells and surface water bodies. Sampling locations were selected during a reconnaissance trip to the area conducted in August 2011. Due to privacy concerns of the homeowners and residents, actual well locations are not provided in this QAPP. Additional sampling points may be included in the future and will be noted in any subsequent QAPP revisions. Figure 2 shows the map locations of proposed sampling points. Up to 38 domestic wells and three surface water locations are targeted for sampling. Water analysis will be conducted for a range of organic and inorganic constituents, including Gasoline Range Organics (GRO), Diesel Range Organics (DRO), volatile organic compounds (VOCs), semi-volatile organic compounds (SVOCs), glycols, alcohols, carboxylic acids, dissolved gases (methane, ethane, propane, n-butane), and major and trace cations and anions, dissolved organic and inorganic carbon, stable isotope compositions of C and H in methane (if detected), O and H isotope compositions of water, stable C isotope composition of dissolved inorganic carbon, and strontium isotope ratios. Included in this set of measurements are a selection of components of hydraulic fracturing fluids (e.g., potassium, barium, glycols, alcohols, naphthalene, and boron), potentially mobilized naturally occurring substances such as

arsenic, manganese, and other trace metals, and general water quality parameters (e.g., pH, TDS, major anions and cations). Some of the chemicals used by hydraulic fracturing companies in Pennsylvania are listed in Table 1. Of the target analytes noted above, those that are critical analytes supporting the primary objective of the project (i.e., to determine if ground-water resources in the selected areas of Bradford-Susquehanna Counties have been impacted by hydraulic fracturing processes) are defined in Table 2. A tiered approach will be applied to the use of glycol data. Initially, the data will be considered as "screening" data as the method is under development and is not yet validated. Once the method is validated, the glycol data will no longer be considered as "screening" data. A tiered approach will also be applied to the VOC and SVOC data. See footnote to Table 2.

Methods for sampling ground water and surface water are described in Section 2.2. Water analyses will be conducted at the R.S. Kerr Environmental Research Center (Ada, OK), U.S. EPA Regional laboratories located in Fort Meade (MD) and Golden (CO), USGS laboratories located in Denver (CO), and Isotech Laboratories located in Champaign (IL). Analytical methods are discussed in Section 2.4.

It is anticipated that data collected from this case study will be incorporated into the larger Hydraulic Fracturing report to be submitted to the U.S. Congress. It is also expected that these data will be utilized in EPA reports, conference proceedings and journal articles. In addition, data collected in this case study may be used in policy and regulation efforts by EPA and state regulatory agencies.

A proposed schedule for field activities is provided in Table 3. This table will be updated in subsequent revisions of the QAPP should they be necessary.

1.4 Project Quality Objectives and Criteria

The primary quality objectives of this case study relate to analytical measurements including precision, accuracy, and sensitivity. These topics and associated quality objectives are discussed in sections 2, 3, and 4.

1.5 Special Training/Certification

A current HAZWOPER certification is required for on-site work. HAZWOPER training and yearly refresher training is provided to GWERD personnel at an appropriate training facility chosen by GWERD SHEMP (Safety, Health, and Environmental Management Program) manager. The HAZWOPER training records and documentation are kept by the GWERD SHEMP manager. A HAZWOPER certificate and wallet card is provided to each person completing the training.

The laboratories performing critical analyses in support of this case study must demonstrate their competency prior to performing such analyses. Competency may be demonstrated through documentation of certification/accreditation or some other means as determined to be acceptable by project participants. The EPA GP laboratory and the on-site contractor laboratories (operated by Shaw) at RSKERC will be used to analyze select critical analytes listed in Table 2. These laboratories have demonstrated competency through the implementation of ORD PPM 13.4, *Quality Assurance/Quality Control Practices for ORD Laboratories Conducting Research*, which includes external independent assessments. These laboratories are also routinely subjected to internal assessments and performance evaluation (PE) samples. The Region VIII Laboratory will be used to analyze those critical analytes listed in Table 2. This laboratory has been subjected to the National Environmental Laboratory Accreditation Program (NELAP) accreditation process through the state of Texas and is expected to soon be granted approval. The USEPA Region 3 Laboratory will be used to analyze glycols, which is not identified as critical at this time. However, the lab is accredited under the National Environmental Laboratory Accreditation Program (NELAP) through the state of New Jersey. The particular method being used by Region 3 for glycols is not accredited, but the analyst follows all the requirements for an accredited method. Initial data reported from the glycol analysis will be flagged as "screening" data from a method that is currently being developed. Once the data are validated, they will no longer be flagged as "screening" data. Isotech Laboratories and USGS laboratories will not provide data for critical analytes.

1.6 Documents and Records

Data reports will be provided electronically on Excel spreadsheets. Shaw's raw data is kept on-site at the GWERD and will be provided on CD/DVD to Ralph Ludwig. Raw data for sub-contracted and regional laboratories shall be included with the data reports. Calibration and QC data and results shall be included. Field notebooks will be kept as well as customized data entry forms if needed. All information needed to confirm final reported data will be included.

Records and documents expected to be produced include: field data, chain-of-custody (COC), QA audit reports for field and laboratory activities, data reports, raw data, calibration data, QC data, interim reports, and a final report.

All field and laboratory documentation shall provide enough detail to allow for reconstruction of events. Documentation practices shall adhere to ORD PPM 13.2, "*Paper Laboratory Records*." Because this is a QA Category 1 project, all project records require permanent retention per Agency Records Schedule 501, *Applied and Directed Scientific Research.* Records shall be stored in Ralph Ludwig's office at the GWERD until they are transferred to GWERD's Records Storage Room. At some point in the future, records will be transferred to a National Archive facility.

2.0 Data Generation and Acquisition

2.1 Sampling Process Design (Experimental Design)

2.1.1 Background on Geology, Hydrology, and Geochemistry

Background information on the geology and hydrology of the study area has been summarized by Williams et al. (1998). The most important sources of groundwater in the study area are stratified drift aquifers. These can occur as unconfined or confined aquifers with lacustrine deposits serving as confining layers. The unconfined aquifers are sand and gravel primarily of outwash origin while the confined aquifers are sands and gravel of ice-contact origin buried beneath the lacustrine deposits. The lacustrine confining units locally exceed 100 ft in thickness. Bedrock and till are the basal confining units of the stratified-drift aquifer systems. Bedrock is of the Devonian, Mississipian, and Pennsylvania age. Devonian bedrock includes from oldest to youngest Loch Haven, Catskill, and Chadakoin Formations with the study area being underlain primarily by the Loch Haven and Catskill Formations. Specific capacity data indicate wells completed in stratified-drift aquifers have specific capacities generally an order of magnitude greater than those completed in the till or bedrock. The median specific capacity in unconfined stratified-drift aquifers is 24 gallons per minute per foot of drawdown and 11 gallons per minute per foot of drawdown in confined stratified aquifers.

Groundwater in the study area is of the calcium bicarbonate type where unrestricted flow occurs (e.g. unconfined and confined stratified drift, shallow bedrock, and till) and of the sodium chloride type in zones of restricted flow (e.g. deeper bedrock, some areas of overlying till and confined stratified drift). Wells completed into zones with more restricted flow contain higher total dissolved solids, dissolved barium, and dissolved chloride with median concentrations of 830 mg/L, 2.0 mg/L, and 349 mg/L, respectively. Iron and manganese concentrations from wells in the study area frequently exceed secondary MCLs (0.3 mg/L and 0.05 mg/L, respectively). Only wells completed in the unconfined stratified drift and the Catskill formation bave median iron and manganese concentrations lower than the USEPA secondary MCLs.

2.1.2 Ground-Water and Surface Water Monitoring

The ground-water and surface water sampling component of this project is intended to provide a survey of water quality in the area of investigation. GWERD will survey any existing data and speak to landowners to determine suitable ground water wells in the area for the study. Sampling locations were selected by interviewing individuals about their water quality and timing of water quality changes in relation to gas production activities. The locations of the domestic wells and surface water bodies to be sampled are shown in Figure 2. The domestic

wells will be sampled from homeowner taps or using a down-hole pump (Proactive Monsoon or equivalent) to retrieve water samples. In some cases, both methods of sampling may be used for a single well to allow for comparison of selected parameter data. The timing of the ground-water sampling events is anticipated to start in the fall of 2011 and continue to the fall/winter of 2012. The minimum number of sampling events to determine if an impact is present is estimated to be four sampling events. Updates to sampling plans and events will be communicated in subsequent revisions to the QAPP. All information regarding domestic well construction collected in future parts of the ongoing site history investigation will be reported in revisions to the QAPP.

2.2 Sampling Methods

2.2.1 Water Sampling

Domestic wells will be sampled using existing dedicated (home owner) pumps already present in the wells with sample collection occurring from the nearest tap to the well and/or by lowering a submersible pump (Proactive Monsoon or equivalent) down the well. Whenever possible, drawdown of the water table will be tracked by taking water level measurements every 10 to 15 minutes during well purging. The water level measurements will follow the RSKSOP-326 standard operating procedure. Water levels will be recorded in a field notebook during purging prior to sampling.

2.2.1.1 Domestic wells

The following is the preferred methodology that will he used for the domestic wells.

1) At each sampling site, GPS coordinates will be collected with a handheld device. Photos will be taken and stamped with the date. Pertinent information about each well will be recorded where possihle (e.g., well diameter, configuration, etc.). If possible, the ground-water level will be measured using a Solinst water level indicator (or equivalent) and recorded. In many cases, well construction details will not be available and water level measurements will not be possible. The existing homeowner well pump, where possible, will be used to purge the well. The rate of pumping will be determined by measuring the water volume collected after a unit of time into a large graduated cylinder or equivalent container. In some cases (e.g. where the domestic well has been out of use and has no functional pump), purging will be conducted using a separate submersible pump (Proactive Monsoon or equivalent) introduced into the well. In cases where the screen volume can be calculated, three screen volumes will be targeted as the purge volume. In cases where the length of screen is not known or is too large (thus making purging of three screen volumes impractical), professional judgment will be used and the well will be purged until stabilization of geochemical parameters occurs. Stabilization of geochemical parameters will be assessed by reducing the flow rate to <2 L/min following

initial purging and subsequently connecting the tubing to the flow cell and YSI 5600 multiparameter probe (or equivalent probes). Following completion of well purging, groundwater samples will be collected either from a homeowner tap located upstream of any home water treatment systems or directly from the well using a separate submersible pump (Proactive Monsoon or equivalent). The pump will be thoroughly rinsed with distilled water between sampling wells and dedicated tubing will be used for each well.

2) The YSI probe (or equivalent probes) will be used to track the stabilization of pH, oxidation-reduction potential (ORP), specific conductance (SC), dissolved oxygen (DO), and temperature. In general, the criteria that will be used to determine when parameters have stabilized are listed in Table 4. These criteria are initial guidelines; professional judgment in the field will be used to determine on a well-by-well basis when stabilization occurs. The time-dependent changes in geochemical parameters recorded by the YSI probe will be logged by the handheld instrument and recorded on log sheets or in field notebooks.

3) Once stabilization occurs, the final values for pH, ORP, specific conductance, dissolved oxygen, and temperature will be recorded.

4) After the values for pH, ORP, SC, DO, and temperature have been recorded, the flow cell will be disconnected. A series of unfiltered samples will be collected in the sequence as follows:

   a. Duplicate 40 mL VOA vials (amber glass) will be collected, without headspace, for VOC analysis using RSKSOP-299v1 or RSKSOP-259v1. Trisodium Sodium Phosphate (TSP) will be added to the VOA vial prior to shipping to the field as a preservative. Acid will not be used as a preservative due to a concern of acid hydrolysis of some analytes. The samples will be stored and shipped on ice to Shaw, NRMRL-Ada's on-site contractor for GC-MS analysis.

   b. Duplicate 60 mL serum bottles will be collected, without headspace, for dissolved gas analysis (e.g., hydrogen, carbon dioxide, ethane, methane, n-butane, propane). The bottles will be filled while being held inverted and submerged in a 5 gallon bucket. The filled bottles will be pulled from the bucket: 2 drops of sulfuric acid will added as a preservative and the bottle will be immediately sealed with a crimp cap. The samples will be stored and shipped on ice to Shaw, NRMRL-Ada's on-site contractor for analysis.

   c. Duplicate 40 mL VOA vials (amber glass) will be collected for organic acid analysis using RSKSOP-112v6. Trisodium Sodium Phosphate (TSP) will be added to the VOA vial prior to shipping to the field as a preservative. The samples will be stored and shipped on ice to Shaw, NRMRL-Ada's on-site contractor for HPLC analysis.

d. Duplicate 1 L amber glass bottles will be collected for semi-volatile organic compounds (Region VIII SOP No. ORGM-515). These samples will be stored and shipped on ice to EPA Region VIII Laboratory for analysis.

e. Duplicate 1L amber glass bottles will be collected for diesel range organic (DRO) analysis. These samples will be preserved with HCl, pH <2, and shipped on ice to EPA Region VIII Laboratory for analysis.

f. Duplicate 40 mL amber VOA vials will be collected without headspace for gasoline range organic analysis (GRO). These samples will be preserved with HCl, pH <2, and shipped on ice to EPA Region VIII Laboratory for analysis.

g. Duplicate 40 mL amber VOA vials will be collected for glycol analysis. These samples will be stored and shipped on ice to EPA Region III Laboratory for analysis.

h. A 1L plastic bottle containing a caplet of benzalkonium chloride for preservation will be collected for carbon and hydrogen isotope analyses of dissolved methane. This sample will be shipped, with bottle inverted, on ice to Isotech Laboratories.

i. A 125 mL plastic bottle will be filled for total metals analysis. Analysis of these samples will be by ICP-OES for Al, Ag, As, B, Be, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Sr, Ti, Tl, V, Zn, Si, and S and by ICP-MS for Cd, Cr, As, Cu, Pb, Ni, Se, Hg, U, and Tl. These samples will be preserved by adding concentrated HNO_3 to pH<2 (pH test strips will be used as spot checks on samples to confirm that the sample pH is <2). The samples will be stored and shipped on ice to Shaw, NRMRL-Ada's on-site contractor for analysis.

j. A 1-liter plastic beaker will be filled for selected analyses to be conducted in the field. Field measurements will consist of turbidity, alkalinity, ferrous iron, and dissolved sulfide. Turbidity (Standard Method 180.1) will be measured using a HACH 2100Q portable turbidimeter (or equivalent instrument). Alkalinity will be measured by titrating ground water with 1.6N H_2SO_4 to the bromcresol green-methyl red endpoint using a HACH titrator (HACH method 8203, equivalent to Standard Method 2320B for alkalinity). Ferrous iron will be measured using the 1,10-phenanthroline colorimetric method (HACH DR890 spectrometer, HACH method 8146, equivalent to Standard Method 3500-Fe B for wastewater). Dissolved sulfide will be measured using the methylene blue colorimetric method (HACH DR890 spectrometer; HACH method 8131, equivalent to Standard Method 4500-S^{2-} D for wastewater).

k. A 1 L amber plastic bottle will be filled with no preservative added. This sample is an archive sample and will be shipped back to GWERD and stored in a freezer. The archive sample may be used by other parts of the HF study team to support the larger hydraulic fracturing investigation. As an example, analytical methods are being

developed by the National Exposure Research Laboratory (NERL). These archived samples could be useful as test samples as those method development studies proceed. Use of these samples would be elaborated in future QAPP revisions.

