

GWERD QUALITY ASSURANCE PROJECT PLAN

Title: Hydraulic Fracturing Retrospective Case Study, Marcellus Shale, Washington County, PA

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<u>/S/</u>	<u>5/6/2013</u>
Richard Wilkin, Principal Investigator	

APPROVALS:

<u>/S/</u>	<u>5/6/2013</u>
David Jewett, Branch Chief	

<u>/S/</u>	<u>5/6/2013</u>
Kelly Smith, GWERD Research Lead for Case Studies	

<u>/S/</u>	<u>5/6/2013</u>
Steve Vandegrift- GWERD QA Manager	

Distribution List:

Russell Neill, EPA/ORDINRMRL/GWERD
Steve Acree, EPA/ORDINRMRL/GWERD
Zell Peterman, U.S. Geological Survey
Alex Kirkpatrick, Student Contractor
Sujith Kumar, CB&I
Shauna Bennett, CB&I QC Coordinator*
Gregory Oberley, EPA Region VIII

Tony Lee, EPA/ORD/NRMRL/GWERD
Randall Ross, EPA/ORD/NRMRL/GWERD
Chris Ruybal, Student Contractor
Cherri Adair, EPA/ORD/NRMRL/GWERD
Mark White, EPA/ORD/NRMRL/GWERD
Cynthia Caporale, EPA Region III
Mark Burkhardt, EPA Region VIII

*will distribute to CB&I staff

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EPA does not consider this internal planning document an official Agency dissemination of information under the Agency's Information Quality Guidelines, because it is not being used to formulate or support a regulation or guidance; or to represent a final Agency decision or position. This planning document describes the overall quality assurance approach that will be used during the research study. Mention of trade names or commercial products in this planning document does not constitute endorsement or recommendation for use.

The EPA Quality System and the HF Research Study

EPA requires that all data collected for the characterization of environmental processes and conditions are of the appropriate type and quality for their intended use. This is accomplished through an Agency-wide quality system for environmental data. Components of the EPA quality system can be found at <http://www.epa.gov/quality/>. EPA policy is based on the national consensus standard ANSI/ASQ E4-2004 *Quality Systems for Environmental Data and Technology Programs: Requirements with Guidance for Use*. This standard recommends a tiered approach that includes the development and use of Quality Management Plans (QMPs). The organizational units in EPA that generate and/or use environmental data are required to have Agency-approved QMPs. Programmatic QMPs are also written when program managers and their QA staff decide a program is of sufficient complexity to benefit from a QMP, as was done for the study of the potential impacts of hydraulic fracturing (HF) on drinking water resources. The HF QMP describes the program's organizational structure, defines and assigns quality assurance (QA) and quality control (QC) responsibilities, and describes the processes and procedures used to plan, implement and assess the effectiveness of the quality system. The HF QMP is then supported by project-specific QA project plans (QAPPs). The QAPPs provide the technical details and associated QA/QC procedures for the research projects that address questions posed by EPA about the HF water cycle and as described in the *Plan to Study the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources* (EPA/600/R-11/122/November 2011/[www.epa.gov/hydraulic fracturing](http://www.epa.gov/hydraulic%20fracturing)). The results of the research projects will provide the foundation for EPA's 2014 study report.

This QAPP provides information concerning the Flowback and Produced Water stages of the HF water cycle as found in Figure 1 of the HF QMP and as described in the HF Study Plan. Appendix A of the HF QMP includes the links between the HF Study Plan questions and those QAPPs available at the time the HF QMP was published.

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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, Washington County, PA. An organizational chart for the project is presented in Figure 1.

Dr. Richard Wilkin, U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Robert S. Kerr Environmental Research Center, Ada, OK. Dr. Wilkin is the principal investigator of 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. David Jewett, U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Robert S. Kerr Environmental Research Center, Ada, OK.

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.

Mr. Tony Lee, Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Robert S. Kerr Environmental Research Center, Ada, OK. Mr. Lee is responsible for assisting in ground water and surface water sampling. 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.

Mr. Chris Ruybal, Student Contractor, Ada, OK. Mr. Ruybal is responsible for assisting in ground water sampling. 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.

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Wilkin in understanding ground water flow directions. 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. Wilkin 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, Robert S. Kerr Environmental Research Center (RSKERC), Ada, OK. Mr. Neill is responsible for operation of the Geoprobe rig during ground water sampling and core collection. His HAZWOPER certification is current.

Mr. Mark White, 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. 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. Wilkin with health and safety issues related to the study. Her HAZWOPER certification is current.

Dr. Sujith Kumar, CB&I, Ada, OK. Dr. Kumar is responsible for overseeing the analytical work performed under GWERD's on site analytical contract (stable isotopes, low molecular weight acids, and dissolved gases).

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

Ms. Cynthia Caporale, USEPA Region III Analytical Laboratory, Laboratory Branch Chief/Technical Director. Ms. Caporale will act as a liaison between the Region III 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. Alan Eichler, Pennsylvania Department of Environmental Protection, Mr. Eichler 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 III 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.

Ms. Debbie Fazio, ALS Environmental, Fort Collins, CO. Ms. Fazio is a point of contact with the ALS Environmental laboratory contracted for radiometric analyses.

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 VIII office.

Mr. Barry Evans, U.S. Environmental Protection Agency- Region VII, Kansas City, KS. As the Project Officer, Mr. Evans is responsible for the coordination of case study samples with the Region VII contract laboratory (subcontractor to ARDL, Inc.) for metals and VOC analysis.

Ms. Susan Mravik, 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. Mravik is responsible for assisting with data management by transferring data from the PI to CB&I. CB&I then uploads the data to a secure server. Ms. Mravik also assists the PIs by tracking the status of laboratory analysis of samples, data reports, ADQs, and final QA approvals of data.

Ms. Cynthia Sonich-Mullin, U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory. Ms. Sonich-Mullin is the Director of NRMRL. Ms. Sonich-Mullin will approve all data releases to stakeholders and the public. In addition, when disputes occur she is the ultimate decision maker within NRMRL.

Dr. Gary Foley, U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Robert S. Kerr Environmental Research Center (RSKERC), Ada, OK. Dr. Foley is the Acting Director of RSKERC.

Ms. Kelly Smith, U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Robert S. Kerr

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Environmental Research Center (RSKERC), Ada, OK. Ms. Smith is the GWERD Research Lead for case studies, replacing Dr. David Jewett. Ms. Smith assists in the coordination of communications and contract laboratories between RSKERC and NRMRL Management.

Dr. Alice Gilliland, U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory. Dr. Gilliland was appointed by the NRMRL lab director to serve as the NRMRL Coordinator for all Hydraulic Fracturing research activities within NRMRL. Dr. Gilliland also will assist in management oversight of data summaries.

Ms. Lauren Drees, U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Laboratory Support and Accountability Staff, Cincinnati, OH. Ms. Drees will assist Mr. Vandegrift with the quality assurance review of the Quality Assurance Project Plan (QAPP), assisting with audits, and QA review and validation of data summaries and the final report. Ms. Drees also initiates dispute resolution at the NRMRL level when it cannot be resolved at the Division level within GWERD.

Ms. Holly Ferguson, U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Environmental Technology Assessment, Verification and Outcomes Staff, Cincinnati, OH. Ms. Ferguson will assist Mr. Vandegrift with the quality assurance review of the Quality Assurance Project Plan (QAPP), conducting or assisting with audits, and QA review and validation of data summaries and the final report.

Ms. Michelle Latham, U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Water Supply and Water Resources Division, Cincinnati, OH. Ms. Latham will be responsible for developing communication documents about the Case Studies.

Dr. Wilkin 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. Dr. Wilkin is responsible for tracking laboratory activities, ensuring that samples are received, working with the laboratories to address issues with sample analysis, and ensuring that data reports are received.

1.2 Problem Definition/Background

The retrospective case study in southwest Pennsylvania will investigate the potential impacts of hydraulic fracturing and processes related to hydraulic fracturing on drinking

water resources in Washington County, PA near the town of Hickory. Background information on the retrospective case studies in relation to the national hydraulic fracturing study can be found in “*Plan to Study the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources*” (EPA/600/R-11/122; November 2011/www.epa.gov/hydraulic_fracturing).

The location of this case study was selected in response to complaints about appearance, odors and taste associated with water in domestic wells. Potential sources of ground-water contamination include activities associated with oil and gas production such as leaking or abandoned pits, gas well completion and enhancement techniques, improperly plugged and abandoned wells, as well as activities associated with residential or agricultural practices. Several phases of investigation for this case study are anticipated. This iterative approach is being adopted so that early in the investigation screening investigations will take place (i.e., sampling domestic wells, surface water bodies), particularly 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 contamination or 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 result. On the other hand, if contamination is detected, confirmation sampling would be planned, but also additional studies and methods might be adopted to track the source of contamination, whatever that 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 Washington County, PA have been impacted by hydraulic fracturing processes and the related secondary objective which is to determine the likely pathway(s) of contaminant migration.

In Phase I, selected domestic wells and surface water bodies will be sampled over several events 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 May 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. Phases 1 and 2 are equivalent to Tier 2 and 3, respectively, in the *Plan to Study the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources* (EPA/600/R-11/122/November 2011/www.epa.gov/hydraulic_fracturing).

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), and additional analytes. Phase I sampling is expected to begin in July 2011.

- Version 0 of this QAPP (dated 7/21/2011) 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. QAPP revisions will be posted on the EPA Hydraulic Fracturing website.
- Version 1 of this QAPP includes minor revisions to sampling methodologies and additional analyses prior to a second sampling trip planned for March 2012 (Table 1). An Addendum to Version 1 (dated 12/20/2012) was prepared to document QC acceptance criteria for the reanalysis of samples for metals by ICP-MS for the March 2012 sampling event.
- Version 2 of this QAPP describes additional quality assurance and quality control associated with water sampling and chemical analysis for the May 2013 sampling event (Table 1). As indicated in Table 4, a sampling event was planned for July 2012 but did not take place due to an inability to coordinate the sampling effort within the desired timeframe.

In May 2011, the PI and Technical Research Lead for Case Studies visited with homeowners in the area and selected potential sites for sampling. In June 2011, the PI and Technical Lead for Case Studies met with representatives of the Pennsylvania Department of Environmental Protection and EPA Region III to provide background on the overall HF Study Plan and specifics about the case study in Washington County. This study will be conducted in conjunction with the Pennsylvania Department of Environmental Protection; U.S. Environmental Protection Agency, Region III; 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 - Washington County is located in the southwest corner of Pennsylvania, about 28 miles to the southwest of downtown Pittsburgh. According to the census results of 2000, the population density in Washington County was about 240 people per square mile. Washington County is currently experiencing oil and natural gas exploration targeting the Marcellus Shale. 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 that 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 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). In Washington County, the depth to the Marcellus Shale ranges from about 5000 to 7000 feet below ground surface.

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 May 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 sampling points. On Figure 2, the blue dots represent surface water sampling locations and the yellow dots represent domestic well sampling locations. A total of 17 domestic wells and up to 6 surface water locations are targeted for sampling. For the May 2013 sampling event, a total of up to 17 domestic wells and 2 surface water locations will be sampled subject to access conditions. Water analysis will include a range 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, strontium isotope ratios, and radiometric analyses (gross alpha, gross beta, Ra-226, and Ra-228). 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, redox status, major anions and cations). Some of the chemicals used by hydraulic fracturing companies in Pennsylvania are listed in Table 2. Of the target analytes noted above, those that are critical analytes supporting the primary objective (i.e., to determine if ground-water resources in Washington County, PA have been impacted by hydraulic fracturing processes) of the project are defined in Table 3. 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

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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 3.

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), ALS Environmental in Fort Collins (CO), Region VII contract laboratory, subcontractor to ARDL, Inc. in Mount Vernon (IL), 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 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 4. 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, such as precision, accuracy, and sensitivity. These topics, and associated quality objectives, are discussed in sections 2, 3, and 4.

Systematic planning was performed in the development of this QAPP and the QAPP captures the results of that planning. The elements of a systematic planning approach are presented in Section 3.3.8.1 of the *EPA Quality Manual for Environmental Programs*, CIO 2012-P-01-0, May 5, 2000. Each of these elements is addressed in this QAPP.

SOPs are internal working documents that are not typically made publically available. The majority of these, however, have been made publically available on the EPA Region VIII web site for a separate research effort:
<ftp://ftp.epa.gov/r8/pavilliondocs/LabSOPsAndLabProducedReports/AnalyticalMethodologyUsed-RobertSKerrLaboratory/>.

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 (when this is available for the type of analysis) or some other means as determined to be acceptable by project participants. This could include quality documentation, such as laboratory manuals, Quality Management Plans, and detailed SOPs. Information about the Agency's policy on assuring laboratory competency can be found at http://www.epa.gov/fem/lab_comp.htm. The EPA GP laboratory and the CB&I laboratories, on-site contractor laboratory at RSKERC, will be used to analyze select critical analytes listed in Table 3. 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 3. This laboratory is accredited by the National Environmental Laboratory Accreditation Program (NELAP) through the state of Texas. The USEPA Region III 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 III for glycols is not accredited, but the laboratory follows all the requirements for an accredited method by using EPA Methods 8000C and 8321 for method development and QA/QC. Initial data reported from the glycol analysis will be flagged as "screening" data from a method that is currently being developed. Once the method is validated, they will no longer be flagged as "screening" data. The Region VII contract laboratory (subcontractor to ARDL, Inc.) will be used to analyze for metals and VOCs. The laboratory must be accredited by NELAP for these parameters. Isotech Laboratories, ALS Environmental, and USGS laboratories will not provide data for critical analytes.

1.6 Documents and Records

Data reports will be provided electronically as Excel spreadsheets or Adobe pdf documents. CB&I's raw data is kept on-site at the GWERD and will be provided on CD/DVD to the PI. 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 in spreadsheets.

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 PI's office in 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 Geologic and Hydrological Information

Background information on the geology and hydrology of Washington County is summarized from reports published by Newport (1973) and Williams et al. (1993). The geologic units in Washington County include sedimentary rocks of Pennsylvanian (Monongahela and Conemaugh Groups) and Permian (Washington Formation) age, including sandstone, siltstone, limestone, shale and coal, and unconsolidated Quaternary deposits. The Quaternary deposits consist of alluvium which overlies bedrock in some of the major stream valleys of the county. The alluvium is generally less than 60 feet thick and is made up of clay, silt, sand, gravel, and cobbles derived primarily from local bedrock.