5) Next a high capacity ground water filter (0.45-micron) will be attached to the end of the tubing and a series of filtered samples will be collected. Prior to filling sample bottles, at least 100 mL of ground water will be passed through the filter to waste. A series of unfiltered samples will be collected in the sequence as follows:

   a. A 60 mL clear plastic bottle will be filled for analysis of $\delta^{13}C$ of dissolved inorganic carbon. This sample will be shipped on ice to Isotech Laboratories.

   b. A 125 mL plastic bottle will be filled for dissolved metals analysis. Analysis of these samples will be by ICP-OES for Al, Ag, As, B, Be, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Sr, Ti, Tl, V, Zn, Si, and S and by ICP-MS for Cd, Cr, As, Cu, Pb, Ni, Se, Hg, U, and Tl. These samples will be preserved by adding concentrated HNO_3 to pH<2 (pH test strips will be used as spot checks on samples to confirm that the sample pH is <2). The samples will be stored and shipped on ice to Shaw, NRMRL-Ada's on-site contractor for analysis.

   c. One 30 mL clear plastic bottle for CE (capillary electrophoresis) sulfate, chloride, bromide and fluoride. No preservative will be added. The samples will be stored and shipped on ice to the RSKERC general parameters lab.

   d. One 30 mL clear plastic bottle for nitrate + nitrite and ammonium (Flow Injection Analysis). This sample will be preserved with sulfuric acid to pH<2 (pH test strips will be used as spot checks on samples to confirm that the sample pH is <2). The samples will be stored and shipped on ice to the RSKERC general parameters lab.

   e. Duplicate 40 mL glass VOA vials will be collected for analysis of dissolved inorganic carbon (DIC). No preservative added will be added to these samples. The samples will be stored and shipped on ice to the RSKERC general parameters lab.

   f. Duplicate 40 mL glass VOA vials will be collected for analysis of dissolved organic carbon (DOC). These samples will be preserved with phosphoric acid to pH<2. The samples will be stored and shipped on ice to the RSKERC general parameters lab.

   g. A 20 mL glass VOA will be collected for analysis of $\delta^{18}O$ and $\delta^{2}H$ of water using isotope ratio mass spectroscopy (IRMS). The sample will be stored and shipped on ice to Shaw, NRMRL-Ada's on-site contractor for analysis.

h. A 500 mL clear plastic bottle will be filled for Sr isotope analysis using thermal ionization mass spectroscopy (no acid preservation). The sample will be stored and shipped on ice to the USGS laboratory in Denver, CO.

See Tables 4 and 5 for numbers of sample bottles needed for each sample type and field QC samples for ground and surface water sampling.

2.2.1.2 Surface Water (Spring) Samples

Figure 2 includes locations of springs that may be sampled. Sample sets collected from the springs would be identical to the sample sets collected from the domestic wells as per Section 2.2.1.1. Although springs have been identified for possible sampling, it may not be possible to collect water from springs during a given sampling event due to seasonal flow issues. Samples will be collected from springs by submerging sample bottles just below the water surface (grab samples) or by extracting water from beneath the surface with dedicated tubing attached to a peristaltic pump (or equivalent). Sampling from springs will be performed as to minimize any capture of sediment. Water samples for dissolved metals, all isotope analyses (except dissolved methane), anions, nutrients, and inorganic/organic carbon will be filtered using a peristaltic pump and a high-capacity (0.45 micron) capsule filter. Dedicated tubing will be used for all sampling and filtration. The readings from the YSI will be recorded by inserting the probe set with protective cover directly into the surface water body and allowing readings to stabilize or by directing surface water through the peristaltic pump and the YSI flow cell until reading stabilization has occurred. Again the logging function will be utilized and readings will be recorded in a field notebook.

2.3 Sample Handling and Custody

2.3.1 Water Sample Labeling

Each well will be uniquely labeled. Samples collected from each well will include the unique label, the date, the initials of the sampler, and designation of the sample type, e.g., "metals" and preservation technique (when applicable). This information will be recorded onto labeling tape, using water-insoluble ink, affixed to each sample bottle. Samples will be labeled as follows. Ground water samples will be labeled NEPAGWxx-mmyy. The xx will move in sequence (i.e., 01, 02, etc.). The mmyy will record the month and year (i.e., 0711 for July 2011). If the same points are sampled in subsequent trips, the number designation will remain the same (linked to the site), but the date and month will change accordingly. Duplicate samples will be marked by a lower case d (e.g., NEPAGW05d-0711). Labeling of surface water samples will follow the same approach, except instead of GW, SW will be used in the identification (i.e., NEPASW01-0711).

2.3.2 Water Sample Packing, Shipping, and Receipt at Laboratories

Samples collected from each location will be placed together into sealed Ziploc plastic bags. The bags will be placed on ice and into coolers. Glass bottles will be packed with bubble wrap to prevent breakage. The coolers will be sent via Fedex or UPS, overnight, to the appropriate lab with chain of custody forms (see Figure 3) and custody seals.

R.S. Kerr Environmental Research Center
919 Kerr Research Drive
Ada, OK 74820
1-580-436-8920
ATTN: Kacie Bennett
(for samples analyzed by both Shaw and EPA General Parameters Laboratory)

Upon receipt at RSKERC, all samples shall be logged in and distributed to appropriate analysts by Shaw using RSKSOP-216v2, *Sample Receipt and Log-in Procedures for the On-site Analytical Contractor.* Before opening the ice chests the custody seal is checked by the sample custodian to verify it is intact. Ice chests are opened and the temperature blank is located to take the temperature and it is noted whether or not ice is still present. Chain-of-custody (COC) forms and samples are removed. Samples are checked against the COC. The observations concerning temperature, custody seal, if ice was not present, and any sample discrepancies are noted on the COC and the sample custodian signs the form. A copy of the COC is distributed to the PI and Shaw retains a copy. The PI should be notified immediately if samples arrive with no ice and/or the temperature records from the temperature blank is greater than 12^0 C.

Sample receipt and log-in at the Region 8 laboratory shall be conducted as described in their SOP, *Sample Receipt and Control Procedure*, #GENLP-808 Rev. 1.0 and the Region 8 Quality Manual, #QSP-001 Rev. 1.0.

EPA Region 8 Lab
16194 West 45^{th} Drive
Golden, CO 80403
1-303-312-7767
ATTN: Jesse Kiernan

Sample receipt and log-in at the Region 3 laboratory shall be conducted as described in their SOP, *Sample Scheduling, Receipt, Log-in, Chain of Custody, and Disposal Procedures, R3-QA061.*

EPA Region 3 Lab
701 Maples Road
Ft. Meade, MD 20755-5350
1-410-305-3032

ATTN: Kevin Martin

Samples for isotope analysis of dissolved inorganic carbon and methane will be sent to:

Isotech Laboratories, Inc.
1308 Parkland Court
Champaign, IL 61821
1-817-362-4190
ATTN: Sher Dixon

Upon receipt, Isotech signs the chain-of-custody form, inventories and logs-in samples, and assigns each a unique number. Signed chain-of-custody forms will be returned to Ralph Ludwig.

Samples for Sr isotope analysis will be sent to:

Zell Peterman
U.S. Geological Survey
6th and Kipling Sts.
MS 963 Box 25046 DFC
Denver, CO 80225
1-303-236-7883

When the samples are received, the samples are inventoried and checked against the chain-of-custody forms. The date of receipt is indicated on the forms and returned to Ralph Ludwig. The samples are assigned a laboratory number and a cross list is prepared that correlates the assigned number with the field number. The samples are then transferred to their secured chemical laboratory for analysis.

2.4 Analytical Methods

2.4.1 Ground and Surface Water

Water samples will be collected and analyzed using RSKERC standard operating procedures (RSKSOPs) at RSKERC and EPA Methods at the Region VIII laboratory (Table 4). Region III's LC-MS-MS method for glycols is under development with the intent to eventually have a validated, documented method.

Analysis at RSKERC includes inductively coupled plasma – optical emission spectroscopy (ICP-OES; for cations), inductively coupled plasma – mass spectroscopy (ICP-MS; for trace metals), capillary electrophoresis (CE, for anions), flow injection analysis (FIA, for N-series), carbon analysis using combustion and infrared detection, gas chromatography (GC, for dissolved gas analysis), isotope ratio mass spectrometry (for $\delta^{18}O$ and $\delta^{2}H$ of water), gas chromatography-mass

spectroscopy (GC-MS) for VOCs, and HPLC analysis for carboxylic acids. Analysis by the EPA Region VIII laboratory includes GC for GRO, DRO, and GC-MS for semivolatiles with appropriate sample preparation and introduction techniques. These analytical methods to be used for water samples are presented in Table 4.

Samples will be submitted to Isotech Lahoratories for analysis of stable isotope ratios of dissolved inorganic carbon ($\delta^{13}C$) by gas stripping and isotope ratio mass spectrometry (IRMS) and $\delta^{13}C$ of methane (C1), as well as $\delta^{2}H$ of methane. Isotech Laboratories will follow their own in-house Standard Operating Procedures, including: Isotech, SOP112v2, $^{13}C/^{12}C$ Determination of DIC, 05/26/2011; Isotech, SOP100v0, Offline Hydrocarbon Gas Preparation System, Gamma Bench, 12/27/2010; Isotech SOP101v0, Offline Gas Preparation System, Alpha Bench, 10/21/2003; Isotech SOP103v0, Delta Plus Mass Spectrometer, Dual Inlet Analysis of δD, 2/22/2010; and, Isotech SOP104, Delta S Mass Spectrometer, Dual Inlet Analysis of $\delta^{13}C$, (in preparation). A Statement of Work will be provided to Isotech with relevant information presented here:

> Samples of ground water and surface water will be provided from multiple sites in Bradford-Susquehanna Counties, PA. Isotech will not be required to determine the concentration of inorganic carbon or dissolved gases in the samples. The isotope analyses are intended to provide information about the carbon cycle in the systems. The measurements will be for $\delta^{13}C$ of dissolved inorganic carbon, the $\delta^{13}C$ value of methane and $\delta^{2}H$ of hydrogen in methane.
>
> Samples will be provided from domestic wells or ground-water monitoring wells located in Bradford-Susquehanna Counties, PA. Isotech will be notified two weeks in advance of the sample collection activities. Duplicate samples will be collected in 10% of the wells, or as otherwise indicated in approved QAPPs (Quality Assurance Project Plans). The total number of samples submitted for $\delta^{13}C$ of dissolved inorganic carbon and for dissolved gas analysis will be approximately 40 for each sampling event. In addition to field duplicates, Isotech shall select samples for a laboratory duplicate analysis for both DIC and dissolved gases in each submitted set to fulfill attached QA/QC requirements (Tahle 11 and 12). These samples need to be from our submitted sample sets and not from another site or sample queue.
>
> The inorganic carbon samples will be collected into 60 mL plastic bottles (filtered, unpreserved); the dissolved gas samples will be sampled into 1 L plastic bottles provided by Isotech Laboratories. The bottles will be filled with ground water and those for dissolved gas analysis will be preserved with a caplet of benzalkonium chloride. It is expected that the concentration of DIC and dissolved gases will be high enough in the samples so that these volumes will be adequate for the analyses. Isotech will identify those samples in which concentrations are not high enough for these measurements. For the dissolved gas samples, the bottles will be transported so that the aqueous solution will

be on top of the bottle closure, i.e., the bottles will be transported upside down. All samples will be transported on ice.

Isotech Laboratories will submit a final report at completion of analysis which includes: tabulation of final results, list of SOPs used (title and SOP #), and full data packages. Full data packages (can be provided at a later date, within 30 days of issuing final results) shall be provided on CD for all sample analyses to allow for reconstruction of analysis: Chain-of-custody forms, calibration data, QA/QC data, raw data, data reduction, data qualifiers, deviations from method requirements, deviations from QC acceptance criteria, and these deviations' impact to reported results. The full data packages shall be sent to Ralph Ludwig (ludwig.ralph@epa.gov) and copied to the GWERD QA Manager, Steve Vandegrift. Results are expected within five weeks of the receipt of the samples.

Region III's LC-MS-MS method for glycols is under development with the intent to eventually have a validated, documented method. Aqueous samples are injected directly on the HPLC after tuning MS/MS with authentic standards (2-butoxyethanol, di-, tri-, and tetraethylene glycols) and development of the HPLC gradient. The HPLC column is a Waters (Milford MA) Atlantis dC18 3um, 2.1 x 150mm column (p/n 186001299). HPLC gradient is with H_2O and CH_3CN with 0.1% formic acid. The 3 glycols are run on a separate gradient than the 2-hutoxyethanol. All details of instrument conditions will be included in the case file. EPA SW-846 Method 8000B and C are used for basic chromatographic procedures. A suitable surrogate has not been identified. Since there is no extraction or concentration step in sample preparation, extraction efficiency calculations using a surrogate are not applicable. If a suitable surrogate is found, it will be used to evaluate matrix effects. Custom standard mix from Ultra Scientific, (Kingstown RI) is used for the instrument calibration . The working, linear range varies for each compound, but is about 10-100 µg/L and may change with further development. Initial calibration (IC) is performed before each day's sample set; calibration verification is done at the beginning, after every 10 sample injections, and at the end of a sample set. The system is tuned with individual authentic standards (at 1 mg/L concentration) of each compound according to the manufacturer's directions using the Waters Empower "Intellistart" tune/method development program in the MRM (multiple reaction monitoring) ESI+ (electrospray positive) mode. Tune data is included in the case file. Target masses, transition data and voltages determined in each tune for each compound are compiled into one instrument method. Only one MS tune file (which determines gas flow rates and source temperatures) may be used during a sample set. For these samples, the tetraethylene glycol tune is used as it provides adequate response for all targets. Due to differences in optimal chromatographic separation, the three glycols are analyzed in one run and 2-butoxyethanol is analyzed separately. The mobile phases for both analyses are comprised of DI water, acetonitrile and formic acid. Exact mass calibration of the instrument is done annually with the preventive maintenance procedure. Custom mix, supplied by Accustandard (New Haven, CT), is used as a second source verification (SSV). The SSV is run after IC. Matrix spikes and matrix spike duplicates are also performed.

Strontium isotope ratios will be determined at the USGS laboratory using thermal ionization mass spectrometry (TIMS). A description of the method is provided in Appendix A (Isotope Support for the EPA Hydraulic Fracturing Study by the U.S. Geological Survey (USGS) Denver, CO).

The RSKSOPs and their associated target analyte list are presented in Table 6. For these analyses, the only surrogates used are for the VOC analysis. Surrogate compounds used are p-bromofluorobenzene and 1,2-dichlorobenzene-d4, spiked at 100 ug/L.

For the semi-volatiles, the target analyte list is presented in Table 7. Surrogates used include phenol-d6, 2-fluorophenol, 2,4,6-tribromophenol, nitrobenzened5, 2-fluorobiphenyl, and p-terphenyl-d14. The concentrations used for the surrogates shall be spiked at 5 µg/mL. For samples containing components not associated with the calibration standards, non-target peaks will be reported as tentatively identified compounds (TICs) based on a library search. Only after visual comparison of sample spectra with the nearest library search results will tentative identifications be made. Guidelines for making tentative identification are:

- A peak must have an area at least 10% as large as the area of the nearest internal standard.
- Major ions in the reference spectrum (ions >10% of the most abundant ion) should be present in the sample spectrum.
- The relative intensities of the major ions should agree within ±20%. (Example: For an ion with an abundance of 50% in the reference spectrum, the corresponding sample ion abundance must be between 30 and 70%.)
- Molecular ions present in the reference spectrum should be present in the sample spectrum.
- Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of co-eluting compounds. Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

Commercial standards for DRO calibration is locally procured DF #2 (source: Texaco station). Surrogates used in DRO include o-terphenyl at a spiking concentration of 10 µg/L.

Commercial standards for GRO calibration are BTEX, MTBE, naphthalene, and gasoline range hydrocarbons (purchased as certified solutions) and unleaded gasoline from Supelco (product number 47516-U). Surrogates used in GRO include 4-bromofluorobenzene at spiking concentrations of 50 µg/L.

2.5 Quality Control

2.5.1 Quality Metrics for Aqueous Analysis

For analyses done at RSKERC, QA/QC practices (e.g., blanks, calibration checks, duplicates, second source standards, matrix spikes, and surrogates) are described in various in-house Standard Operating Procedures (RSKSOPs) and summarized in Table 8. Matrix spikes sample spiking levels are determined at the discretion of the individual analysts (based on sample concentrations) and are included with the sample results. Corrective actions are outlined in the appropriate SOPs and when corrective actions occur in laboratory analysis it will be documented and the PI will be notified as to the nature of the corrective action and the steps taken to correct the problem. The PI will review this information and judge if the corrective action was appropriate.

For analyses done by the Region VIII laboratory, QA/QC requirements are (Table 9):

(1) Samples shall be processed and analyzed within the following holding times (from date sampled):

Semivolatiles: 7 days until extraction, 30 days after extraction

DRO: 14 days until extraction*, 40 days after extraction

GRO: 14 days*

*With acid preservation

(2) Data verification shall be performed by the Region VIII laboratory to ensure data meets their SOP requirements.

(3) Complete data package shall be provided electronically on disk, including copies of chain-of-custody forms, copy of method or Standard Operating Procedure used, calibration data, raw data (including notebook pages), QC data, data qualifiers, quantitation (reporting) and detection limits, deviations from method, and interpretation of impact on data from deviations from QC or method requirements. (All documentation needed to be able to re-construct analysis.)

(4) Detection limits (DL) and quantitation (reporting) limits (RL) for the semi-volatiles are as provided in Table 7. The DL and RL for DRO and GRO are both at 20 µg/L.