Ground water in Washington County occurs in both artesian and water-table aquifers. Well yields range from a fraction of a gallon per minute to over 350 gallons per minute. Water-bearing zones are generally no deeper than 150 feet below ground surface. Ground-water flow in the shallow aquifer system generally follows topography, moving from recharge areas near hilltops to discharge areas in valleys. Depth to water varies from about 20 to 60 feet below land surface depending on topographic setting. The quality of ground water in Washington County is variable and depends on factors such as formation lithology and residence time. For example, recharge ground water sampled from hilltops and hillsides is typically calcium-bicarbonate type and usually low in total dissolved solids (~500 mg/L). Ground water from valley settings in areas of discharge is typically sodium-bicarbonate or sodium-chloride type with higher values of total dissolved solids (up to 2000 mg/L). Williams et al. (1993) report that concentrations of iron and manganese are frequently above the U.S. EPA's recommended maximum contaminant levels (RMCLs) in the ground water from Washington County. In their study over 33% of water samples had iron concentrations greater than the RMCL (0.3 ppm) and 30% of water samples had manganese concentrations above the RMCL (0.05 ppm). Hard water was also reported as being a common problem in the county. Dissolved solids concentrations in more than one third of the wells sampled by Williams et al. (1993) exceeded 500 mg/L. Concentrations of arsenic, cadmium, chromium, copper, lead, mercury, selenium, silver, and zinc were less than drinking water levels established by the U.S. EPA.

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 are shown in Figure 2. The domestic wells will be sampled using downhole pumps or via homeowner taps. It is believed that most domestic wells are screened between 50 and 200 feet below ground surface. It is anticipated that the monitoring wells will be sampled by GWERD over a period of about 3 years. The timing of the ground-water sampling events is anticipated to start in the summer/fall of 2011 and continue to the spring of 2013 (Table 4). The 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 dedicated pumps (home owner) or where possible by accessing the well directly using pumps lowered down the well casing. By purging the wells with down-hole pumps, the water intake location within the well casing will be controlled. 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 be used for the domestic wells. If it is not possible to use this approach, then these wells will be sampled from the homeowner's tap (ensuring that the tap is not downstream from a water treatment system such as a water softener).

- 1) At each sampling site, GPS coordinates will be collected with a handheld device (Garmin Vista HCx; ± 3 -10 m). Photos will be taken and stamped with the date. Pertinent information about well will be recorded where possible (e.g., depth, well diameter, configuration, etc.). The ground-water level will next be measured using a Solinst water level indicator (or equivalent) and recorded. In cases where a remote pump can be used, the pump will be hooked up with new polyethylene tubing. Tubing will be changed in between each well and the pump will be rinsed with distilled water. The pump (Proactive Hurricane or equivalent) will be lowered down the well casing to a level selected in the field (generally at the middle of the screened section of the well) and powered on. In most cases, well construction details will not be available. The goal in domestic well sampling is

generally to purge 3 well casing volumes prior to sampling. In cases where the well volume can be calculated, 3 well volumes will be targeted as the purge volume. In other cases professional judgment will be used in the field and consider variables such as water volume pumped, water level drawdown, and stabilization of geochemical parameters. In all cases, the water volume pumped will be tracked by recording time and purge rate. It is expected that the pump will yield an initial flow rate of up to approximately 2 L/min. This flow will pass through a flow cell equipped with a YSI 5600 multiparameter probe (or equivalent probes). The rate of pumping will be determined by measuring the water volume collected after approximately 15 seconds into a 4 L graduated cylinder; the desirable pumping rate through the flow cell should be less than 2 L/min. The pumping rate will ideally maintain minimal drawdown. Draw down will be monitored by measuring the water level (where possible) approximately every 10 to 15 minutes. In addition to changing the pump tubing between sampling locations, the pump will be decontaminated using Liquinox detergent and triple-rinsing with tap water followed by deionized water.

- 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 following criteria will be used to determine when parameters have stabilized: pH change of less than or equal to 0.02 units per minute; oxidation-reduction potential change of less than or equal to 0.002 V per minute; specific conductance change of less than or equal to 1% per minute. 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. Four 40 mL VOA vials (amber glass, precleaned, certified) will be collected, without headspace, for VOC analysis using EPA Method 8260B. Hydrochloric acid (HCl; Optima) will be added to the VOA vial after sample collection to obtain a pH < 2 for sample preservation. The samples will be stored and shipped on ice to the Region VII contract with ARDL, Inc. for GC-MS analysis.

- b. Duplicate 60 mL (nominal volume) serum bottles will be collected, without headspace, for dissolved gas analysis (e.g., methane, ethane, propane, n-butane). The bottles will contain a pressed pellet of trisodium phosphate as a preservative and will be sealed with a crimp cap. The serum bottles will be filled and capped underwater in a clean 5 gallon bucket filled with purge water. The samples will be stored and shipped on ice to CB&I, NRMRL-Ada's on-site contractor for analysis. During the final sampling event (planned for May 2013), an additional 2 samples will be collected at selected sites known to have concentrations of dissolved methane by filling and capping the serum bottles without submerging them in the 5 gallon bucket. The serum bottles will also contain TSP as a preservative. In this way, a comparison of dissolved gas results will be obtained by using the two sampling methodologies. To maintain data consistency with previous sampling events, the data summary for the final sampling event will include dissolved gas data for samples collected underwater (submerged serum bottles). The final report will provide the results of the comparison of dissolved gas sampling methods combined with other case study results.
- c. Duplicate 40 mL VOA vials (clear glass, precleaned) will be collected, without headspace, for low molecular weight organic acid analysis using RSKSOP-112v6. 1 M sodium hydroxide will be added in the field as a preservative. The samples will be stored and shipped on ice to CB&I, NRMRL-Ada's on-site contractor for HPLC analysis.
- d. Duplicate 1 L amber glass bottles (precleaned, certified) will be collected for semi-volatile organic compounds (Region VIII SOP No. ORGM-515). Samples will be preserved by storing on ice until shipment. These samples will be shipped on ice to the EPA Region VIII Laboratory for analysis.
- e. Duplicate 1 L amber glass bottles (precleaned, certified) will be collected for diesel range organic (DRO) analysis. These samples will be preserved with HCl (Optima), pH <2, and shipped on ice to the EPA Region VIII Laboratory for analysis.
- f. Duplicate 40 mL amber VOA vials (precleaned, certified) will be collected without headspace for gasoline range organic analysis (GRO). These samples will be preserved with HCl (Optima), pH <2, and shipped on ice to the EPA Region VIII Laboratory for analysis.
- g. Duplicate 40 mL amber VOA vials (precleaned, certified) will be collected for glycol analysis. These samples will be stored and shipped on ice to the EPA Region III Laboratory for analysis.

- h. A 1 L plastic bottle containing a caplet of benzalkonium chloride for preservation will be collected for carbon and hydrogen isotope analyses of dissolved methane. The bottle will be filled underwater in a clean 5 gallon bucket. This sample will be shipped, with bottle inverted, on ice to Isotech Laboratories.
- i. A 1 L plastic bottle will be filled for analysis of radium-226. The sample will be preserved by adding HNO₃ (Optima) to pH<2. The sample will be shipped to ALS Environmental.
- j. A 2 L plastic bottle will be filled for analysis of radium-228. The sample will be preserved by adding HNO₃ (Optima) to pH<2. The sample will be shipped to ALS Environmental.
- k. A 1 L plastic bottle will be filled for analysis of gross alpha and gross beta analysis. The sample will be preserved by adding HNO₃ (Optima) to pH<2. The sample will be shipped to ALS Environmental.
- l. A 1 L plastic bottle will be filled unfiltered for the analysis of total metals concentrations. Analysis of these samples will be by ICP-OES (EPA Method 200.7) for Ag, B, Ba, Be, Ca, Co, Fe, K, Li, Mg, Mn, Na, P, Si, Sr, Ti, and Zn; by ICP-MS (EPA Method 6020A) for Al, As, Cd, Cr, Cu, Mo, Ni, Pb, Sb, Se, Sr, Th, Tl, U, and V; and Hg using cold vapor method (EPA Method 7470A). These samples will be preserved using concentrated HNO₃ (Optima) to a 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 a lab designated under the EPA Region VII contract with ARDL, Inc. Cold shipment and storage is not required for these samples but the samples will be shipped in ice chests packed with ice. The total metal samples will be digested in accordance to the method outlined in EPA Method 200.7.
- m. A 1-liter plastic beaker will be filled for field analyses. Field measurements will consist of turbidity, alkalinity, ferrous iron, and dissolved sulfide. Turbidity (EPA 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 H₂SO₄ to the bromcresol green-methyl red endpoint using a HACH titrator (HACH method 8203, equivalent to EPA Method 310.1 for alkalinity). Ferrous iron will be measured using the 1,10-phenanthroline colorimetric method (HACH DR/2010 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 DR/2010 spectrometer; HACH method 8131, equivalent to Standard Method 4500-S²⁻ D for wastewater).

- n. Next a series of field-filtered samples will be collected using 0.45-micron filter capsules. A 60 mL clear plastic bottle will be filled for analysis of $\delta^{13}\text{C}$ of dissolved inorganic carbon. This sample will be filtered in the field with a high-capacity 0.45-micron capsule filter, and shipped on ice to Isotech Laboratories.
- o. A 1 L plastic bottle will be filled filtered for dissolved metals concentrations. Analysis of these samples will be by ICP-OES (EPA Method 200.7) for Ag, B, Ba, Be, Ca, Co, Fe, K, Li, Mg, Mn, Na, P, Si, Sr, Ti, and Zn; by ICP-MS (EPA Method 6020A) for Al, As, Cd, Cr, Cu, Mo, Ni, Pb, Sb, Se, Sr, Th, Tl, U, and V; and Hg using cold vapor method (EPA Method 7470A). These samples will be preserved using concentrated HNO_3 (Optima) to a $\text{pH} < 2$ (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 a lab designated under the EPA Region VII contract with ARDL, Inc. Cold shipment and storage is not required for these samples but the samples will be shipped in ice chests packed with ice.
- p. One 30 mL clear plastic bottle for CE (capillary electrophoresis) sulfate, chloride, bromide and fluoride. No preservative will be added. The samples will be filtered in the field with a high-capacity 0.45-micron capsule filter, and stored and shipped on ice to the RSKERC general parameters lab.
- q. One 60 mL clear plastic bottle for nitrate + nitrite, ammonium, and TKN (Total Kjeldahl Nitrogen). This sample will be preserved with sulfuric acid (Optima; pH test strips will be used as spot checks on samples to confirm that the sample pH is < 2). The samples will be filtered in the field with a high-capacity 0.45-micron capsule filter, and stored and shipped on ice to the RSKERC general parameters lab.
- r. Duplicate 40 mL glass VOA vials (precleaned, certified) will be collected for analysis of dissolved inorganic carbon (DIC). No preservative added will be added to these samples. The samples will be filtered in the field with a high-capacity 0.45-micron capsule filter, and stored and shipped on ice to the RSKERC general parameters lab.
- s. Duplicate 40 mL glass VOA vials (precleaned, certified) will be collected for analysis of dissolved organic carbon (DOC). These samples will be preserved with phosphoric acid (HPLC Grade) to $\text{pH} < 2$. The samples will be filtered in the field with a high-capacity 0.45-micron capsule filter, and stored and shipped on ice to the RSKERC general parameters lab.

- t. A 20 mL glass VOA will be collected for analysis of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ of water using isotope ratio mass spectroscopy (IRMS) or cavity ring-down spectrometry (CRDS will be used on samples collected in the second and subsequent sampling events using RSKSOP334v0). The sample will be stored and shipped on ice to CB&I, NRMRL-Ada's on-site contractor for analysis.
- u. 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 filtered in the field with a high-capacity 0.45-micron capsule filter, and stored and shipped on ice to the USGS laboratory in Denver, CO.
- v. 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. The archive samples were collected during the first field; it is anticipated that this archive sample will not be collected during subsequent sampling trips.

See Tables 5 and 6 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 and Monitoring Well Samples

Figure 2 shows the location of several surface bodies that will be sampled (blue dots). The same set of samples will be collected as described in section 2.2.1.1. In all cases these surface water samples will be collected from flowing streams that were identified during the May 2011 reconnaissance trip to the site. A total of six sites were targeted for sampling; depending on seasonal flow in these streams, it may not be possible to collect water from all sites during sampling visits. The streams are typically less than 0.5 m deep. Sample bottles will be submerged into the surface water just below the surface and filled as grab samples. The locations of the sampling sites will be recorded with a handheld GPS device. The site will be photographed. General observations about the flow and the stream depth will be recorded in a field notebook. The sampling will be performed as to minimize any capture of sediment into the sampling bottles. Water samples for dissolved metals, all isotope analyses (except methane and radium), anions, nutrients, and inorganic/organic carbon will be filtered using a peristaltic pump and a high-capacity (0.45 micron) capsule filter. Clean tubing will be used prior to sampling and filtration. The readings from the YSI will be recorded by inserting the probe set with

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protective cover directly into the surface water body and allowing readings to stabilize. Again the logging function will be utilized and readings will be recorded in a field notebook.

It is anticipated that several monitoring wells installed around some of the gas production pads and impoundment areas will be sampled. Right now the details on the construction of these wells are not known nor is it known whether EPA will have permission to sample these wells. If these wells are sampled, additional details will be included in subsequent revisions of the QAPP. Sample collection will follow the same guidelines as described above for the domestic well sampling.

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 a 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 SWPAGWxx-yyyy. The xx will move in sequence (i.e., 01, 02, etc.). The yyyy will record the month and year (e.g., 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., SWPAGW05d-0711). Labeling of surface water samples will follow the same approach, except instead of GW, SW will be used in the identification (e.g., SWPASW01-0711).

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, overnight, to the appropriate lab with chain of custody forms (see Figure 3) and custody seal.

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

Upon receipt at RSKERC, all samples shall be logged-in and distributed to appropriate analysts by CB&I 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) form 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 CB&I retains a copy. 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 6°C.

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

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

EPA Region 3 Lab
701 Mapes Road
Ft. Meade, MD 20755-5350
1-410-305-3032
ATTN: Kevin Martin

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

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

Sample receipt and log-in at Isotech shall be conducted as described in their SOP, *Sample Receiving*, SOP205 Revision 0.

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 Rick Wilkin. 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.

Samples for Ra isotope analysis and gross alpha/beta analysis will be sent to:

ALS Environmental
225 Commerce Drive
Fort Collins, CO 80524

Sample receipt and log-in at ALS Environmental shall be conducted as described in their SOP, *Log-in and Distribution of Samples and Workorders*, ALS SOP202 Rev 12.

Samples to be shipped to the EPA Region VII contract with ARDL, Inc. will be overnight delivered via UPS or Fedex, to the contract laboratory awarded the work, with appropriate chain of custody forms (see Figure 3) and the cooler will be sealed with custody seals. Sample receipt and log-in will be conducted per contract lab SOPs.