(5) The laboratory shall be subject to an on-site QA audit and analysis of Performance Evaluation samples. If the laboratory is currently analyzing Performance Evaluation (Proficiency Testing) samples, a request will be made for these data. If they are not actively involved in analyzing these samples, then they shall be provided by RSKERC.

(6) See Table 9 for QC types and performance criteria.

Corrective Actions: If any samples are affected by failure of a QC sample to meet its performance criteria, the problem shall be corrected and samples will be re-analyzed. If re-analysis is not possible (such as lack of sample volume), the PI shall be notified. The data will be qualified with a determination as to impact on the sample data. Failures and resulting corrective actions shall be reported.

For analyses done by the Region III laboratory, QA/QC requirements are (see Tables 10 and 11):

(1) Samples shall be analyzed within the holding time of 14 days.

(2) Data verification shall be performed by the Region III laboratory to ensure data meets the method requirements.

(3) Complete data package shall be provided electronically on disk , including copies of chain-of-custody forms, copy of method or Standard Operating Procedure used, calibration data, raw data (including notebook pages), QC data, data qualifiers, quantitation (reporting) and detection limits, deviations from method, and interpretation of impact on data from deviations from QC or method requirements. (All documentation needed to be able to re-construct analysis.)

(4) Detection and reporting limits are still to being determined, but most will be between 10 and 50 ug/L (Table 10).

(5) The laboratory shall be subject to an on-site QA audit if the glycol data becomes "critical" at a later data after method validation.

(6) Until the method is validated, the data will be considered "screening" data.

Corrective Actions: If any samples are affected by failure of a QC sample to meet its performance criteria, the problem shall be corrected and samples will be re-analyzed. If re-analysis is not possible (such as lack of sample volume), the PI shall be notified. The data will be qualified with a determination as to impact on the sample data. Failures and resulting corrective actions shall be reported.

For analyses done by Isotech Laboratories, QA/QC requirements are (Table 12 and Table 13):

(1) Data verification shall be performed by Isotech Laboratories to ensure data meets their SOP requirements.

(2) Complete data packages shall be provided electronically including tabulation of final results, copies of chain-of-custody forms, list of SOPs used (title and SOP #), calibration data, QA/QC data, data qualifiers, deviations from method, and interpretation of impact on data from deviations from QC or method requirements.

(3) See Tables 12 and 13 for QC types and performance criteria

Corrective Actions: If any samples are affected by failure of a QC sample to meet its performance criteria, the problem shall be corrected and samples will be re-analyzed. If re-analysis is not possible (such as lack of sample volume), the PI shall be notified. The data will be qualified with a determination as to impact on the sample data. Failures and resulting corrective actions shall be reported.

For analyses done by USGS, QA/QC requirements are (Table 14):

(1) Data verification shall be performed by USGS to ensure data meets their SOP requirements.

(2) Complete data packages shall be provided electronically including tabulation of final results, copies of chain-of-custody forms, list of SOPs used (title and SOP #), calibration data, QA/QC data, data qualifiers, deviations from method, and interpretation of impact on data from deviations from QC or method requirements.

(3) See Table 14 for QC types and performance criteria

Corrective Actions: If any samples are affected by failure of a QC sample to meet its performance criteria, the problem shall be corrected and samples will he re-analyzed. If re-analysis is not possible (such as lack of sample volume), the PI shall be notified. The data will be qualified with a determination as to impact on the sample data. Failures and resulting corrective actions shall be reported.

2.5.2 Measured and Calculated Solute Concentration Data Evaluation

The computer program AqQA (RockWare Inc., version 1.1.1) may be used as a check on the quality of solute concentration data. Two methods would be used. First, the specific

conductance values measured in the field will be compared to a calculated value that is based on anion- and cation-specific resistivity constants and the measured concentrations of anions and cations in specific ground-water samples. The agreement between the measured and calculated values should be within 15%. The second method will be to calculate the charge balance for each solution. This is done by summing and comparing the net positive and negative charge from the measured concentrations of anions and cations. The agreement should be within 10%. Poor agreement would suggest that some major solute(s) is not accounted for in the analytical measurements or could otherwise point to errors in the analytical work. At the discretion of the PI, discrepancies of this manner will be either flagged or the identity of other sample components and/or reason(s) for poor agreement will be investigated.

2.5.3 Detection Limits

Detection limits for the various analytes are listed in the RSKERC Standard Operating Procedures for these methods and are listed in Table 6. Any updates to these detection limits will be provided in their data reports. Detection limits for the analyses done by Region VIII and III are discussed in Section 2.5.1. They are adequate for project objectives. For isotope measurements, detection limits do not apply. However, enough mass of the element of interest must be included in the sample. For example, 100 ng of Sr is required to determine the isotope ratio of Sr in a sample. In most cases, mass limitations are not expected for isotope measurements, except for the case of methane in samples that are low in dissolved methane.

2.5.4 QA/QC Calculations

% Recovery or Accuracy

$$\%REC=\frac{m}{n}\times 100$$

Where m = measurement result
n = True Value (a certified or known value) of standard or reference

Precision

Precision is described by Relative Percent Difference (RPD) as previously defined.
The Relative Percent Difference (RPD) is calculated based on the following:

$$RPD=\frac{2(a-b)}{a+b}\times 100$$

where a = sample measurement and b = duplicate sample measurement and a > b.

Matrix Spike Recovery

Matrix spikes sample spiking levels are determined at the discretion of the individual analysts (based on sample concentrations) and are included with the sample results.

$$\%\text{Recovery} = \frac{\text{spiked sample concentration-native sample concentration}}{\text{spiked sample concentration}} \times 100$$

2.6 Instrument/Equipment Testing, Inspection, and Maintenance

Laboratory instrumentation used for analysis of project analytes are in routine use and are tested for acceptable performance prior to analyzing actual samples through the analysis of standards and QC samples. Field instruments are tested prior to use in the field by calibrating or checking calibration with standards. Routine inspection and maintenance of these instruments is documented in instrument logbooks. RSKSOPs provide details on instrument testing and corrective actions.

2.7 Instrument/Equipment Calibration and Frequency

RSKERC calibration and calibration frequency are described in RSKSOPs (RSKERC Standard Operating Procedures). For the Region III and VIII laboratories, these requirements are identified in their SOPs and in Tables 9 and 11, and for the USGS laboratory in Table 14. Field instruments (meters for pH, specific conductance, ORP, and DO) are calibrated (per manufacturer's instructions) or checked for calibration daily prior to use, mid-day, and at the end of the day after the last sample measurement. Calibration standards (pH 4.00 and 7.00 buffers, 1413 uS/cm conductivity standard, ORP standard) shall be traceable to NIST, if available, and verified that all dated calibration standards are not beyond their expiration date and will not expire during the field trip. Prior to deployment in the field each test meter will be checked that it is in good working order. Calibration data will be recorded in a bound waterproof notebook and personnel making entries will adhere to the GWERD Notebook policy. Calibration of instruments will be performed daily prior to initiation of sample collection and will be performed according to manufacturer's instructions and will be recorded in the field notebook. In addition, calibration checks will be performed using known standards or buffers before use and at the end of the day. With the exception of pH, all checks must be within ±10% of known concentrations and in the case of pH must be within ±0.2 pH units. These calibration checks will be recorded in the field notebook. If a calibration check fails, this will be recorded in the field notebook and the possible causes of the failure will be investigated. Upon investigation corrective action will be taken and the instrument will be recalibrated. Samples taken between the last good calibration check and the failed calibration check will be flagged to indicate there was a problem. Duplicate field measurements are not applicable to measurements in flow through cell (RSKSOP-211v3, *Field Analytical QA/QC*).

Hach spectrophotometers (ferrous iron and sulfide) and turbidimeters (turbidity) will be inspected prior to going to the field and their function verified. These instruments are factory-calibrated and will be checked in the lab prior to going to the field per the manufacturer's instructions. For the Hach spectrophotometers this will consist of checking the accuracy and precision of iron measurements. The ferrous iron accuracy will be checked by measuring a 1 mg Fe/L standard (using FerroVer® total iron reagent) and the results should be between 0.90 -1.10 mg Fe/L. The precision will be tested using the standard performing the measurement three times on this solution. The single operator standard deviation should be ±0.05 mg Fe/L. Turbidity will be checked against turbidity standards supplied by Hach (or equivalent). In addition, blanks (deionized water) will be run at the beginning of the day and at the end of the day. The values for the blanks will be recorded in the field notebook and any problems associated will be recorded. If blanks have detectable concentrations of any analyte, the sample cells will be decontaminated and a new blank will be run. This process will continue until there is no detectable analytes in the blanks. Alkalinity measurements will use a 1.6N H_2SO_4 solution to titrate samples and standards in the field. The titrator will be checked using a 100 mg/L standard made from Na_2CO_3 or $NaHCO_3$. The analyzed value should be in the range of 90-110 mg/L. Duplicates will be performed once a day or on every tenth sample. Duplicate acceptance criteria are RPD< 15. The values obtained for each duplicate sample will be recorded in the field notebook and RPD will be calculated (section 2.5.4) and recorded in the field notebook. If the duplicate samples fail an additional duplicate sample will be taken and reanalyzed. If the additional duplicate samples fail to meet the QC criteria, then the instruments will be checked and corrective action taken. The corrective actions will be recorded in the field notebook. Samples collected between the last valid duplicate sample and the failed duplicate sample will be flagged.

2.8 Inspection/Acceptance of Supplies and Consumables

RSKSOPs and Region VIII SOPs provide requirements for the supplies and consumables needed for each method. The analysts are responsible for verifying that they meet the SOP requirements. Water used for field blanks, equipment blanks, and trip blanks will be taken from the RSKERC (NANOPure). Water will be filled into a high-capacity carboy and taken to the field.

2.9 Non-direct Measurements

At this stage of the project there are no non-direct measurements anticipated. Limited water quality data were provided by some of the homeowners. Because these data will not be reported as part of this project, but instead used as background information for the site, data quality will be considered acceptable if it has met QA/QC requirements of the labs that performed the analyses.

2.10 Data Management

The PI is responsible for maintaining data files, including their security and integrity. All files (both electronic and hard copy) will be labeled such that it is evident that they are for the retrospective hydraulic fracturing project in Bradford-Susquehanna Counties, PA.

Data will be submitted to Ralph Ludwig as either hard copies (field notes), or electronically (laboratory data) in Excel spreadsheets on CD or DVD or via email. Data in hard copy form will be manually entered into Excel spreadsheets on Ralph Ludwig's computer or designated GWERD staff computer and will given to the PI. The PI, a technician, or student will conduct this task. Data will be spot-checked (frequency of 10%) by Ralph Ludwig to ensure accuracy. If errors are detected during the spot-check, the entries will be corrected. Detection of an error will prompt a more extensive inspection of the data, which could lead to a 100% check of the data set being entered at that time if multiple errors are found.

Data in electronic form shall be electronically transferred to the spreadsheets. Data will be spot-checked (frequency of 10%) by the PI to ensure accuracy of the transfer. If errors are detected during the spot-check, the entries will be corrected. Detection of an error will prompt a more extensive inspection of the data, which could lead to a 100% check of the data set being entered at that time if multiple errors are found.

2.10.1 Data Analysis, Interpretation, and Management

Data validation will consist of initial and final review of data. Initial review will include continuous oversight during field collection of data by the principal investigator to avoid common transcription errors associated with recording of data. Final review will include evaluation of all collected data for suitability in data interpretation. It will include but is not limited to the following activities: (1) assessment of data completeness, (2) review of log books and forms used for data logging, and (3) review of calibration and standard checks.

2.10.2 Data Recording

Data collected during the ground-water investigation will be recorded into field notebooks and entered into Microsoft Excel spreadsheets. Water quality data will also be entered into AqQA a program for evaluating ground water quality and for evaluating data validity. Graphs will be produced using Excel or Origin to show key data trends.

2.10.3 Data Storage

As this is a Category I project, all data and records associated with this project will be kept permanently and will not be destroyed. All data generated in this investigation will be stored electronically in Microsoft Excel and backed up in RSKERC's local area network 'M' drive. All paper-based records will be kept in the PI's offices. If the project records are archived, the PI

will coordinate with GWERD management and GWERD's records liaison and contract support regarding the compiling of all data and records.

2.10.4 Analysis of Data

All data collected associated with groundwater and surface water sampling will be summarized in Microsoft Excel spreadsheets. Data in spreadsheets will be spot-checked (10% of samples) against original data reports by selecting random data points for comparison to verify accuracy of data transfer. If errors are detected during the spot-check, the entries will be corrected. Detection of an error will prompt a more extensive inspection of the data, which could lead to a 100% check pf the data set being entered at that time if multiple errors are found. When possible, data sets will be graphically displayed using Excel and/or Origin to reveal important trends.

3.0 Assessment and Oversight

3.1 Assessments and Response Actions

Technical Systems Audits (TSAs), Audits of Data Quality (ADQs), and Performance Evaluations (if not currently done) will be conducted early in the project to allow for identification and correction of any issues that may affect data quality. TSAs will be conducted on both field and laboratory activities. Laboratory TSAs will focus on the critical target analytes. Detailed checklists, based on the procedures and requirements specified in this QAPP, related SOPs, and EPA Methods will be prepared and used during these TSAs. These audits will be conducted with contract support from Neptune and Co., with oversight by Steve Vandegrift, QAM.

ADQs will be conducted on a representative sample of data for the critical target analytes. These will also be performed by the Neptune and Co., with oversight by Steve Vandegrift, QAM. See Section 4.2 for additional discussion on ADQs.

Performance Evaluations (PE) will be conducted on critical target analytes for those that are available commercially.

See Section 3.2 for how and to whom assessment results are reported.

Assessors do not have stop work authority; however, they can advise the PI if a stop work order is needed in situations where data quality may be significantly impacted, or for safety reasons. The PI makes the final determination as to whether or not to issue a stop work order.

For assessments that identify deficiencies requiring corrective action, the audited party must provide a written response to each finding and observation to the PI and QA Manager, which shall include a plan for corrective action and a schedule. The PI is responsible for ensuring that audit findings are resolved. The QA Manager will review the written response to determine their appropriateness. If the audited party is other than the PI, then the PI shall also review and concur the corrective actions. The QA Manager will track implementation and completion of corrective actions. After all corrective actions have been implemented and confirmed to be completed; the QA Manager shall send documentation to the PI and his supervisor that the audit is closed. Audit reports and responses shall be maintained by the PI in the project file and the QA Manager in the QA files, including QLOG.

3.1.1 Assessments

TSAs will be conducted on both field and laboratory activities. Detailed checklists, based on the procedures and requirements specified in this QAPP, SOPs, and EPA Methods will be prepared and used during these TSAs. One field TSA will be done. It is anticipated this will take place during the sampling events in October 2011 or April 2012. The laboratory audit will take place when samples are in the laboratory's possession and in process of being analyzed.

Laboratory TSAs will focus on the critical target analytes (Table 2) and will be conducted on-site at RSKERC (involves both EPA and Shaw-operated labs) and at the Region VIII laboratory which will analyze for semi-volatile organic, DRO and GRO analyses. It is anticipated this will take place after the first sampling event. However, laboratory TSAs will not be repeated if they have been done previously for another HF case study and significant findings were not identified.

ADQs will be conducted on a representative sample of data for the critical target analytes. These will begin with the first data packages to ensure there are no issues with the data and to allow for appropriate corrective actions on subsequent data sets if needed.

Performance Evaluations will be conducted on critical target analytes for those that are available commercially. Shaw and the EPA GP Lab analyzes PE samples routinely on a quarterly basis. The Region VIII laboratory is currently analyzing Performance Evaluation (aka Proficiency Testing) samples twice a year and data from the past two studies have been provided to the QAM. Glycols analyzed by Region III are not critical, but even if they become critical, PE samples are not available commercially, so PEs will not be done by their laboratory for glycols. Strontium isotopes analyzed by the USGS laboratory are not critical, and as such, PEs will not be done.

3.1.2 Assessment Results

At the conclusion of a TSA, a debriefing shall he held between the auditor and the PI or audited party to discuss the assessment results. Assessment results will be documented in reports to the PI, the PIs first-line manager, and the Technical Research Lead for case studies. If any serious problems are identified that require immediate action, the QAM will verbally convey these problems at the time of the audit to the PI.

The PI is responsible for responding to the reports as well ensuring that corrective actions are implemented in a timely manner to ensure that quality impacts to project results are minimal.

3.2 Reports to Management

All final audit reports shall be sent to the Technical Research Lead for case studies , the first-line manager of Ralph Ludwig, and copied to Ralph Ludwig. Audit reports will be prepared by the QA Manager with input from the QA support contractor where audit performance was delegated. Specific actions will be identified in the reports.

4.0 Data Validation and Usability

4.1 Data Review, Verification, and Validation

Criteria that will be used to accept, reject, or qualify data will include specifications presented in this QAPP, including the methods used and the measurement performance criteria presented in Tables 5, 8, 9, 11, 12, 13, and 14. In addition, sample preservation and holding times will be evaluated against requirements in Table 4.

Data will not be released outside of RSKERC until all study data have been reviewed, verified and validated as described below. The PI is responsible for deciding when project data can be shared with interested stakeholders in conjunction with the GWERDs Director's approval.

4.2 Verification and Validation Methods

Data verification will evaluate data at the data set level for completeness, correctness, and conformance with the method. Data verification will be done by those generating the data. This will begin with the analysts in the laboratory and the personnel in the field conducting field measurements, monitoring the results in real-time or near real-time. At RSKERC, Shaw's, verification includes team leaders, the QC coordinator, and the program manager. For the EPA GP Lab at RSKERC, data verification includes peer analysts in the GP lab and the team leader. Shaw's and the EPA GP Lab's process goes beyond the verification level, as they also evaluate the data at the analyte and sample level by evaluating the results of the QC checks against the RSKSOP performance criteria.

For the Region VIII laboratory, QA/QC requirements include data verification prior to reporting and detailed description can be found in the QSP-001-10 QA Manual (Burkhardt and Batschelet, 2010). Results are reported to the client electronically, unless requested otherwise. Electronic test results reported to the client include the following: data release memo from the analysts, LQAO, and Laboratory Director (or their Designees) authorizing release of the data from the Laboratory, and a case narrative prepared by the analysts summarizing the samples received, test methods, QC notes with identification of noncompliance issues and their impact on data quality, and an explanation of any data qualifiers applied to the data.

The Region III laboratory data verification and validation procedure is described in detail in their Laboratory Quality Manual (Metzger et al., 2011). Briefly, the procedure is as follows. The actual numeric results of all quality control procedures performed must be included in the case file. The data report and narrative must describe any limitations of the data based on a comprehensive review of all quality control data produced. A written procedure or reference must be available for the method being performed and referenced in the narrative. If the method to be performed is unique, the procedures must be fully documented and a copy included in the case file. Results must be within the method, procedure, client or in-house limits. At least one blank (BLK), duplicate analysis, and spiked sample must be carried through the entire method or procedure. Peer reviewers complete the On-Demand Data Checklist. The data report must

document the accuracy and precision of the reported data by applying qualifier codes, if applicable, and include a summary of the quality control in the case file.

For field measurements, Ralph Ludwig will verify the field data collected. For isotope measurements, Isotech and USGS will verify the data collected; these data are not considered to be critical.

The laboratories shall contact the PI upon detection of any data quality issues which significantly affect sample data. They shall also report any issues identified in the data report, corrective actions, and their determination of impact on data quality.

Data validation is an analyte- and sample-specific process that evaluates the data against the project specifications as presented in the QAPP. Data validation (i.e., audit of data quality) will be performed by a party independent of the data collection activity. Neptune and Company, a QA support contractor, will conduct data validation on a representative sample of the critical analytes with oversight by the QAM. Data packages for the critical analytes that have been accepted by Ralph Ludwig as ready to use or report shall be provided to Steve Vandegrift, QAM, who will coordinate the data validation with Neptune. Neptune shall evaluate data against the QAPP specifications. Neptune will use NRMRL SOP #LSAS-QA-02-0, "Performing Audits of Data Quality" as a guide for conducting the data validation. The outputs from this process will include the validated data and the data validation report. The report will include a summary of any identified deficiencies and a discussion on each individual deficiency and any effect on data quality and recommended corrective action.

As part of the data validation process, the synthesis of data and conclusions drawn from the data will be reviewed by the RSKERC Case Study Team (minimally will include case study PIs, Technical Research Lead for case studies, and GWERD Division Director) prior to release of this information or data to entities outside of RSKERC. Once reviewed by the RSKERC Case Study Team in coordination with the GWERD Division Director, the GWERD Division Director will approve its release.

4.3 Reconciliation with User Requirements

The PI, Ralph Ludwig, shall analyze the data, as presented below. Ralph Ludwig shall also review the results from the data verification and validation process. The PI shall make a determination as to whether or not the data quality has met project requirements and therehy the user requirements. If there are data quality issues that impact their use, the impact will be evaluated by the PI. If corrective actions are available that would correct the issue, the PI will make the determination to implement such actions. For example, the PI may have the option to re-sample or re-analyze the affected samples. If not, then the PI will document the impact in the final report such that it is transparent to the data users how the conclusions from the project are affected.

The types of statistical analyses that may be performed include summary statistics (mean, median, standard deviation, minimum, maximum, etc.) if applicable. In addition, the data will be plotted graphically over time and trends in the data will be analyzed, for example increasing or decreasing concentrations of a particular analyte.

Data will be presented in both graphical and tabular form. Tabular forms of the data will include Excel spreadsheets for raw data and tables containing the processed data. Graphical representations of the data will not only include time-series plots, but also Durov and Piper Diagrams for major anions and cations. In addition, concentrations of data could be plotted on surface maps of the Washington County site showing well locations and concentrations of analytes.

5.0 References

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RSKSOP-194v4. Gas Analysis by Micro Gas Chromatograph (Agilent Micro 3000). 13 p.

RSKSOP-211v3. Field Analytical QA/QC. 4 p.

RSKSOP-112v6. Standard Operating Procedure for Quantitative Analysis of Low Molecular Weight Acids in Aqueous Samples by HPLC. 22 p.

RSKSOP-213v4. Standard Operating Procedure for Operation of Perkin Elmer Optima 3300 DV ICP-OES. 22 p.

RSKSOP-214v5. Quality control procedures for general parameters analysis using Lachat Flow Injection analysis (FIA), 10 p.

RSKSOP-216v2. Sample Receipt and Log-In Procedures for the On-Site Analytical Contractor. 5 p.

RSKSOP-257v3. Operation of Thermo Elemental PQ Excell ICP-MS. 16 p.

RSKSOP-276v3. Determination of Major Anions in Aqueous Samples Using Capillary Ion Electrophoresis with Indirect UV Detection and Empower 2 Software. 11 p.

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6.0 Tables

Table 1. Known constituents of the hydraulic fracturing fluids used in Pennsylvania.

1,2,4-Trimethylbenzene Glycol Ethers (includes 2BE)	Glycol Ethers (includes 2BE)
1,3,5 Trimethylbenzene Guar gum	Guar gum
2,2-Dibromo-3-Nitrilopropionamide Hemicellulase Enzyme	Hemicellulase Enzyme
2.2-Dibromo-3-Nitrilopropionamide Hydrochloric Acid	Hydrochloric Acid
2-butoxyethanol Hydrotreated light distillate	Hydrotreated light distillate
2-Ethylhexanol Hydrotreated Light Distilled	Hydrotreated Light Distilled
2-methyl-4-isothiazolin-3-one Iron Oxide	Iron Oxide
5-chloro-2-methyl-4-isothiazotin-3-one Isopropanol	Isopropanol
Acetic Acid Isopropyl Alcohol	Isopropyl Alcohol
Acetic Anhydride Kerosine	Kerosine
Acie Pensurf Magnesium Nitrate	Magnesium Nitrate
Alchohol Ethoxylated Mesh Sand (Crystalline Silica)	Mesh Sand (Crystalline Silica)
Alphatic Acid Methanol	Methanol
Alphatic Alcohol Polyglycol Ether Mineral Spirits	Mineral Spirits
Aluminum Oxide Monoethanolamine	Monoethanolamine
Ammonia Bifluoride Naphthalene	Naphthalene
Ammonia Bisulfite Nitrilotriacetamide	Nitrilotriacetamide
Ammonium chloride Oil Mist	Oil Mist
Ammonium Salt Petroleum Distallate Blend	Petroleum Distallate Blend
Ammonia Persulfate Petroleum Distillates	Petroleum Distillates
Aromatic Hydrocarbon Petroleum Naphtha	Petroleum Naphtha
Aromatic Ketones Polyethoxylated Alkanol (1)	Polyethoxylated Alkanol (1)
Boric Acid Polyethoxylated Alkanol (2)	Polyethoxylated Alkanol (2)
Boric Oxide Polyethylene Glycol Mixture	Polyethylene Glycol Mixture
Butan-1-01 Polysaccharide	Polysaccharide
Citric Acid Potassium Carbonate	Potassium Carbonate
Crystalline Silica: Cristobalite Potassium Chloride Crystalline Silica: Cristobalite Potassium Chloride	Potassium Chloride
Crystalline Silica: Quartz Potassium Hydroxide	Potassium Hydroxide
Dazomet Prop-2-yn-1-01	Prop-2-yn-1-01
Diatomaceus Earth Propan-2-01	Propan-2-01
Diesel (use discontinued) Propargyl Alcohol	Propargyl Alcohol
Diethylbenzene Propylene	Propylene
Doclecylbenzene Sulfonic Acid Sodium Ash	Sodium Ash
E B Butyl Cellosolve Sodium Bicarbonate	Sodium Bicarbonate
Ethane-1,2-diol Sodium Chloride	Sodium Chloride
Ethoxlated Alcohol Sodium Hydroxide	Sodium Hydroxide
Ethoxylated Alcohol Sucrose	Sucrose
Ethoxylated Octylphenol Tetramethylammonium Chloride	Tetramethylammonium Chloride
Ethylbenzene Titaniaum Oxide	Titaniaum Oxide
Ethylene Glycol Toluene	Toluene
Ethylhexanol Xylene	Xylene
Ferrous Sulfate Heptahydrate	
Formaldehyde	
Glutaraldehyde	

From the Pennsylvania Department of Environmental Protection website (http://www.dep.state.pa.us, accessed June 13, 2011)

Table 2. Critical analytes.

Analyte	Analysis Method	Laboratory Performing the Analysis
Gasoline Range Organics (GRO)	ORGM-506 r1.0, EPA Method 8015D	EPA Region VIII Laboratory
Diesel Range Organics (DRO)	ORGM-508 r1.0, EPA Method 8015D	EPA Region VIII Laboratory
Volatile Organic Compounds (VOC)*	RSKSOP-299v1 or -259v1	Shaw Environmental
Semivolatile Organic Compounds (SVOC)	ORGM-515 r1.1, EPA Method 8270D	EPA Region VIII Laboratory
Metals (As, Se, Sr, Ba, B)	RSKSOP-213v4 &-257v2 or -332v0	Shaw Environmental
Major Cations (Ca, Mg, Na, K)	RSKSOP-213v4	Shaw Environmental
Major Anions (Cl, NO_3^-+NO_2^-, SO_4^{2-})	RSKSOP-276v3 (NO_3^-+NO_2^- by RSKSOP-214v5)	RSKERC general parameters lab

*ethanol, isopropyl alcohol, tert-butyl alcohol, naphthalene, acrylonitrile (acrylonitrile is being added to RSKSOP-299)

Only those SVOC compounds in Table 7 that have DL, RL, and Control Limits listed may be used as critical analytes. Others only as screening data.

Both VOC and SVOC have many target analytes and initially all are considered as critical (with exception for SVOC noted above). A tiered approach will be used to further refine the identification of specific compounds as critical. Data from the first sampling events will be evaluated by the PI to determine if there are specific compounds that are identified in these samples which would warrant their specific identification as critical to narrow the list. These will be identified in a subsequent QAPP revision.

GRO analysis provides data for not only TPH as gasoline, but several other compounds. Only TPH as gasoline will be considered critical from this analysis.

Table 3. Tentative schedule of field activities for the hydraulic fracturing case study in SW Pennsylvania.

Media	Oct-Nov 2011	April 2012	July 2012	Sept 2012
Groundwater	X	X	X	X
Surface Water	X	X	X	X

Table 4. Ground and surface water sample collection.

Sample Type	Analysis Method (EPA Method)	Sample Bottles/# of bottles*	Preservation/ Storage	Holding Time(s)
Dissolved gases	RSKSOP-194v4 &-175v5 (No EPA Method)	60 mL serum bottles/2	No Headspace H_2SO_4, pH<2; refrigerate 6°C[††]	14 days
Metals (filtered)	RSKSOP-213v4 &-257v3 or 332v0 (EPA Methods 200.7 and 6020)	125 mL plastic bottle/1	HNO_3, pH<2; room temperature	6 months (Hg 28 days)
Metals (unfiltered)	RSKSOP179v2; RSKSOP-213v4 &-257v3 or 332v0 (EPA Methods 200.7 and 6020)	125 mL plastic bottle/1	HNO_3, pH<2; room temperature	6 months (Hg 28 days)
SO_4, Cl, F, Br	RSKSOP-276v3 (EPA Method 6500)	30 mL plastic/1	Refrigerate ≤6°C	28 days
NO_3 + NO_2, NH_4	RSKSOP-214v5 (EPA Method 350.1 for NH_4, 353.1 for NO_3 + NO_2)	30 mL plastic/1	H_2SO_4, pH<2; refrigerate ≤6°C	28 days
DIC	RSKSOP-330v0 (EPA Method 9060A)	40 mL clear glass VOA vial/2	refrigerate ≤6°C	14 days
DOC	RSKSOP-330v0 (EPA Method 9060A)	40 mL clear glass VOA vial/2	H_3PO_4, pH<2; refrigerate ≤6°C	28 days
Volatile organic compounds (VOC)	RSKSOP-299v1 or -259v1 (EPA Method 5021A plus 8260C)	40 mL amber glass VOA vial/2	No Headspace TSP[†], pH>10; refrigerate ≤6°C	14 days
Low Molecular Weight Acids	RSKSOP-112V6 (No EPA Method)	40 mL glass VOA vial/2	TSP[†], pH>10; refrigerate ≤6°C	30 days
O, H stable isotopes of water	RSKSOP-296v0 (No EPA Method)	20 mL glass VOA vial/1	Refrigerate at ≤6°C	stable
$\delta^{13}C$ of inorganic carbon	Isotech: gas stripping and IRMS (No EPA Method)	60 mL plastic bottle/1	Refrigerate ≤6°C	No information
$\delta^{13}C$ and $\delta^{2}H$ of methane	Isotech: gas stripping and IRMS (No EPA Method)	1 L plastic bottle/1	Caplet of benzalkonium chloride; refrigerate ≤6°C	No information
$^{87}Sr/^{86}Sr$ analysis	Thermal ionization mass spectrometry (No EPA Method)	500 mL plastic bottle/1 and 2 for every 10 samples	Refrigerate ≤6°C	No information
Semi-volatile organic compounds	ORGM-515 r1.1, EPA Method 8270D	1L Amber glass bottle/2 and for every 10 samples of ground water need 2 more bottles for one selected	Refrigerate ≤6°C	7 days until extraction, 30 days after

		sample, or if <10 samples collected, collect 2 more bottles for one select sample		extraction
DRO	ORGM-508 r1.0, EPA Method 8015D	1L Amber glass bottle/2 and for every 10 samples of ground water need 2 more bottles for one selected sample, or if <10 samples collected, collect 2 more bottles for one select sample	HCl, pH<2; refrigerate ≤6°C	7 days until extraction, 40 days after extraction
GRO	ORGM-506 r1.0, EPA Method 8015D	40 mL amber glass VOA vial/2 and for every 10 samples of ground water need 2 more bottles for one selected sample, or if <10 samples collected, collect 2 more bottles for one select sample	No headspace; HCl, pH<2; refrigerate ≤6°C	14 days
Gylcols	Region III method** (No EPA Method)	40 mL amber glass VOA vial/2	Refrigerate ≤6°C	14 days
Archive	NA	1 L plastic amber	Freeze ≤-10°C; freezer at lab	NA

† trisodium phosphate
†† above freezing point of water
*Spare bottles made available for laboratory QC samples and for replacement of compromised samples (broken bottle, QC failures, etc.).

**under development

Table 5. Field QC samples for water samples.