2.4 Analytical Methods

2.4.1 Ground and Surface Water

Water samples will be collected and analyzed using the methods identified in Table 5. SOPs are internal working documents that are not typically publically available. The majority of these, however, have been made available on the EPA Region VIII web site for a separate research effort:

<ftp://ftp.epa.gov/r8/pavilliondocs/LabSOPsAndLabProducedReports/AnalyticalMethodologyUsed-RobertSKerrLaboratory/>.

Analysis at RSKERC includes capillary electrophoresis (CE, for anions), flow injection analysis (FIA, for Nitrogen-series analyses), carbon analysis using combustion and infrared detection, gas chromatography (GC, for dissolved gas analysis), isotope ratio mass spectrometry or cavity ring-down spectrometry (CRDS to be used for the third and any subsequent sampling events for $\delta^{18}\text{O}$ and $\delta^2\text{H}$ of water), and HPLC analysis for low molecular weight acids. The analytical methods to be used for water samples are presented in Table 5. The RSKSOPs and their associated target analyte list are presented in Table 7 and QA/QC requirements are listed in Table 8.

Samples will be submitted to Isotech Laboratories for analysis of stable isotope ratios of dissolved inorganic carbon ($\delta^{13}\text{C}$) by gas stripping and isotope ratio mass spectrometry (IRMS) and $\delta^{13}\text{C}$ of methane (C1), and $\delta^2\text{H}$ of methane. Isotech Laboratories will follow their own in-house Standard Operating Procedures, including: Isotech, SOP112v2, $^{13}\text{C}/^{12}\text{C}$ 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 $\delta^{13}\text{C}$, (in preparation). A Statement of Work will be provided to Isotech with relevant information presented here:

Samples of ground water will be provided for isotopic analyses of dissolved inorganic carbon (DIC) and methane. The vendor shall not be required to determine the concentration of inorganic carbon or dissolved gases in the samples. The isotope analyses are intended to provide information on the carbon cycle in the system. The measurements will be for $\delta^{13}\text{C}$ of dissolved inorganic carbon, $\delta^{13}\text{C}$ value of C1, and the $\delta^2\text{H}$ of hydrogen in methane. These analyses will support the Hydraulic Fracturing Case Study in southwestern, PA. This project is being conducted under a Category 1 QAPP ("Hydraulic Fracturing Retrospective Case Study, Marcellus Shale, Washington County, PA; QA ID no. G-16403).

Samples will be provided from domestic wells and surface water bodies located in Washington County, Pennsylvania. The wells and surface water bodies will be sampled during the week of [date of sampling]. The vendor will be notified at least one week in advance of the sample collection activities. Duplicate samples will be collected in 10% of the wells, or as otherwise indicated in the approved QAPP. A total of up to 25 samples will be submitted for $\delta^{13}\text{C}$ of dissolved inorganic carbon and up to 25 samples are planned for methane gas analysis. In addition to field duplicates, it is expected that the vendor will select samples for laboratory duplicate analysis in each submitted set to fulfill QA/QC requirements. 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 will be high enough in the samples so that these volumes will be adequate for the analyses. It is likely that many of the samples submitted for methane isotopic analysis will not contain measureable concentrations of methane and therefore no analysis will be possible. 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.

The vendor shall determine the stable carbon isotope ratio of DIC and carbon and hydrogen in methane in the water samples as described above using gas stripping and isotope ratio mass spectrometry. Isotech Laboratories will follow their own in-house Standard Operating Procedures, including: Isotech, SOP112v2, $^{13}\text{C}/^{12}\text{C}$ 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 $\delta^{13}\text{C}$, (in preparation).

Analyses of the laboratory duplicates shall agree within 1 permil $^{13}\delta\text{C}$ and within 3 permil $^2\delta\text{H}$, or less. The measured value of the stable carbon and hydrogen isotope ratio in calibration standards shall be within 0.5 permil or less and 3 permil or less, respectively, of the nominal value in the calibration standards. QA/QC requirements are summarized in the attached tables.

The contractor's results shall be considered acceptable if samples are analyzed as described in previous section and QA/QC requirements as summarized in the attached Tables are met and data deliverables as described below are provided.

Isotech Laboratories shall 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. Results of the analysis shall be reported to Rick Wilkin via e-mail at wilkin.rick@epa.gov within five weeks of the receipt of the samples. The full data packages shall be copied to the GWERD QA Manager, Steve Vandegrift.

Samples will be submitted to ALS Environmental for analysis of radium-226 (EPA Method 903.1, Radium-226 in Drinking Water Radon Emanation Technique), radium-228 (EPA Method 904.0, Radium-228 in Drinking Water), gross alpha and gross beta (EPA Method 900.0, Gross Alpha and Gross Beta Radioactivity in Drinking Water).

ALS Environmental will follow their own in-house Standard Operating Procedures, including: ALS SOP783v9, Radium-226 in aqueous and soil matrices – Radon emanation technique; ALS SOP746v9, Determination of radium-228 according to EPA Method 904.0 or SW846 Method 9320 with modifications; ALS SOP702v20, Preparation of gross alpha and gross beta in environmental matrices; and, ALS SOP724v11, Analysis of alpha and beta emitting radionuclides by gas flow proportional counter. A Statement of Work will be provided to ALS Environmental with relevant information presented here:

This work is a service for analysis of groundwater samples for radium-226, radium-228, and gross alpha and gross beta analysis. EPA scientists will provide groundwater samples and the

contractor shall analyze the samples and return electronic files showing the results of the sample analysis.

Radiological information on groundwater samples is required to aid in characterizing groundwater samples in wells as part of EPA's national hydraulic fracturing study. This will allow for construction of conceptual models for study areas of interest.

EPA will provide the contractor with groundwater samples in 1L polyethylene bottles for radium-226 and gross alpha/beta analysis and in a one 1-L bottle plus one 500 mL (or 2-L) polyethylene bottle for Ra-228 analysis. All samples will be preserved in the field with HNO₃ to pH <2. Bottles will subsequently be placed in an ice chest (without ice) and shipped to the laboratory within a few days of collection. Samples will be submitted in lots of about 10 beginning [date of sampling].

The contractor shall provide these services; analysis of radium-226 in groundwater samples using EPA Method 903.1; analysis of radium-228 in groundwater samples using EPA Method 904.0; and analysis of gross alpha and gross beta using EPA Method 900.0. The laboratory shall have current accreditation for the methods through NELAP or other nationally-recognized accrediting organization and provide documentation of this accreditation. The laboratory shall indicate the frequency and provider of their Proficiency Testing (aka Performance Evaluation) samples for the stated methods and shall provide results from the last two rounds for these methods. The laboratory shall provide copies of their QA Manual and copies of the applicable Standard Operating Procedures. The Laboratory's Quote shall include costs to provide full data packages described in the Deliverables paragraph. The minimum laboratory required reporting and detection limits and the minimum laboratory QA/QC requirements are provided in the attached tables. Sample requirements shall be included also (sample volumes, bottle types, preservation, holding times, etc.). The laboratory should be aware that they are subject to a QA audit during the course of the period of performance.

Contractor's results shall be considered acceptable if the samples were analyzed using the EPA Methods as stated in the previous paragraph and all of the laboratory's SOP QA/QC requirements are met, as well as those in the attached tables, and data deliverables as described below are provided. They shall meet the holding time requirement of six months (however, the required delivery of results is within five weeks as indicated in next section).

A final report at completion of analysis shall include: tabulation of final results in Excel spreadsheets, list of methods or 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 and are required to include: copies of signed Chain-of-custody forms, calibration data, control charts for calibration checks and backgrounds of detectors used, QA/QC data, raw data (including applicable log book entries), 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 copied to the GWERD QA Manager, Steve Vandegrift.