QC Sample	Purpose	Method	Frequency	Acceptance Criteria/Corrective Action*
Trip Blanks (VOCs and Dissolved Gases only)	Assess contamination during transportation.	Fill bottles with reagent water and preserve, take to field and returned without opening.	One in each ice chest with VOA and dissolved gas samples.	<RL*; if >RL, PI will determine if significant relative to sample data.
Equipment Blanks	Assess contamination from field equipment, sampling procedures, decon procedures, sample container, preservative, and shipping.	Apply only to samples collected via equipment, such as filtered samples: Reagent water is filtered and collected into bottles and preserved same as filtered samples.	One per day of sampling	<RL; if >RL, PI will determine if significant relative to sample data.
Field Duplicates	Represent precision of field sampling, analysis, and site heterogeneity.	One or more samples collected immediately after original sample.	One in every 10 samples, or if <10 samples collected for a water type (ground or surface), collect a duplicate for one sample	Report duplicate data; if RPD > 30 for results greater than 5xRL then affected data will be flagged as needed.
Temperature Blanks	Measure temperature of samples in the cooler.	Water sample that is transported in cooler to lab.	One per cooler.	Record temperature; condition noted on COC form***
Field Blanks**	Assess contamination introduced from sample container with applicable preservative	In the field, reagent water is collected into sample containers with preservatives.	One per day of sampling	<RL*; if >RL, PI will determine if significant relative to sample data.

* Reporting limit or Quantitation Limit

** Blank samples will not be collected for isotope measurements, including O, H, C, and Sr.

*** The PI should be notified immediately if samples arrive with no ice and/or if the temperature recorded from temperature blanks is greater than or equal to 12 °C. These samples will be flagged accordingly.

Table 6. RSKERC detection limits for various analytes.

Analyte	Method	MDL (µg/L)	QL or LOQ (µg/L)
VOCs			
Vinyl chloride	RSKSOP-299v1	0.18	0.50
Ethanol	RSKSOP-299v1	12.4	100
1,1-Dichloroethene	RSKSOP-299v1	0.11	0.50
Acetone	RSKSOP-299v1	0.63	1.00
Isopropyl alcohol	RSKSOP-299v1	6.40	25.0
Carbon disulfide	RSKSOP-299v1	0.07	0.50
Methylene chloride	RSKSOP-299v1	0.14	1.00
t-Butyl alcohol	RSKSOP-299v1	2.81	5.00
Methyl t-butyl ether	RSKSOP-299v1	0.41	1.00
t-1,2-Dichloroethene	RSKSOP-299v1	0.11	0.50
1,1-Dichloroethane	RSKSOP-299v1	0.08	0.50
Diisopropyl ether	RSKSOP-299v1	0.12	1.00
Ethyl t-butyl ether	RSKSOP-299v1	0.17	1.00
c-1,2-Dichloroethene	RSKSOP-299v1	0.14	0.50
Chloroform	RSKSOP-299v1	0.07	0.50
1,1,1-Trichloroethane	RSKSOP-299v1	0.09	0.50
Carbon tetrachloride	RSKSOP-299v1	0.10	0.50
Benzene	RSKSOP-299v1	0.07	0.50
1,2-Dichloroethane	RSKSOP-299v1	0.16	0.50
t-Amyl methyl ether	RSKSOP-299v1	0.15	1.00
Trichloroethene	RSKSOP-299v1	0.15	0.50
Toluene	RSKSOP-299v1	0.10	0.50
1,1,2-Trichloroethane	RSKSOP-299v1	0.18	0.50
Tetrachloroethene	RSKSOP-299v1	0.10	0.50
Chlorobenzene	RSKSOP-299v1	0.09	0.50
Ethyl benzene	RSKSOP-299v1	0.07	1.00
m/p-Xylene	RSKSOP-299v1	0.17	2.00
o-Xylene	RSKSOP-299v1	0.06	0.50
Isopropyl benzene	RSKSOP-299v1	0.06	0.50
1,3,5-Trimethylbenzene	RSKSOP-299v1	0.06	0.50
1,2,4-Trimethylbenzene	RSKSOP-299v1	0.06	0.50
1,3-Dichlorobenzene	RSKSOP-299v1	0.10	0.50
1,4-Dichlorobenzene	RSKSOP-299v1	0.08	0.50
1,2,3-Trimethylbenzene	RSKSOP-299v1	0.12	0.50
1,2-Dichlorobenzene	RSKSOP-299v1	0.13	0.50
Naphthalene	RSKSOP-299v1	0.12	0.50
Vinyl chloride	RSKSOP-259v1	0.22 (0.07)*	0.50
Ethanol	RSKSOP-259v1	44.7 (24.7)	100 (50)
1,1-Dichloroethene	RSKSOP-259v1	0.08 (0.08)	0.50
Acetone	RSKSOP-259v1	Not Analyzed	Not Analyzed

Isopropyl Alcohol	RSKSOP-259v1	9.72 (11.4)	50.0
Methylene Chloride	RSKSOP-259v1	0.24 (0.13)	1.00 (0.5)
t-Butyl alcohol	RSKSOP-259v1	1.85 (3.21)	5.00
Methyl t-butyl ether	RSKSOP-259v1	0.05 (0.11)	0.50
t-1,2-Dichloroethene	RSKSOP-259v1	0.20 (0.08)	1.0
1,1-Dichloroethane	RSKSOP-259v1	0.09 (0.10)	0.50
Diisopropyl ether	RSKSOP-259v1	0.09 (0.15)	0.50
Ethyl-t-butyl ether	RSKSOP-259v1	0.10	1.0
c-1,2-Dichloroethene	RSKSOP-259v1	0.04 (0.05)	0.50
Chloroform	RSKSOP-259v1	0.03	0.50
1,1,1-Trichloroethane	RSKSOP-259v1	0.28 (0.09)	1.00 (0.50)
Carbon tetrachloride	RSKSOP-259v1	0.05 (0.07)	0.50
Benzene	RSKSOP-259v1	0.03 (0.11)	0.50
1,2-Dichloroethane	RSKSOP-259v1	0.12 (0.17)	1.00 (0.50)
t-Amyl methyl ether	RSKSOP-259v1	0.08 (0.05)	0.50 (1.00)
Trichloroethene	RSKSOP-259v1	0.05 (0.04)	0.50
Toluene	RSKSOP-259v1	0.03 (0.07)	0.50
Tetrachloroethene	RSKSOP-259v1	0.09 (0.06)	1.00 (0.50)
Chlorobenzene	RSKSOP-259v1	0.07 (0.03)	0.50
Ethyl benzene	RSKSOP-259v1	0.43 (0.09)	(5.00) (0.50)
m/p-Xylene	RSKSOP-259v1	0.09 (0.16)	1.00
o-Xylene	RSKSOP-259v1	0.06 (0.08)	0.50
1,3,5-Trimethylbenzene	RSKSOP-259v1	0.08	0.50
1,2,4-Trimethylbenzene	RSKSOP-259v1	0.12 (0.08)	0.50
1,3-Dichlorobenzene	RSKSOP-259v1	0.29 (0.02)	0.50
1,4-Dichlorobenzene	RSKSOP-259v1	0.33 (0.05)	0.50
1,2,3-Trimethylbenzene	RSKSOP-259v1	0.18 (0.08)	0.50
1,2-Dichlorobenzene	RSKSOP-259v1	0.23 (0.07)	1.00 (0.50)
Naphthalene	RSKSOP-259v1	0.34 (0.07)	5.00 (0.50)
n-Propanol	RSKSOP-259v1	11.1 (NA)	50.0 (NA)
i-Butanol	RSKSOP-259v1	9.73 (15.6)	50.0
n-Butanol	RSKSOP-259v1	6.69 (15.5)	50.0
2,5-Dimethylfuran	RSKSOP-259v1	0.03 (0.07)	0.50
Metals ICP-MS		MDL (µg/L)	QL or LOQ (µg/L)

As	RSKSOP-257v3/-332v0	0.050	0.167
Be	RSKSOP-257v3/-332v0	0.005	0.015
Analyte	Method	MDL (µg/L)	QL or LOQ (µg/L)
Cd	RSKSOP-257v3/-332v0	0.020	0.067
Cr	RSKSOP-257v3/-332v0	0.037	0.124
Cu	RSKSOP-257v3/-332v0	0.287	0.957
Fe	RSKSOP-257v3/-332v0	0.105	0.350
Hg	RSKSOP-257v3/-332v0	0.019	0.064
Mn	RSKSOP-257v3/-332v0	0.037	0.124
Mo	RSKSOP-257v3/-332v0	0.008	0.027
Ni	RSKSOP-257v3/-332v0	0.048	0.160
Pb	RSKSOP-257v3/-332v0	0.043	0.143
Sb	RSKSOP-257v3/-332v0	0.014	0.047
Se	RSKSOP-257v3/-332v0	0.159	0.530
Sr	RSKSOP-257v3/-332v0	0.012	0.040
Tl	RSKSOP-257v3/-332v0	0.04	0.013
V	RSKSOP-257v3/-332v0	0.003	0.010
Zn	RSKSOP-257v3/-332v0	0.072	0.240
U	RSKSOP-257v3/-332v0	0.002	0.007
Ce	RSKSOP-257v3/-332v0	0.006	0.020
Metals ICP-OES		MDL (mg/L)	QL or LOQ (mg/L)
Na	RSKSOP-213v4	0.046	0.154
K	RSKSOP-213v4	0.029	0.097
Ca	RSKSOP-213v4	0.026	0.087
Mg	RSKSOP-213v4	0.013	0.044
Fe	RSKSOP-213v4	0.013	0.044
Mn	RSKSOP-213v4	0.001	0.004
Co	RSKSOP-213v4	0.001	0.004
Mo	RSKSOP-213v4	0.001	0.004
Al	RSKSOP-213v4	0.024	0.080
As	RSKSOP-213v4	0.007	0.024
Se	RSKSOP-213v4	0.007	0.024
Cd	RSKSOP-213v4	0.001	0.004
Be	RSKSOP-213v4	0.001	0.004
Cu	RSKSOP-213v4	0.002	0.007
Sb	RSKSOP-213v4	0.008	0.027
Cr	RSKSOP-213v4	0.001	0.004
Ni	RSKSOP-213v4	0.001	0.004
Zn	RSKSOP-213v4	0.005	0.017
Ag	RSKSOP-213v4	0.003	0.010
Tl	RSKSOP-213v4	0.009	0.030
Pb	RSKSOP-213v4	0.003	0.010
Sr	RSKSOP-213v4	0.001	0.004

Analyte	Method	MDL (mg/L)	QL or LOQ (mg/L)
V	RSKSOP-213v4	0.002	0.007
Ba	RSKSOP-213v4	0.001	0.004
B	RSKSOP-213v4	0.005	0.017
Ti	RSKSOP-213v4	0.001	0.004
Si	RSKSOP-213v4	0.019	0.064
P	RSKSOP-213v4	0.011	0.037
S	RSKSOP-213v4	0.026	0.087
U	RSKSOP-213v4	0.009	0.030
Dissolved Gases**		MDL (µg/L)	QL or LOQ (µg/L)
Methane	RSKSOP-194v4 & RSKSOP-175v5	0.08	1.5
Ethylene	RSKSOP-194v4 & RSKSOP-175v5	0.56	4.11
Ethane	RSKSOP-194v4& RSKSOP-175v5	0.20	2.91
Acetylene	RSKSOP-194v4 & RSKSOP-175v5	2	18.7
Carbon Dioxide	RSKSOP-194v4& RSKSOP-175v5	20.4	262
Propane	RSKSOP-194v4& RSKSOP-175v5	0.24	4.1
n-Butane	RSKSOP-194v4& RSKSOP-175v5	0.22	5.22
Hydrogen	RSKSOP-194v4& RSKSOP-175v5	0.01	0.33
Anions/Nutrients		MDL (mg/L)	QL or LOQ (mg/L)
Br^-	RSKSOP-276v3	0.248	1.00
Cl^-	RSKSOP-276v3	0.118	1.00
SO_4^{2-}	RSKSOP-276v3	0.226	1.00
$NO_3^- + NO_2^-$	RSKSOP-214v5	0.014	0.10
F^-	RSKSOP-276v3	0.052	0.20
NH_4^+	RSKSOP-214v5	0.012	0.05
Low Molecular Weight Acids	Method	MDL (mg/L)	QL (mg/L)
Lactate	RSKSOP-112v6	0.020	0.100
Isobutyrate	RSKSOP-112v6	0.018	0.100
Acetate	RSKSOP-112v6	0.011	0.100

Propionate	RSKSOP-112v6	0.022	0.100
Formate	RSKSOP-112v6	0.015	0.100
Butyrate	RSKSOP-112v6	0.025	0.100

*For RSKSOP-259, MDL and QL values are provided for two different instruments identified as "CAIN" and "ABEL." Those in parentheses are for "ABEL." If there is no difference only one value is listed.

** Aqueous concentrations are dependent on headspace volume, aqueous volume, temperature, pressure, etc. These limits were calculated based on 60 mL bottle, 6 mL headspace, 25 degrees, headspace pressure of 1 atmosphere, and using the "created" headspace calculations.

Table 7. Region VIII detection and reporting limits and LCS and MS control limits for semi-volatile organic compounds (SVOC) using Method 8270.

Analyte	Detection Limits		Control Limits			
	DL (µg/L)	RL (µg/L)	Mean	Standard Deviation	Lower Control Limit	Upper Control Limit
1-Chloronaphthalene						
1,2-Dibromo-3-chloropropane						
1,2-Dichlorobenzene	0.218	0.500	67.3	11.4	33	102
1,2-Dinitrobenzene						
1,2-Diphenylhydrazine			84.8	9.4	57	113
1,2,4-Trichlorobenzene	0.208	0.500	71.7	11.6	37	107
1,2,4,5-Tetrachlorobenzene						
1,3-Dichlorobenzene	0.226	0.500	64.8	10.9	32	98
1,3-Dinitrobenzene						
1,4-Dichlorobenzene	0.225	0.500	64.8	10.9	32	98
1,4-Dinitrobenzene						
2-Chloronaphthalene	0.167	0.500				
2-Chlorophenol	0.243	0.500	71.3	11.4	37	106
2-Fluorobiphenyl (Surrogate)			79.9	10.6	48	112
2-Fluorophenol (Surrogate)			63.7	14.8	19	108
2-Methylnaphthalene	0.190	0.500	75.0	9.5	46	104
2-Methylphenol	0.217	0.500	73.3	11.7	38	109
2-Nitroaniline	0.118	0.500	81.8	11.2	48	115
2-Nitrophenol	0.197	0.500	75.8	12.4	39	113
2,3,4,6-Tetrachlorophenol						
2,4-Dichlorophenol	0.185	0.500	76.3	9.6	48	105
2,4-Dimethylphenol	0.142	0.500	68.8	13.5	28	109
2,4-Dinitrophenol	2.00	2.00	75.8	20.6	14	138
2,4-Dinitrotoluene	0.086	0.500	84.3	11.2	51	118
2,4,5-Trichlorophenol	0.151	0.500	79.7	10.3	49	111
2,4,6-Tribromophenol (Surrogate)			82.9	13.6	42	124
2,4,6-Trichlorophenol	0.166	0.500	80.7	10.7	49	113
2,6-Dichlorophenol			82.7	11.3	49	117
2,6-Dinitrotoluene	0.091	0.500				
3-Methylphenol	0.189	0.500	71.3	13	32	110
3-Nitroaniline	0.394	0.500	72.6	17.7	19	126
3,3'-Dichlorobenzidine			65.2	15.3	19	111
4-Bromophenyl phenyl ether	0.108	0.500	82.9	10.2	52	113
4-Chloroaniline	0.546	1.00	62.2	15.6	15	109
4-Chloro-3-methylphenol	0.165	0.500	78.6	10.7	47	111
4-Chlorophenyl phenyl ether	0.120	0500	80.6	10.3	50	111
4-Methylphenol	0.189	0.500	71.3	13.0	32	110
4-Nitroaniline	0.320	0.500	77.2	13.7	36	118
4-Nitrophenol	0.085	0.500				

4,4'-DDD						
4,4'-DDE						
4,4'-DDT						
4,4'-Methylenebis (2-chloroaniline)						
4,4'-Methylenebis (N,Ndimethylaniline)						
4,6-Dinitro-2-methylphenol	0.202	0.500	84.9	15.0	40	130
Acenaphthene	0.147	0.500	77.6	10.1	47	108
Acenaphthylene	0.139	0.500	78.5	9.4	40	107
Acetophenone						
Aldrin						
Aniline						
Anthracene	0.088	0.500	83.0	9.7	54	112
Azinphos-methyl						
Azobenzene	0.102	0.500				
Benzoic acid						
Benz(a)anthracene	0.079	0.500	82.7	8.9	56	109
Benzo(b)fluoranthene	0.081	0.500	81.8	12.1	45	118
Benzo(k)fluoranthene	0.088	0.500	84.6	13.2	45	124
Benzo(g,h,i)perylene	0.098	0.500	80.5	14.1	38	123
Benzo(a)pyrene	0.083	0.500	81.3	9.5	53	110
Benzyl alcohol			71.0	13.8	30	112
α-BHC						
β-BHC						
δ-BHC						
γ-BHC (Lindane)						
Bis(2-chloroethoxy)methane	0.183	0.500	76.2	10.2	46	107
Bis(2-chloroethyl) ether	0.238	0.500	73.3	12.3	37	110
Bis(2-chloroisopropyl) ether	0.426	0.500	78.2	17.5	26	131
Bis(2-ethylhexyl) phthalate	0.500	1.00	84.2	14.0	42	126
Butyl benzyl phthalate	0.190	0.500	81.1	11.7	46	116
Carbaryl						
Carbazole	0.084	0.500	82.5	11.4	48	117
Chlorobenzilate						
Chrysene	0.079	0.500	82.1	8.9	55	109
Dibenz(a,h)anthracene	0.110	0.500	84.7	14.1	42	127
Dibenzofuran	0.133	0.500	80.3	8.8	54	107
Di-n-butyl phthalate	0.153	0.500				
Dichlorovos						
Dieldrin						
Diethyl phthalate	0.099	0.500	79.2	12.9	41	118
Dimethyl phthalate	0.107	0.500	75.9	16.9	25	127
Dinoseb						
Diphenylamine						
Di-n-butyl phthalate			84.8	10.3	54	116
Di-n-octyl phthalate	0.188	0.500	87.4	16.6	37	137
Disulfoton						

Endosulfan I						
Endosulfan II						
Endosulfan sulfate						
Endrin						
Endrin aldehyde						
Endrin ketone						
Fluoranthene	0.094	0.500	85.2	10.4	54	116
Fluorene	0.120	0.500	80.6	10.3	50	112
Heptachlor						
Heptachlor epoxide						
Hexachlorobenzene	0.116	0.500	82.3	10.0	52	112
Hexachlorobutadiene	0.225	0.500	65.2	12.6	27	103
Hexachlorocyclopentadiene	0.202	0.500				
Hexachloroethane	0.196	0.500	60.9	11.1	28	94
Indeno(1,2,3-cd)pyrene	0.093	0.500	84.3	13.6	43	125
Isophorone	0.167	0.500	81.0	10.5	50	112
Malathion						
Methoxychlor						
Mevinphos						
Naphthalene	0.212	0.500	70.8	10.5	39	102
Nitrobenzene	0.233	0.500	76.8	10.8	44	109
Nitrobenzene-d5 (Surrogate)			76.0	11.8	41	111
N-Nitrosodi-n-butylamine	0.187	0.500				
N-Nitrosodiethylamine						
N-Nitrosodimethylamine			67.9	41.1	26	110
N-Nitrosodiphenylamine			79.6	10.6	48	111
N-Nitrosodi-n-propylamine			80.9	15.7	34	128
N-Nitrosomethylethylamine						
Parathion						
Pentachlorobenzene						
Pentachlorophenol	0.199	0.500	77.6	13.3	38	117
Phenanthrene	0.107	0.500	84.0	11.0	51	117
Phenol	0.246	0.500				
Phorate						
Pronamide						
Pyrene	0.087	0.500	88.6	13.2	49	128
Pyridine						
Terbufos						
Terphenyl-d14 (Surrogate)			92.7	14.0	51	135
Trifluralin						
®-(+)-Limonene	0.054	0.100				
1,3-Dimethyl adamantine	0.028	0.100				
2-Butoxyethanol	0.054	0.100				
Adamantane	0.033	0.100				
Squalene	0.565	1.00				
Terpiniol	0.031	0.100				
Tri(2-butoxyethyl)phosphate	0.133	0.200				

Table 8. RSKERC QA/QC requirements summary* from SOPs.

Measurement	Analysis Method	Blanks (Frequency)	Calibration Checks (Frequency)	Second Source (Frequency)	Duplicates (Frequency)	Matrix Spikes (Frequency)
Dissolved gases	RSKSOP-194v4 &-175v5*	≤MDL (He/Ar blank, first and last in sample queue; water blank before samples)	85-115% of known value (After helium/Ar blank at first of analysis queue, before helium/Ar blank at end of sample set, and every 15 samples)	85-115% of known value (After first calibration check)	RPD≤20 (Every 15 samples)	NA
Metals (filtered & undigested)	RSKSOP-213v4	<QL for 80% of metals (Beginning and end of each sample queue, 10-15 samples)	90-110% of known value (Beginning and end of each sample queue, 10-15 samples)	PE sample acceptance limits or 90-110% of known value (Immediately after first calibration check)	RPD<10 for 80% of metals; for results <5x QL, difference of ≤ QL (Every 15 samples)	90-110% Rec. for 80% of metals w/ no individual exceeding 50-150% Rec. (one per sample set, 10-15 samples)
Metals (unfiltered & digested)	RSKSOP-213v4	<10xMDL	See "undigested"	See "undigested"	RPD<20 for 80% of metals; for results <5x QL, difference of ≤ QL (Every 15 samples)	80-120% Rec. for 80% of metals w/ no individual exceeding 50-150% Rec. (one per sample set, 10-15 samples)
Metals (filtered & undigested)	RSKSOP-257v3 and -332v0	<QL for 80% of metals; none >10xMDL	90-110% of known value (Beginning and end of each sample	PE sample acceptance limits or 90-110% of known value	RPD<10 for 80% of metals; for results <5x QL,	90-110% Rec. for 80% of metals w/ no

		(Beginning and end of each sample queue, 10-15 samples)	queue, 10-15 samples)	(Immediately after first calibration check)	difference of ≤ QL (Every 15 samples)	individual exceeding 70-130% Rec. (one per sample set, 10-15 samples)
Metals (unfiltered & digested)	RSKSOP-257v3 and -332v0	<ICP MDL for RSKSOP-213v4	See "undigested"	See "undigested"	RPD<20* for 80% of metals; for results <5x QL, difference of ≤ QL (Every 15 samples) *35 for solids	80-120% average rec. with at least 50% of individuals within 50-150% rec. for pre-digestions and 70-130% rec. for all results for post-digestions (one per sample set, 10-15 samples)
SO_4, Cl, F, Br	RSKSOP-276v3	<MDL (Beginning and end of each sample queue)	90-110% Rec. (Beginning, end, and every 10 samples)	PE sample acceptance limits (One per sample set)	RPD<10 (every 15 samples)	80-120% Rec. (one per every 20 samples)
$NO_3 + NO_2$, NH_4	RSKSOP-214v5	<½ lowest calib. std. (Beginning and end of each sample queue)	90-110% Rec. (Beginning, end, and every 10 samples)	PE sample acceptance limits (One per sample set)	RPD<10 (every 10 samples)	80-120% Rec. (one per every 20 samples)
DIC/DOC	RSKSOP-330v0	<½QL (after initial calib., every 10-15 samples, and at end)	80-120% of known value (after initial calib., every 10-15 samples, and at end)	80-120% of known value (Immediately after calibration)	RPD<10 (every 15 samples)	80-120% Rec. (one per 20 or every set

Volatile organic compounds (VOC)**	RSKSOP-299v1 and -259v1	<MDL (Beginning and end of each sample set)	80-120% Rec. (Beginnmg, end, and every 20 samples)	80-120% of known value (Once at beginning and also at end for -259v1)	-299v1: RPD<20 -259v1: RPD<25 (every 20 samples)	70-130% Rec. (every 20 samples)
Low Molecular Weight Acids	RSKSOP-112v6	<MDL (Beginning of a sample queue; every 10 samples; and end of sample queue)	85-115% of the recovery (Prior to sample analysis; every 10 samples; end of sample queue)	85-115% of recovery (Prior to sample analysis)	< 15 RPD (Every 20 samples through a sample queue)	80-120 % recovery (Every 20 samples through a sample queue)
O, H stable isotopes of water***	RSKSOP-296v1	NA	Difference of calibrated/true < 1‰ for δ^2H & < 0.2‰ for $\delta^{18}O$ (Beginning, end and every tenth sample)	Working stds calibrated against IAEAstds.† (Beginning, end, and every tenth sample)	Standard deviation ≤ 1‰ for δ^2H and < 0.2‰ for $\delta^{18}O$ (every sample)	NA

* This table only provides a summary; SOPs should be consulted for greater detail.
**Surrogate compounds spiked at 100 ug/L: p-bromofluorobenzene and 1,2-dichlorobenzene-d4, 85-115% recovery.
***Additional checks: internal reproducibility prior to each sample set, std dev ≤ 1 ‰ for δ^2H and ≤ 0.1 for $\delta^{18}O$
†International Atomic Energy Agency (VSMOW, GISP, and SLAP)
Corrective actions are outlined in the SOPs.
MDL = Method Detection Limit
QL = Quantitation Limit
PE = Performance Evaluation

Table 9. Region VIII laboratory QA/QC requirements for semi-volatiles, GRO, DRO.

QC Type	Semivolatiles	DRO	GRO	Frequency
Method Blanks	<RL Preparation or Method Blank, one with each set of extraction groups. Calibration Blanks are also analyzed	<RL Preparation or Method Blank	<RL Preparation or Method Blank and IBL	At least one per sample set
Surrogate Spikes	Limits based upon DoD statistical study (rounded to 0 or 5) for the target compound analyses.	60-140% of expected value	70-130% of expected value	Every field and QC sample
Internal Standards Verification.	Every sample, EICP area within -50% to +100% of last ICV or first CCV.	NA	NA	Every field and QC sample
Initial multilevel calibration	ICAL: minimum of 6 levels (.25 -12.5 ug/L) , one is at the MRL (0.50 ug/L), prior to sample analysis (not daily) RSD ≤20%, r^2 ≥0.990	ICAL: 10-500 ug/L RSD<=20% or r^2>=0.990	ICAL: .25-12.5 ug/L for gasoline (different range for other compounds) RSD<=20% or $r^{\wedge 2}$>=0.990	As required (not daily if pass ICV)
Initial and Continuing Calibration Checks	80-120% of expected value	80-120% of expected value	80-120% of expected value	At beginning of sample set, every tenth sample, and end of sample set
Second Source Standards	ICV1 70-130% of expected value	ICV1 80-120% of expected value	ICVs 80-120% of expected value	Each time calibration performed
Laboratory Control Samples (LCS)	Statistical Limits from DoD LCS Study (rounded to 0 or 5) or if SRM is used based on those certified limits	Use an SRM: Values of all analytes in the LCS should be within the limits determined	Use and SRM: Values of all analytes in the LCS should be within the limits determined by the supplier. Otherwise 70-130% of expected value	One per analytical batch or every 20 samples, whichever is greater

		by the supplier. Otherwise 70-130% of expected value		
Matrix Spikes (MS)	Same as LCS	Same as LCS	70-130% of expected value	One per sample set or every 20 samples, whichever is more frequent
MS/MSD	% Recovery same as MS RPD ≤ 30	% Recovery same as MS RPD ≤ 25	% Recovery same as MS RPD ≤ 25	One per sample set or every 20 samples, whichever is more frequent
Reporting Limits*	0.1 µg/L (generally)[1] for target compounds HF special compounds are higher	20 µg/L[1]	20 µg/L[2]	NA

[1]Based on 1000 mL sample to 1 mL extract

[2]Based on a 5 mL purge

*see QAPP Table 7

Table 10. Region III detection and reporting limits for glycols.

Analyte‡	Detection Limit (µg/L)†	Reporting Limit (µg/L)†
2-butoxyethanol	NA	NA
diethylene glycol	NA	NA
triethylene glycol	NA	NA
tetraethylene glycol	NA	NA

† Detection and reporting limits are still being determined, most will be between 10 and 50 pbb.

‡ The samples are analyzed according to OASQA On Demand Procedures- See the QA manual for procedures. See Section 13.1.4.2 Procedure for Demonstration of Capability for "On-Demand" Data (Metzger et al., 2011)

Table 11. Region III laboratory QA/QC requirements for glycols.

QC Type	Performance Criteria	Frequency
Method Blanks	<RL	One per every 20 samples
Solvent Blanks	<RL	One per every 10 samples
Initial and Continuing Calibration Checks	80-120% of expected value	At beginning of sample set, after every tenth sample, and end of sample set
Second Source Standards	80-120% of expected value	Each time calibration performed
Laboratory Control Samples (LCS)	80-120% of expected value	One per analytical batch or every 20 samples, whichever is greater
Matrix Spikes (MS)	70-130% of expected value	One per sample set or every 20 samples, whichever is more frequent
MS/MSD	RPD $\leq$ 25	One per sample set or every 20 samples, whichever is more frequent

RL = Reporting Limit

Corrective Actions: If any samples are affected by failure of a QC sample to meet its performance criteria, the problem shall be corrected and samples will be re-analyzed. If re-analysis is not possible (such as lack of sample volume), the data will be qualified with a determination as to impact on the sample data.

Table 12. Isotech laboratory QA/QC Requirements for $\delta^{13}C$ of DIC (Dissolved Inorganic Carbon)

QC Type	Performance Criteria	Frequency
Mass Spec Calibration Check	Difference of calibrated/true $\leq$ 0.5‰	One @ beginning of day, and one after samples analyzed
Mass Spec Zero Enrichment Check	0 +/- 0.1 ‰	Once a day
Lab Duplicates	$\leq$ 1 ‰	1 per every 5 samples**

*Working standards calibrated against IAEA (International Atomic Energy Agency) standard LSVEC and NBS-19; referenced to $\delta^{13}C$ of the Peedee belemnite (NIST material).

**If < 5 samples are submitted, run a duplicate regardless of total number.

Corrective Actions: If any samples are affected by failure of a QC sample to meet its performance criteria, the problem shall be corrected and samples will be re-analyzed. If re-analysis is not possible (such as lack of sample volume), the data will be qualified with a determination as to impact on the sample data.

Table 13. Isotech Laboratory QA/QC Requirements for $\delta^{13}C$ of dissolved methane and δD of dissolved methane.

QC Type	Performance Criteria	Frequency
Mass Spec Calibration Check	Difference of calibrated/true $\leq$ 0.5‰ for $\delta^{13}C$ and $\leq$ 3‰ for δD	One @ beginning of day and after samples are analyzed for $\delta^{13}C$*; one @ beginning of day and every tenth sample for δD**
Mass Spec Zero Enrichment Check	0 +/- 0.1 ‰ for $\delta^{13}C$ and 0 +/- 1 ‰ for δD	Once a day for $\delta^{13}C$ and every tenth sample for δD
Lab Duplicates	$\leq$ 1 ‰ for $\delta^{13}C$ and $\leq$ 3‰ for δD	1 per every 10 samples***
Preparation System Check/Reference Standards	$\leq$ 1 ‰ for $\delta^{13}C$ and $\leq$ 3‰ for δD	One per every 10 samples

*Working standards calibrated against IAEA (International Atomic Energy Agency) standard LSVEC and NBS-19; referenced to $\delta^{13}C$ of the Peedee belemnite (NIST material).

**Working standards calibrated against VSMOW, SLAP, and GISP; referenced to VSMOW.

***If < 10 samples are submitted, run a duplicate regardless of total number.

Corrective Actions: If any samples are affected by failure of a QC sample to meet its performance criteria, the problem shall be corrected and samples will be re-analyzed. If re-analysis is not possible (such as lack of sample volume), the data will be qualified with a determination as to impact on the sample data.

Table 14. USGS laboratory QA/QC requirements for $^{87}Sr/^{86}Sr$ analysis using TIMS*

QC Type	Performance Criteria	Frequency
Blanks	<1 ng per analysis	One per month during period of sample analyses. An unacceptable blank disqualifies all analyses back to previous acceptable blank.
Initial and Continuing Calibration Checks using USGS laboratory standard EN-1** ("operational" checks)	The value is expected to repeat to ± 0.003 percent (3 sigma) in replicate analyses of the $^{87}Sr/^{86}Sr$.	EN-1 is analyzed once for every 10 analyses of unknowns or more frequently.
Lab Duplicates		In a given suite of samples, any "unexpected" values are automatically repeated. Blind duplicates are analyzed every 15 to 20 samples.

*Thermal Ionization Mass Spectrometry

**Internal standard EN-1 (contained Sr is that of modern sea water)

Corrective Actions: If any samples are affected by failure of a QC sample to meet its performance criteria, the problem shall be corrected and samples will be re-analyzed. If re-analysis is not possible (such as lack of sample volume), the data will be qualified with a determination as to impact on the sample data.