Results of the analysis will be reported to Rick Wilkin via e-mail at wilkin.rick@epa.gov or other contact as indicated with sample set within five weeks of the receipt of the samples. Return UPS or Fedex labels will be included with each set so that ice chests can be shipped back to RSKERC at no charge. Rick Wilkin (or other contact) shall be contacted within 48 hours of problems with sample analyses, such as loss of sample, QC failures, etc.

Region III's LC-MS-MS method for glycols (see Tables 9 and 10) 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 H₂O and CH₃CN with 0.1% formic acid. The 3 glycols are run on a separate gradient than the 2-butoxyethanol. 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 steps 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 10-1000 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 are 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).

Analysis by the EPA Region VIII laboratory includes GC for GRO and DRO and GC-MS for semi-volatiles. For the semivolatiles the target analyte list is presented in Table 11 and QA/QC requirements are listed in Table 12. Surrogates used include phenol-d6, 2-fluorophenol, 2,4,6-tribromophenol, nitrobenzene-d5, 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 co-eluting peaks. Data system library reduction programs can sometimes create these discrepancies.

A commercial standard 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.

The samples analyzed by the Region VII contract with ARDL, Inc. include metals by Inductively Coupled Plasma – Mass Spectrometry (ICP-MS), Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES), mercury by cold vapor AAS, and volatile organic compounds (VOCs) by purge and trap-GC/MS (for the May 2013

sampling event). The contract laboratory will analyze water samples for Al, As, Cd, Cr, Cu, Mo, Ni, Pb, Sb, Se, Sr, Th, Tl, U, and V by ICP-MS. In addition, the contract laboratory analyze water samples for Ag, B, Ba, Be, Ca, Co, Fe, K, Li, Mg, Mn, Mo, Na, P, S, Sb, Si, Sr, Ti, and Zn by ICP-OES. The contract laboratory will perform the analysis in accordance with the EPA Methods 6020A for ICP-MS and 200.7 for ICP-OES. Both total and dissolved metals will be analyzed. Sample digestion for total metals is done according to EPA Method 200.7. Samples for dissolved metals are not digested. Samples collected for mercury and volatile organic compounds are in accordance with EPA Methods 7470A and EPA Method 8260B, respectively. The target analyte lists for metals and VOC analyses are provided in Tables 13 and 14.

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 12):

- (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 11. 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 (conducted July 2011) and analysis of Performance Evaluation samples. The laboratory is currently analyzing Performance Evaluation (Proficiency Testing) samples and has provided this data

(6) See Table 12 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 9 and 10):

- (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 be determined, but most will be between 10 and 50 µg/L (Table 9).

(5) The laboratory shall be subject to an on-site QA audit if the glycol data become “critical” at a later date 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 15 and Table 16):

- (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 15 and 16 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 17):

- (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 17 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 ALS Environmental, QA/QC requirements are (see Tables 18 and 19):

- (1) Samples shall be processed and analyzed within the following holding times (from date sampled): six months.
- (2) Data verification shall be performed by the ALS Environmental 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) Reporting limits are listed in Table 18.
- (5) The laboratory shall be subject to an on-site QA audit if the radiochemistry data becomes “critical” at a later date.
- (6) See Table 19 for QC types and performance 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 Region VII contract with ARDL, Inc., QA/QC requirements are (see Tables 20-23):

1. Samples shall be processed and analyzed within the following holding times (from date sampled): Metals: 6 months, except Hg (28 days) with acid preservation. VOCs: 14 days with acid preservation.

2. Data verification shall be performed by the contract laboratory to ensure that the data meets the SOW requirements and QA/QC requirements summarized in Tables 20-23.

a. The associated method blank shall not contain target analytes above the associated reporting limit (unless otherwise noted in SOW) and all applicable QC criteria shall be met based on the method utilized (initial calibration, continuing calibration, tune, internal standard, surrogate, etc.).

b. The project plan submitted by the contractor for this project must include the accuracy, precision, and relative percent difference applicable to each target compound/analyte required in the SOW. The submitted limits shall be at least as stringent as those specified in the method being utilized. If the contractor does not have established internal limits for a given parameter, then the limits in the method shall apply.

3. Complete data packages shall be provided electronically by 2:00 pm CST on the 35th day after receipt of the last sample for a given sampling event. (NOTE: If the due date falls on a Holiday, Saturday or Sunday, then the deliverables are due to EPA by 12:00pm on the first subsequent business day). Electronic deliverables shall include all analytical results (field and laboratory QC samples) and the associated narrative. In addition to the normal narrative and Excel spreadsheet required, the laboratory shall provide an electronic "CLP type" data package that includes the written narrative, Forms 1's, QC data, and all supporting raw data. The package shall be organized and paginated. The entire data package shall be provided in a .pdf file format. The complete data package in .pdf format shall be provided within 48 hours of the electronic results and narrative. The associated narrative shall address each of the applicable areas listed below for every parameter group in the task order. This includes a statement that the QA/QC criteria for every applicable area were in control or, conversely, that one or more QC outliers were present. For areas with outliers, the narrative shall specify each parameter which was out of control and the associated samples that were affected. In addition, the narrative shall indicate any and all corrective actions taken and the results of those actions as well as impact on the associated samples (holding times, initial calibration, continuing calibration, surrogates, internal standards, laboratory duplicate, matrix spike/matrix spike duplicate, laboratory control sample, and method blanks).

4. Contract required quantitation limits (CRQL) for the metals and VOCs are provided in Tables 13 and 14.

5. The laboratory shall be subject to an on-site QA audit. A QA audit was conducted in November 2012 on Southwest Research Institute, the subcontractor to ARDL, Inc. If a different laboratory is selected for future, it will be audited. The laboratory must also analyze Performance Evaluation (Proficiency Testing) samples. The laboratory must be NELAP-accredited which are required to analyze these samples twice a year.

6. See Tables 20-23 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 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) will be used as a check on the quality of solute concentration data. Two methods will 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 7. Any updates to these detection limits will be provided in their data reports. Detection limits for the analyses done by Region VIII, Region III, Region VII contract with ARDL, Inc., and ALS Environmental 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

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

Where m = measurement result

n = True Value (a certified or known value) of standard or reference

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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.

For duplicate samples collected in the field, the RPD will only be calculated where analyte concentrations for both samples (primary and duplicate) are >5 times the quantitation level. RPDs are expected to be less than or equal to 30%. If RPDs are greater than 30%, actions will be taken to better understand the reason and data will be flagged. The duplicate samples will be used for the purposes of determining reproducibility. In all cases, results reported in prepared reports or publications will be based on the primary sample. Results for duplicate samples will be reported in QA appendices or supporting material. Analytes detected in various blank samples will be evaluated and flagged, if appropriate, in presentations of data. Generally, blank contamination will be evaluated for significance when blank contaminants are above reporting limits. If they are found at a level within 3 times that found in applicable field samples they will be considered significant and affected sample data will be flagged.

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.

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

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.

SOPs are internal working documents that are not typically publically available. The majority of these, however, have been made available on the EPA Region VIII web site for a separate research effort:

<ftp://ftp.epa.gov/r8/pavilliondocs/LabSOPsAndLabProducedReports/AnalyticalMethodologyUsed-RobertSKerrLaboratory/>.

2.7 Instrument/Equipment Calibration and Frequency

RSKERC calibration and calibration frequency are described in RSKSOPs (RSKERC Standard Operating Procedures) and Table 8. SOPs are internal working documents that are not typically publically available. The majority of these, however, have been made available on the EPA Region VIII web site for a separate research effort:

<ftp://ftp.epa.gov/r8/pavilliondocs/LabSOPsAndLabProducedReports/AnalyticalMethodologyUsed-RobertSKerrLaboratory/>.