7.0 Figures

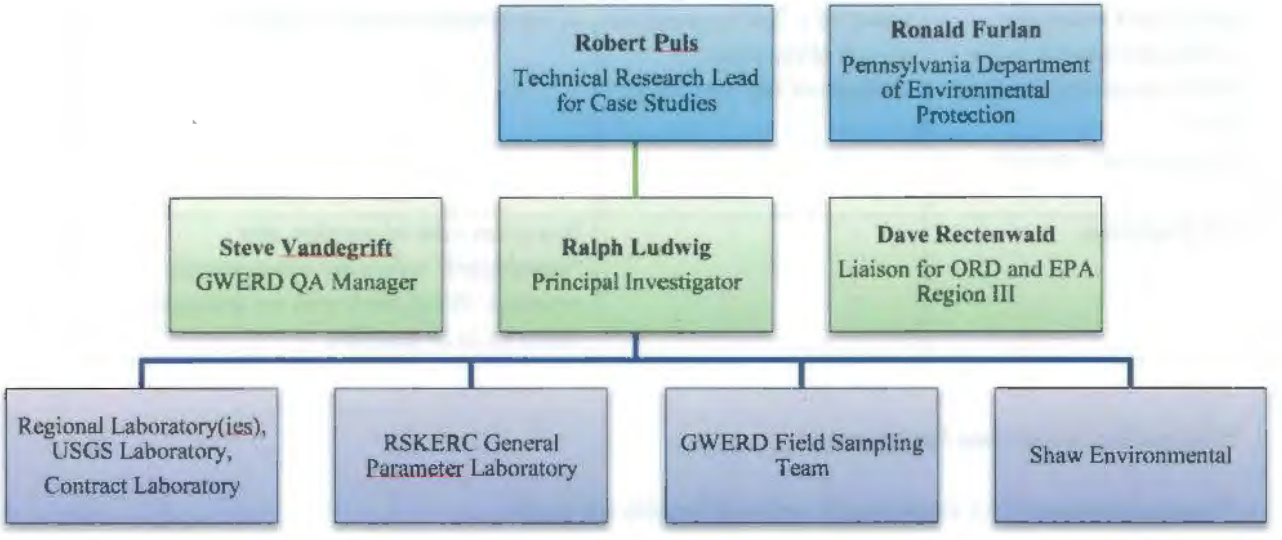

Figure 1. Organizational chart for the Hydraulic Fracturing Retrospective Case Study, Marcellus Shale, Bradford-Susquehanna Counties, PA.

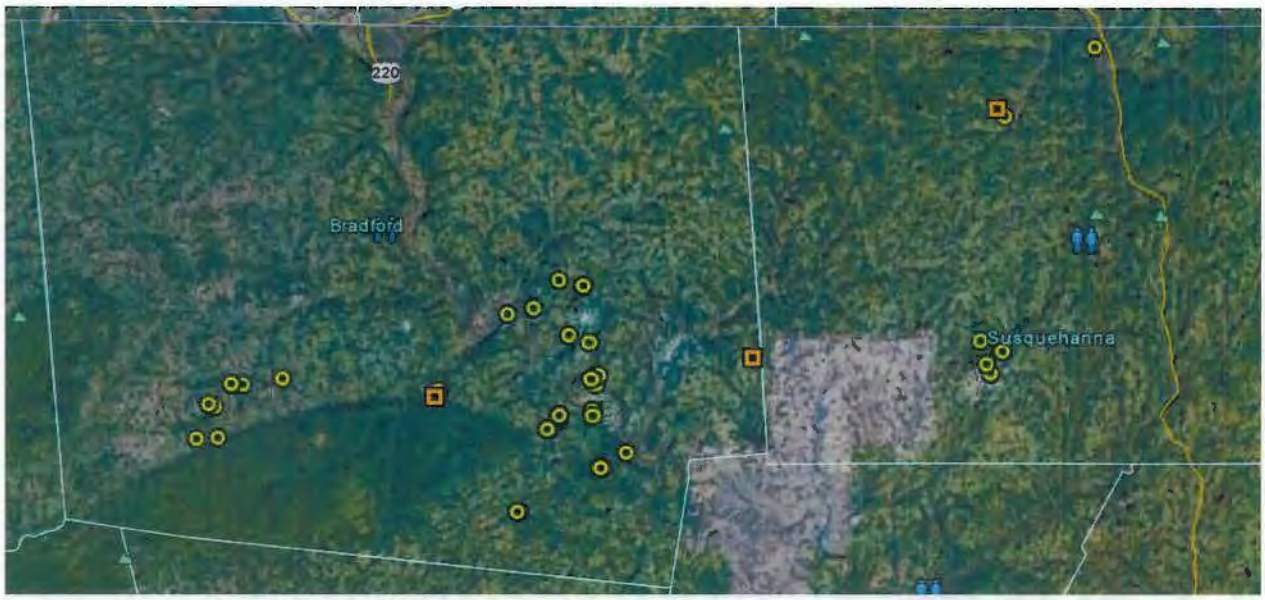

Figure 2. Map showing locations of domestic wells and springs to be sampled in Bradford-Susquehanna Counties, PA. (Circles denote domestic well locations; squares denote spring locations)

USEPA, ORD, NRMRL

Sample Analysis Request and Chain of Custody (COC) Record

Page ___ of ___

Project:
Location:
Project Manager/Phone:

Lab Name:
Address:
Contact Name/Phone:

Shipping Method:
Shipping Tracking Number:

Shipping Date:
Total Number of Shipping Containers:

Sample Number	Sample Matrix/Description	Date/Time Collected	Container Type	Preservative	Number of Containers	Requested Parameters				Special Instructions

Relinquished By: Printed name: _____ Signature: _____ Affiliation: _____ Date: _____ Time: _____
Received By: Printed name: _____ Signature: _____ Affiliation: _____ Date: _____ Time: _____
Comments:

Relinquished By: Printed name: _____ Signature: _____ Affiliation: _____ Date: _____ Time: _____
Received By: Printed name: _____ Signature: _____ Affiliation: _____ Date: _____ Time: _____
Comments:

Pink copy - Field Custodian, Yellow copy - Lab Custodian, White copy - Project Manager

EPA-442 (CIN) (09/08)

Figure 3. Chain of Custody form for submittal of water samples to R.S. Kerr Environmental Research Center.

APPENDIX A

Isotope Support for the EPA Hydraulic Fracturing Study by the U.S. Geological Survey (USGS) Denver CO

Background: Strontium is an alkaline earth element that closely follows calcium in the geochemical and biological cycles. The critical parameter is the $^{87}Sr/^{86}Sr$ ratio which can be determined to a high degree of precision by thermal ionization mass spectrometry (TIMS). ^{86}Sr is a stable isotope of strontium whereas some of the ^{87}Sr is radiogenic from the decay of ^{87}Rb. In hydrologic studies, Sr isotopes are used to study (1) mixing of waters, (2) groundwater evolution due to water-rock interaction, (3) isotopic characterization of aquifers, and (4) weathering including the impact of climate change and acid rain. Numerous examples of each of these are available in the scientific literature. The addition of Sr isotopes to dissolved ion, trace metal, and other isotopic analyses (e.g., O and H) provides a powerful combination for addressing critical hydrologic and hydrochemical problems as shown by the selected references.

USGS Capability: Researchers in USGS isotope laboratories have been analyzing Sr isotopes for nearly a half century with ever increasing precision as instrumentation continually improves. The laboratory in Denver has two state-of-the-art TIMS and clean laboratories for these analyses. During the past 20 years, the USGS Geochemistry Team has worked on the Yucca Mountain Project under a stringent Quality Assurance/Quality Control program, and the team continues to use the DOE-approved technical procedures (attached).

Application to Hydraulic Fracturing Study: Formation water is typically many times more saline than fresh water and commonly more saline than ocean water. When hydraulic fracturing fluids are injected into rock units, it mixes with the formation water, and the flowback water typically has a high salinity. Potential contamination of groundwater can occur from the injection water which commonly contains a number of proprietary chemical compounds and flowback water which is a mixture of injection water and formation water. Use of Sr isotopes to detect contamination associated with the hydraulic fracturing process requires samples of (1) uncontaminated groundwater, (2) hydrofracking water, and (3) flowback water.

Scope and Cost of Analyses: Depending on the isotopic variability of the three water types, we anticipate that several tens of samples would be required for each site study. The cost of $575 per sample will include the following:

1 A high precision $^{87}Sr/^{86}Sr$ analysis with a 2-sigma uncertainty of ±0.00002.

2 ICPMS analysis of Sr concentration (coefficient of variation of ±5 percent).

3 Sr isotope measurements of USGS standard EN-1 which is analyzed every six samples. The $^{87}Sr/^{86}Sr$ values for EN-1 allow precise interlaboratory comparisons of analyses. These data will be compiled and included in the report.

4 For each study site, a report describing the isotopic results and their implications can be prepared.

5 Other isotopes (O, H, C, U, Pb) and other dissolved ions and trace metal concentrations can be determined by the USGS laboratories in Denver if needed.

6 USGS personnel can participate or advise in the specific site studies and sample collection if needed by the EPA.

Brenot, A., Baran, N., Petelet-Giraud, E., Negrel, P., 2008, Interaction between different water bodies in a small catchment in the Paris Basin (Breville, France): Tracing multiple Sr sources through Sr isotopes coupled with Mg/Sr and Ca/Sr ratios: Applied Geochemistry, v. 23, p. 58-75.

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Gosselin, D.C., Harvey, F. Edwin, Frost, Carol, Stotler, Randy, Macfarlane, P. Allen, 2004, Strontium isotope geochemistry of groundwater in the central part of the Dakota (Great Plains) aquifer, USA: Applied Geochemistry, v. 19, 359-357.

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Shand, P., Darbyshire, D.P.F., Love, A.J., Edmunds, W.M., 2009, Sr isotopes in natural waters: Applications to source characterisation and water-rock interaction in contrasting landscapes. Applied Geochemistry v. 24, p.574-586

Singleton, M.J., Maher, K., DePaolo, D.J., Conrad, M.E., and Dresel, P.E., 2006, Dissolution rates and vadose zone drainage from strontium isotope measurements of groundwater in the Pasco Basin, WA unconfined aquifer: Journal of Hydrology, v.321, p. 39-58.

Prepared by:

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Rb-Sr Isotope Geochemistry

1. INTRODUCTION. This technical procedure describes the application and use of the Rb-Sr isotope system as a geochronometer and as a tracer of geologic processes and materials including rocks, minerals, water, and various man-made materials that contain Sr. This procedure applies to all U.S. Geological Survey (USGS), Yucca Mountain Project Branch (YMPB) and support personnel who perform these quality-affecting activities in support of the Office of Civilian Radioactive Waste Management (OCRWM) program.

Work initiated in accordance with procedures superseded by this technical procedure will be completed in accordance with this technical procedure. There is no impact to previous activities as a result of this new procedure. Modifications to this procedure shall be processed in accordance with YMPB-USGS-QMP-5.01, Preparation of Technical Procedures.

The utility of the Rb-Sr decay system in geochronology and isotope tracer studies is described by Faure (1986). ^{87}Rb decays to ^{87}Sr with a half-life of 48.8 billion years, and the change in isotopic composition of Sr (measured as $^{87}Sr/^{86}Sr$ where ^{86}Sr is a nonradiogenic isotope) is a function of the time-integrated $^{87}Rb/^{86}Sr$ ratio of the host environment. Geochemically, Rb is an alkali metal that closely follows K, and Sr is an alkaline-earth element with close affinities to Ca.

One form of the basic decay equation follows:

$$(^{87}Sr/^{86}Sr)p = (^{87}Sr/^{86}Sr)i + (^{87}Rb/^{86}Sr)p*(e^{\lambda t} - 1)$$

Where subscripts "p" and "i" refer to "present-day" and "initial", respectively; "t" is time in years; and e is the decay constant for ^{87}Rb ($1.42*10^{-11}$ yr^{-1}).

For geochronologic applications, the above equation is solved for "t" which is the interval of time since the rock or mineral system formed with an initial Sr isotopic composition of $(^{87}Sr/^{86}Sr)i$ assuming closed system evolution (i.e. no loss or gain of parent or daughter isotopes other than by radioactive decay). For tracer studies, the above decay equation may or may not be relevant. Initial Sr isotope values ($^{87}Sr/^{86}Sr)i$ values for igneous rock are valuable for characterizing the sources of magmas from which the rocks formed including possible assimilation of crustal rocks during ascent of the magmas. For this usage, the age of the system and the $(^{87}Rb/^{86}Sr)p$ must be known so that $(^{87}Sr/^{86}Sr)p$ can be corrected for the ingrowth of radiogenic ^{87}Sr. Other materials for which Sr isotopes can be effectively used as tracers or for characterization include calcite deposits such as in veins or caleretes, marine and terrestrial limestones; subsurface and surface waters and other waters such as may occur in a tunnel environment; and other Sr-Ca bearing materials, including cement/concrete and conveyor belts where the isotope ratios are used simply for baseline characterization of materials that may be introduced into a repository and subsequently impact other materials such as dust and condensate.

2. RESPONSIBILITIES.

2.1 Principal Investigator is responsible for assuring compliance with this procedure and for conducting the activities described in this procedure.

2.2 YMPB and Support Personnel are responsible for conducting the activities described in this procedure.

3. INTERFACES. The USGS may receive samples from the YMP Sample Management Facility following procedures for sample transmittal and control.

4. TECHNICAL REQUIREMENTS. Technical requirements of applicable planning documents associated with Rb-Sr Isotope Geochemistry are met through the implementation of this procedure. There are no other technical requirements.

5. ASSOCIATED WORK ACTIVITIES. Other work activities and procedures associated with implementation of this procedure include:

- YMPB-USGS-GCP-25, *Determination of Chemical Composition by Energy Dispersive X-Ray Fluorescence Spectrometry*
- YMPB-USGS-GCP-38, *Determination of Chemical Composition by Inductively Coupled Plasma Mass Spectrometry*
- YMPB-USGS-GCP-42, *Calibration of Laboratory Scales and Analytical Balances*

6. METHODS. The general principles of isotope-dilution techniques are described by Faure (1986). Procedures described herein for the analyses of rock samples in the Rb-Sr laboratory (Denver, Colorado) are similar to those summarized by Peterman and others (1985). Adaptations of these methods are readily made for other materials. The use of high-purity reagents with certifications and ultra-high purity water (18×10^6 ohms resistivity, hereafter referred to as UHP water) facilitates maintenance of a low-blank environment.

6.1 Methods:

6.1.1 Sample Collection and Preparation: Samples analyzed under this procedure will be collected and controlled in compliance with YMPB-USGS-QMP-SII.01, R0 (Identification and Control of Samples). Standard thin sections may be used for preliminary determination of mineralogic composition of some samples. Samples of rock are crushed in a laboratory jaw crusher to particle sizes of 1.0 cm or less. Approximately 100 grams of this material are further reduced to approximately 200 mesh size by pulverizing in a shatterbox using a hardened steel grinding container. To prevent cross contamination among samples, the crushing equipment is cleaned thoroughly between samples by washing and scrubbing using stainless steel brushes.

Other methods of sample preparation including hand picking of grains, can be used as required by the problem and the nature of the samples. For some samples, an approximate 3-gram split of the rock powder can be analyzed for K, Ca, Ti, Rb, Sr, Y, Zr, Nb, La, Ce, and Ba on an energy dispersive X-ray fluorescence (XRF) unit preparatory to isotope dilution analyses in accordance with YMPB-USGS-GCP-25,
Determination of Chemical Composition by Energy Dispersive X-Ray Fluorescence Spectrometry.

6.1.2 Chemical Dissolution: Rb and Sr must be liberated from the host material and isolated from potentially interfering elements for isotopic analyses. The type of material dictates the method of dissolution as described below:

6.1.2.1 Silicate Samples: A few tens to hundreds of milligrams) of silicate powder is weighed for dissolution. A measured amount of Rb and Sr spike solution may be added if isotope-dilution concentrations are required. The spikes consist of known concentration of ^{84}Sr and ^{87}Rb. Sample dissolution is accomplished through a combination of small amounts of concentrated H_2SO_4, HCl, $HClO_4$,or HNO_3 with concentrated HF. After refluxing on a hot plate to dryness the resultant precipitate is brought into solution with HCl or HNO_3 and centrifuged. The supernatant solution is pipetted in small volumes onto an ion-exchange resin column pretreated with HCl or HNO_3. After washing with a measured volume of HCl or HNO_3 acid, the final solution containing the purified Sr is collected in a Teflon beaker and dried on low heat. The sample is transferred to the mass spectrometer laboratory for isotopic analysis.