For the Region III and Region VIII laboratories, these requirements are identified in their SOPs and in Tables 10 and 12, and for the USGS laboratory, Table 17.

For the Region VII contract laboratory, these requirements are identified in their SOPs and in Tables 20-23.

Field instruments (meters for pH, specific conductance, ORP, DO, and temperature) 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, and/or 10.00 buffers, 1413 uS/cm conductivity standard, ORP standard, zero-oxygen calibration check solution) 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 to ensure 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, mid-day, and at the end of the day. With the exception of pH, all checks must be within $\pm 10\%$ 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 cells (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); 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. Dissolved sulfide measurements will be checked by preparing a sodium sulfide solution and measured with a spectrometer. The accuracy and precision will be checked using a standard solution of sodium sulfide prepared that has been titrated using the iodometric method. Accuracy should be within $\pm 10\%$ of the expected concentration and coefficient of variation should be 20% or less. 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, midday, 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 noted. 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. For turbidity, blank measurements of ≤ 1 NTU are acceptable. 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 85-115 mg/L. Duplicates will be performed once a day or on every tenth sample. Duplicate acceptance criteria are $\text{RPD} \leq 15$. 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, Region III and VIII SOPs, Region VII contract laboratory SOPs, and SOPs for ALS Environmental and Isotech as well as the USGS Sr procedure 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 several high-capacity carboys 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 SW Pennsylvania. This will be done in accordance with the ORD PPM 13.2, *Paper Laboratory Records* as well as EPA Records Schedule 501, *Applied and Directed Scientific Research*. Finally, the Hydraulic Fracturing Quality Management Plan Rev. No. 1, Section 5, contains additional information on data management for Hydraulic Fracturing Research.

Data will be submitted to the PI 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 the PI's computer or designated GWERD staff computer and will be saved on a local server. The local server is automatically backed up nightly. Data will be spot-checked by the PI to ensure accuracy. If errors are detected during spot-checks, 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 by the PI to ensure accuracy of the transfer. If errors are detected during spot-checks, 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.

An Excel workbook consisting of multiple spreadsheets will be compiled for each sampling round for each retrospective case study. A standard format for the Excel spreadsheets will be developed for all of the case study data. The Excel spreadsheets will be utilized as the electronic data deliverable (EDD) for downloading the data into an MSAccess database.

2.10.1 Data Recording

Data collected 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.

2.10.2 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.

2.10.3 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. The PI will perform these tasks. 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. During the data verification/validation process an independent 100% transcription check of the data will be initiated by the QA staff (see Section 4.2). If errors are found they will be corrected by the PI and resubmitted to the QA staff to verify that the data corrections were made and the final data are error free. 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 QA contract support with oversight by the GWERD QAM.

ADQs will be conducted on a representative sample of data (typically from the first sampling event) for the critical target analytes. These will also be performed by the EPA QAMs or by a QA support contractor with oversight by the GWERD 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 QAM 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 with the corrective actions. The QAM will track implementation and completion of corrective actions. After all corrective actions have been implemented and confirmed to be completed; the QAM 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 QAM 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. The field TSA took place during the sampling event in March 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 3) and were conducted on-site at RSKERC (involves both EPA and CB&I-operated labs) July 28, 2011 and at the Region VIII laboratory on July 26, 2011 which analyzes for semi-volatile organic, DRO and GRO analyses. Laboratory TSAs will not be repeated if they have been done previously for another HF case study and significant findings were not identified. A laboratory TSA was conducted November 27, 2012 on the Region VII contract laboratory (Southwest Research Institute, subcontractor to ARDL, Inc.).

ADQs will be conducted on a representative sample of data for the critical target analytes. These will be conducted on 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. CB&I and the EPA GP Lab analyze 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. Isotech will not be expected to perform PE sample analysis (which are not available commercially) as their analyses are not classified as critical. ALS Environmental participates in PE sample analysis, but their analysis is not classified as critical. The Region VII contract laboratory will analyze Performance Evaluation samples as this is required for NELAP-accredited laboratories.

3.1.2 Assessment Results

At the conclusion of a TSA, a debriefing shall be 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, the Technical Research Lead for Case Studies, and the HF Program QAM. 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 distributed as in 3.1.2. Audit reports will be prepared by the QAM or the QA support contractor. Those prepared by the QA support contractor will be reviewed and approved by the QAM prior to release. 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 8, 10, 12, 15-23. In addition, sample preservation and holding times will be evaluated against requirements in Table 5.

Data will not be released outside of NRMRL until all study data have been reviewed, verified and validated as described below. NRMRL senior management is responsible for deciding when project data can be shared with interested stakeholders.

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, CB&I'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. CB&I's and the EPA GP Lab 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 Datschelet, 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.

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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 impact on data quality.

For field measurements, the PI 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.

Laboratory data reports are reviewed by the PI for completeness, correctness, and conformance with QAPP requirements. All sample results are verified by the PI to ensure they meet project requirements as defined in the QAPP and any data not meeting these requirements are appropriately qualified in the data summary prepared by the PI. See Table 24 for the Data Qualifiers. The Contract Laboratory Program guidelines on organic (USEPA, 2008) and inorganic (USEPA, 2010) methods data review are used as guidance in application of data qualifiers.

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. Data validation activities may be performed by EPA QAMs or by a QA support contractor with oversight by the GWERD QAM. Data summaries that have been prepared by the PI as well as laboratory data reports and raw data shall be provided to the QAM, who will coordinate the data validation for the critical analytes. The data validation team shall evaluate data against the QAPP specifications. NRMRL SOP #LSAS-QA-02-0, "Performing Audits of Data Quality" will be used as a guide for conducting the data validation. The data validation team will review the information presented in the case narrative, review data, and ensure that appropriate project-specific data qualifiers were added to the data summary tables. The outputs from this process will include the validated data and the data validation report (ADQ 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.

The PI will use the information from these data verification/validation activities to assist in determining what corrective actions are needed and make appropriate revisions to the data summary. Corrective actions may include the option to re-sample or re-analyze the affected samples. If corrective actions are not possible, 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.

After the data validation (ADQ) process is complete, QA staff or designees will perform transcription checks on 100% of the data in the data summary. Transcription check review comments will be provided to the PI and QA staff will verify that the PI's responses are acceptable. The data summary may then be approved by the QAM. Additional editorial reviews may be done, but will have no effect on the data.

4.3 Reconciliation with User Requirements

The PI shall analyze the data, as presented below. The PI shall use the results from the data verification and validation process to assess whether or not the data quality has met project requirements and thereby the user requirements.

However, if there are data quality issues that may impact their use, the impact will be evaluated by the PI, with assistance from QA staff. If there are disagreements between the PI and GWERD QA staff relating to data usability, the issue will follow the dispute resolution process as described in the Hydraulic Fracturing Quality Management Plan.

The types of statistical analyses that will 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 SW Pennsylvania sites showing well locations and concentrations of analytes.

5.0 References

ALS SOP783v9. Radium-226 in Aqueous and Soil Matrices – Radon Emanation Technique – Method EPA 903.1.

ALS SOP746v9. Determination of Radium-228 According to EPA Method 904.0 or SW846 Method 9320, with Modifications.