Alternatively, Rb and Sr concentrations can be determined by ICP-MS, according to YMPB-USGS-GCP-38, *Determination of Chemical Composition by Inductively Coupled Plasma Mass Spectrometry.*

6.1.2.2 Carbonate Samples: Carbonate samples are typically weighed and dissolved in weak HCl or HNO_3 leaving admixed silicates intact. Other methods of leaching include, but are not limited to 10 percent CH_3COOH (acetic acid), or 10 percent disodium EDTA (ethylenedinitrilotetraacetate). For isotope dilution determination, a weighed amount of Sr spike is added to the sample before dissolution. The leachate is separated from the insoluable material by centrifuging and the supernatant liquid is transferred to separate container. After drying the leachate with low heat, the residual is dissolved in a small amount of HNO_3 acid. To estimate the proportion of carbonate in the original sample, the acid-leached residue is washed with ultra high purity (UHP) H_2O, dried and weighed. Ion exchange procedures to isolate Sr from the solution are similar to those described above in Para. 6.1.2.1 for the silicate samples.

6.1.2.3 Water Samples: Water samples are weighed and spiked with Sr isotope (if necessary) then evaporated to dryness in Pyrex or Teflon beakers in an environmental hood. The dried sample is brought up in HNO_3 and centrifuged. A portion of sample solution may be prepared for trace element concentration determination by ICP MS in accordance with YMPB-USGS-GCP-38, *Determination of Chemical Composition by Inductively Coupled Plasma Mass Spectrometry*. Sr is isolated by ion-exchange methods, following the procedures in Para. 6.1.2.1.

6.1.3 Mass Spectrometry: Isotopic analyses of Rb and Sr will be done by thermal ionization mass spectrometry (TIMS). A drop of 1.0N HCl is added to the Sr sample (0.1-5 micrograms of Sr), which was prepared as described above in section. 6.1.2. Prior to loading any solutions the rhenium or tantalum filaments used will be outgassed in a vacuum to remove impurities. The Sr sample is dried on the filaments by passing a low current (1.5-2.0 amps) through the filaments. The rhenium sample filaments are configured with an ionizing filament and placed sample turret of the mass spectrometer. Tantalum filaments are used for single filament runs. Following pump down to a source pressure of approximately 4×10^{-7} mm of Hg, an ion beam is generated by heating the sample filaments with the ionizing filament operating at approximately 1.8×10^{3} C. When a stable Sr beam of approximately 0.5-5 volts of ^{88}Sr is attained, data collection is started. Five or more blocks of data are to be taken until an average $^{87}Sr/^{86}Sr$ value with an uncertainty (95 percent confidence level on the mean) of 0.0001 is attained. The measured ratios will be corrected for mass discrimination by normalizing the $^{86}Sr/^{88}Sr$ ratio to a value of 0.11940 and adjusting the other ratios accordingly.

Rb will also be loaded onto a rhenium sample filaments, configured with an ionizing filament, and installed on the source of the Rb mass spectrometer. Operate the ionizing filament at a lower temperature (approximately 1.5×10^{3} C) than that for Sr. Generally three to five blocks of data will yield a suitable mean value with <0.03 percent variation.

The Sr and Rb isotopic ratios will be combined with data on samples and spike weights to calculate Rb and Sr contents, and $^{87}Rb/^{86}Sr$ and $^{87}Sr/^{86}Sr$ ratios.

6.2 Materials and Equipment: Materials and equipment needed to perform this work include:

6.2.1 Sample Preparation:

- Standard thin sections (For indication only)

- Laboratory jaw crusher
- Spex Shatterbox
- Stainless steel brushes
- Kevex energy dispersive X-ray fluorescence unit (For indication only)
- Steel mortar and pestle
- Microscope for hand picking

6.2.2 Chemical Dissolution:

- Ultra-high purity (UPH) H_2O (18.2×10^6 ohms resistivity)
- Ultrex, Baker Analyzed, C Star Suprapur (EM Science) and/or
- reagents of equivalent or higher purity of the following: H_2SO_4 (concentrated) HF (concentrated) $HClO_4$ (concentrated) HNO_3 (concentrated) HCl (concentrated) CH_3COOH (acetic acid) Disodium EDTA (ethylenedinitrilotetraacetate)
- Platinum dishes
- Teflon covers, jars, beakers, tubes and other equipment
- Electronic analytical balance
- NIST traceable weights
- ^{87}Rb spike solution
- NIST SRM-607 Rb standard
- ^{84}Sr spike solution
- NIST SRM-610 or 611 Sr standard
- Hot plate
- Centrifuge
- Ion-exchange resins and columns
- Parafilm
- Environmental hood or laminaire flow hoods
- Appropriate standard laboratory equipment including, but not limited to: quartz, Teflon, and Pyrex beakers; graduated cylinders; and glass and plastic centrifuge tubes (accuracies in all ranges to ±5 percent)
- NIST glass and rock standards such as, but not limited to, SRM-610, SRM-611 and SRM-987 for strontium and SRM-607 for rubidium.

6.2.3 Mass Spectrometry: Including, but not limited to a thermal ionization mass spectrometer (TIMS) e.g. Finnigan MAT 262 and Thermo Elemental Triton; and an inductively coupled plasma (ICP) mass spectrometer e.g. Thermo Elemental PQ-3:

- Rhenium ribbon
- Tantalum ribbon
- EN-1 standard carbonate
- Biotite or K-feldspar mineral samples
- NIST SRM-987 (for strontium)
- NIST SRM-727 (for rubidium)
- BCR-1 standard rock sample
- High purity elemental standard solutions
- NIST 1643 and 1640 water standards
- Liquid N2

Collected data will be traceable to the M&TE used to collect that data by lab notebooks and

computer printouts from the mass spectrometer.

Special handling of equipment is required, e.g., protective gloves, when appropriate.

6.3 Operational checks: Operational checks will be used to determine if equipment is operational and capable of providing acceptable data. Results of an operational check are acceptable by monitoring the mass spectrometer results.

6.3.1 Chemistry Laboratory/Mass Spectrometer: Evaluation of the effectiveness of the chemistry laboratory procedures is achieved primarily by monitoring the mass spectrometer results on accepted standard materials.

Standard materials include, but are not limited to NIST glass and rock standards such as SRM-610, SRM-611, and SRM-987 for strontium or SRM-607 for rubidium. Operational checks on the mass spectrometers are performed at least every 30 samples or as necessary by analyzing a laboratory standard material For Sr the lahoratory standard is calcium carbonate prepared from a modern *tridacna* (giant clam) shell collected from Enewetok Lagoon and designated EN-1. Sr in the clam shell represents the isotopic composition of modern sea water. Because the $^{87}Rb/^{85}Rb$ ratio is constant in nature, rubidium isotopic measurements are checked by analyzing Rb from an unspiked biotite or K-feldspar. These operational checks of the chemistry and mass spectrometry laboratories shall incorporate components that measure and/or regulate volume, vacuum, filament current/temperature, accelerating voltage, and ion-beam current. If the results of these operational checks are not within acceptable limits per Para. 11 of this procedure, mass spectrometer and/or laboratory operations are suspended until the problem(s) is (are) identified and rectified. If elemental concentrations of the standards indicate a significant change in the spike solution concentration then the affected spikes are re-determined with NIST standards. These checks will be documented in the mass spectrometer logbook.

6.3.2 Analytical Balance: An operational check of the analytical balance will be performed periodically using class 1 weights, which are traceable to NIST certification. Annual calibration will be performed in accordance with YMPB USGS GCP-42, Calibration of Laboratory Scales and Analytical Balances. Operational checks will be documented in a lab notebook.

7. PREREQUISITES, LIMITS, PRECAUTIONS, AND ENVIRONMENTAL CONDITIONS.

7.1 Prerequisites: There are no special prerequisites or precautions associated with the implementation of this procedure. Although a clean area (e.g. HEPA filtered) is necessary for chemistry operations.

7.2 Limits: Mass spectrometers are complex systems composed of a number of sensitive electronic components. Any electronic problem will commonly manifest itself as beam instability during the course of an analysis. This is identified immediately by the operator on the basis of an unstable signal. The instruments will be shut down until the problem is rectified. There are no unconstrained assumptions in the laboratory procedures that have not been experimentally tested during the long-term operation of the facility.

7.3 Precautions: Besides the usual laboratory safety equipment there are no special precautions associated with the implementation of this procedure.

7.4 Environmental Conditions: Water samples should be processed in an environmental hood.

8. ACCEPTANCE CRITERIA. The satisfactory performance of this procedure can be judged by the quantitative replicate analyses of NIST-certified standard samples. Isotope dilution measurements will be accurate to 1 percent of their values (2 sigma) or better. Measurements of $^{87}Sr/^{86}Sr$ will be accurate to 0.015 percent or better. Total laboratory blanks for Rb and Sr will be determined as necessary, and these shall be below 10 nanograms for the data to be accepted.

8.1 Unless otherwise stated, the precision needed for all measurements specified in this procedure is 5 in the last significant figure. Volume and temperature measurements within the chemical dissolution process and measurements of vacuum, filament current/temperature and accelerating voltage within the mass spectrometry analysis are approximate and absolute determination of these parameters is not necessary for successful performance of the analysis. Approximate numbers are provided within this procedure to ensure consistency between samples and standards tested. These measurement parameters are encompassed within the operational checks of the chemistry/mass spectrometry procedures where proper operation of the system is validated by testing standards of known characteristics.

9. SAMPLES. Samples are handled as part of this procedure and shall be identified and controlled in accordance with YMPB-USGS-QMP-SII.01, *Identification and Control of Samples.*

9.1 Identification and Traceability: Samples shall be controlled and tracked in compliance with YMPB-USGS-QMP-SII.01, R0, *Identification and Control of Samples.*

9.2 Control, Storage, and Disposition: Samples shall reside in the custody of the PI, or delegate, who shall store them in a secured area at the Denver Federal Center, Denver, Colorado. Final disposition of individual samples, including transfer to another YMP participant, disposal, or the need for archiving, shall be determined by the PI and shall be documented. Total consumption of a sample during analysis shall also be documented.

9.3 Special Treatment: No special handling, storage and/or shipping are required unless the PI designates the sample(s) as special. Special samples will be treated accordingly and documented.

9.4 Nonconforming Samples: Nonconforming samples will be documented in accordance with YMPB-USGS-QMP-SII.01.

10. SOFTWARE. Software is used in this procedure are an integral part of the mass spectrometer equipment and is verified by system calibrations performed per the requirements of this procedure. Software used in this procedure will be controlled and documented in accordance with YMPB-USGS-QMP-SI.01, *Software Management*.

11. MEASURING AND TEST EQUIPMENT.

11.1 Calibration Requirements: Calibration of selected equipment is required. All calibrations will be performed and documented in accordance with YMPB-USGS-QMP-12.01, *Control of Measuring and Test Equipment*, including application of calibration status stickers and reporting of out of calibration conditions. Measuring and test equipment (M&TE) that requires calibration include:

11.1.1 Mass Spectrometer(s): The mass spectrometer(s) is calibrated independently of the laboratory by analyzing the NIST standards SRM-987 (strontium) and/or SRM-727 (rubidium). These standards are salts of the elements and therefore do not require extensive laboratory preparation. These calibrations will be performed annually or as necessary.

11.1.2 NIST Traceable Weights: NIST traceable weights are calibrated every 5years or as necessary by an OCRWM OQA approved/accepted supplier.

11.1.3 Analytical Balance: The laboratory scales and analytical balances arecalibrated in accordance to YMPB-USGS-GCP-42, *Calibration of Laboratory Scales and Analytical Balances*. Operational checks will bedocumented in a laboratory notebook.

12. CONSUMABLE STANDARDS/MATERIALS. Consumable materials will he purchased from an OCRWM approved vendor, or from a non-OCRWM vendor for which justification is documented

and approved in accordance with YMPB-USGS-QMP-12.01. Each container or consumable will be labeled with shelf-life information and date. Use of consumable standards beyond the expiration dates is possible if the material quality can be verified by the PI or by an OCRWM approved verification plan. Comparison of consumable materials can be verified with the successful analysis of standards and sample materials. Standard materials include, but are not limited to, SRM-987, NBS-611 and other NIST traceable and internationally accepted USGS standard materials. Sr isotope standards do not change with time due to the long half-life of 87Rb and shelf life is not applicable.

13. HANDLING, STORAGE AND SHIPPING OF EQUIPMENT AND CONSUMABLES. No special handling, storage and/or shipping are required. All material and equipment shall be as per listed manufacturer or equivalent and will adhere to all federal, state, and local requirements. Equipment and consumable materials will be handled and stored in a manner consistent with USGS chemical safety policies. Use of acid-storage cabinets, secondary containment, personal protective equipment, and limited access practices will be used as appropriate. Bench-top chemistry is performed under HEPA-filtered air flow in temperature-controlled laboratories. Cleanliness of the labware, lab environment, and consumable reagents is monitored by routine inclusion of total-process blanks (pure spike solution that undergoes the entire chemical digestion and separation processes). No shipping of equipment or consumables is required.

14. ELECTRONIC MANAGEMENT OF INFORMATION. Data will not be released from the laboratory until all samples of a given set have been examined for internal coherence. Mass spectrometric measurements of isotopic ratios are obtained on hard copy as output from the instruments. The relevant ratios are transferred by data entry to electronic media and then retrieved from this media for double back-checking against the mass spectrometer records. Sample weights and spike weights are also entered into electronic media and then double-back checked against entries in the laboratory notebooks. All of the checking is done before the technical data submittal. The maintenance of security and integrity of any electronic data files shall be ensured by using password protected drives which are routinely backed up.

15. RECORDS. The following QA:QA records are submitted by the PI, or delegate, to the Records Processing Center through the Records Management Specialist in accordance with YMPB-USGS-QMP-17.01, *Quality Assurance Records Management*: 15.1 Records Packages: The following may be submitted as part of a records package:

15.1.1 Data Records: The basic completed analytical data sets obtained will consist of the Rb and Sr contents (if applicable) and the $^{87}Sr/^{86}Sr$ ratios of the samples. These are obtained from the mass spectrometer analyses, the sample and spike weights, and the concentrations of the Rb and Sr spike solutions.

- Table of Sr Data
- Record of Mass Spectrometer Run
- Rb-Sr Sample Data Sheet (if appropriate)
- Copy of Calibration Certificates for Weight(s) (if appropriate)
- Copy of Mass Spectrometer Calibration sheet.
- Copy of Inclusive Pages from Laboratory Notebook (pages with inclusive operational check dates, if appropriate)

15.1.2 Supporting Information:

- Calibration documentation identified in Para. 11.1 shall be submitted as supporting information.
- Chemistry laboratory notebooks shall record, at a minimum, sample identification and dates of analyses.
- Mass spectrometer logbooks shall record, at a minimum, sample numbers, dates analyzed, element analyzed, instrument identification, and instrument operator.
- Notebooks and logbooks contain supporting information and are not considered data unless specified so by the PI. If a notebook or logbook contains data, a statement will be noted in the book documenting which information is data. As appropriate, the documentation containing the information shall be submitted as part of the data records package identified in Para. 15.1.1.

Information obtained from the use of standard thin sections and the Kevex energy dispersive XRF unit is used in this procedure for indicative purposes only and does not affect the outcome and quality of the data acquired from the use of this procedure.

15.2 Individual Records: None

16. REFERENCES. References cited in this procedure are listed below.

- YMPB-USGS-QMP-5.01, *Preparation of Technical Procedures*
- YMPB-USGS-QMP-12.01, *Control of Measuring and Test Equipment*

- YMPB-USGS-QMP-17.01, *Quality Assurance Records Management*
- YMPB-USGS-QMP-SI.01, *Software Management*
- YMPB-USGS-QMP-SII.01, *Identification and Control of Samples*

YMPB-USGS-GCP-25, *Determination of Chemical Composition by Energy Dispersive X-Ray Fluorescence Spectrometry*

- YMPB-USGS-GCP-38, *Determination of Chemical Composition by Inductively Coupled Plasma Mass Spectrometry*
- YMPB-USGS-GCP-42, *Calibration of Laboratory Scales and Analytical Balances*
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17. ATTACHMENTS. None.

18. HISTORY OF CHANGES.

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