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ALS SOP724v11. Analysis of Alpha and Beta Emitting Radionuclides by Gas Flow Proportional Counter – Method EPA 900.0

American Public Health Association; American Water Works Association; Water Environment Federation. 1998. Method 3500-Fe B. Phenanthroline Method. In: Standard Methods for the Examination of Water and Waste Water, 20th Ed. Editors Clesceri, L.S.; Greenberg, A.E.; and Eaton, A.D. Washington D.C.

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Metzger, C., Caporale, C., and Bilyeu, J. 2011. Laboratory Quality Manual, Version 8. U.S. Environmental Protection Agency Region 3, Environmental Science Center Environmental Assessment and Innovation Division, Office of Analytical Services and Quality Assurance.

Newport, T. G. 1973. Summary ground-water resources of Washington County, Pennsylvania. Pennsylvania Geological Survey Water Resource Report 38.

RSKSOP-175v5. Sample preparation and calculations for dissolved gas analysis in water samples using a GC headspace equilibration technique. 33 p.

RSKSOP-179v2. Standard operating procedure for total nitric acid extractable metals from aqueous samples by microwave digestion. 9 p.

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-276v4. Determination of major anions in aqueous samples using capillary ion electrophoresis with indirect UV detection and Empower 2 Software. 11 p.

RSKSOP-296v1. Determination of hydrogen and oxygen isotope ratios in water samples using high temperature conversion elemental analyzer (TC/EA), a continuous flow unit, and an isotope ratio mass spectrometer (IRMS), 8 p.

RSKSOP-299v1. Determination of volatile organic compounds (fuel oxygenates, aromatic and chlorinated hydrocarbons) in water using automated headspace gas chromatography/mass spectrometry (Agilent 6890/5973 Quadrupole GC/MS System). 25 p.

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RSKSOP-326v0. Manual measurement of groundwater levels for hydrogeologic characterization. 4 p.

RSKSOP-330v0. Determination of various fractions of carbon in aqueous samples using the Shimadzu TOC-VCPH analyzer. 15 p.

RSKSOP-332v0. Operation of Thermo X Series II ICP-MS. 16 p.

RSKSOP-334v0. Determination of stable hydrogen and oxygen isotope ratios in water samples using a Picarro L2120i cavity ring-down spectrometer (CRDS), in review. 30 p.

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6.0 Tables

Table 1. QAPP revision history.

Revision Number	Date Approved	Revision
0	7/21/2011	New document
1	03/05/2012	Section 1: • Update project organization • Update accreditation information in 1.5 Section 2: • Revise dissolved gas/methane isotope sample collection method and removed hydrogen and carbon dioxide as target analytes • Add radiometric analyses/sample types/bottles/preservation • Clarification of samples for filtration • CRDS will be used in the second and subsequent sampling events for H and O stable isotopes of water instead of IRMS • Add ALS Environmental for analysis of ²²⁶Ra, ²²⁸Ra, gross alpha/beta • Add statement of work for ALS and updated SOW for Isotech • Updated information on Region VIII QA/QC regarding on-site QA audit and PEs • Add RSKSOP-334 for water isotopes • Add ALS QA/QC requirements • Add RPD/Blank sample data analysis • Provided clarification on sulfide and turbidity calibration checks • Deleted 2.10.1 as information is redundant • Provided clarification on ADQ and PE requirements and to whom audit reports are provided Section4: • Added text on data report review and data usability Section 5: • Added references

		Section 6: • Add this table • Added radiochemicals to Table 5, holding times for stable isotopes C, H, Sr and SOP for CRDS • Added DIC/DOC to Table 7 • Replaced Table 8 with update • Provided corrections to QC requirements for DIC/DOC and O,H stable isotopes of water in Table 9 • Replaced Table 10 with update • Addition of tables 16 and 17/ALS QA/QC • Added Table 18
1, Addendum	12/20/2012	Addition of specifications and quality control (QC) acceptance criteria for the reanalysis of samples for metals by Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) for the May 2012 sampling event. The EPA Superfund Analytical Services Contract Laboratory Program (EPA CLP) analyzed water samples for Al, As, Cd, Cr, Cu, Ni, Pb, Sb, Se, Th, Tl, and U by ICP-MS.
2	4/22/2013	• Added EPA disclaimer and information about the EPA Quality System Section 1 • Updated staff assignments, including QA staff, NRMRL management, communications staff, and support staff • Section 1.2: added reference to the EPA HF study plan, added summary of QAPP history • Section 1.4: added information about project planning and SOPs • Section 1.5: added information about Agency policy on lab competency and Region VII contract lab Section 2 • Section 2.1.2: added information about placement of downhole pumps • Section 2.2.1: updated sample collection information, added details about glass bottles (certified, precleaned), added dissolved gas sampling test for final round, added new metals sample information, added sample for TKN • Section 2.4.1: added information about SOPs, updated information relating to Region VIII analysis and the Region VII contract lab analysis • Section 2.5.1: added corrective action information for RSKERC analysis, provide information of the QA/QC requirements of the Region VII contract lab and corrective actions • Section 2.6/2.7: added information about SOPs

		• Section 2.10: added information about lab records management and EPA policy; specified data output in Excel workbook format, specified 100% data checks Section 3: • Section 3.1: edited text; added information about Region VII contract Section 4: • Section 4.1: specified NRMRL management roles regarding data release • Section 4.2: specified Region VII contract lab data validation procedures, clarified data validation process, specified 100% data transcription checks • Section 4.3: clarified conflict resolution process Section 5: • Added references to the EPA HF study plan Section 6: • Updated this Table on the QAPP revision history • Table 3, updated critical analytes (removed SVOCs) • Table 4, updated the schedule • Table 5, updated table for metals and VOCs, added TKN, added Br by additional methods • Table 6, updated information, acceptance criteria language revised to be consistent with data qualifier Table 24; in footnote changed 12° to 6° to be consistent with Table 5 • Table 7, revised RSKERC MDLs and QLs, added TKN, added Br by additional methods • Table 11, updated the Region VIII MDLs and QLs • Added Tables 13 and 14; QL and MDL information for metals and VOC analysis • Added Tables 20-23; Region VII contract lab QA/QC requirements • Updated Table 24, Data qualifiers
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Table 2. 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
Alcohol 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 Distillate Blend	Petroleum Distillate 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	Potassium Chloride
Silica: Cristobalite Potassium Chloride	Potassium Hydroxide
Crystalline Silica: Quartz Potassium Hydroxide	Prop-2-yn-1-01
Dazomet Prop-2-yn-1-01	Propan-2-01
Diatomaceous Earth Propan-2-01	Propargyl Alcohol
Diesel (use discontinued) Propargyl Alcohol	Propylene
Diethylbenzene Propylene	Sodium Ash
Doclecybenzene Sulfonic Acid Sodium Ash	Sodium Bicarbonate
E B Butyl Cellosolve Sodium Bicarbonate	Sodium Chloride
Ethane-1,2-diol Sodium Chloride	Sodium Hydroxide
Ethoxlated Alcohol Sodium Hydroxide	Sucrose
Ethoxylated Alcohol Sucrose	Tetramethylammonium Chloride
Ethoxylated Octylphenol Tetramethylammonium Chloride	Titanium Oxide
Ethylbenzene Titanium Oxide	Toluene
Ethylene Glycol Toluene	Xylene
Ethylhexanol 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 3. Critical analytes.

Analyte	Laboratory Performing the Analysis
Gasoline Range Organics (GRO)	EPA Region VIII laboratory
Diesel Range Organics (DRO)	EPA Region VIII laboratory
Volatile Organic Compounds (VOC)*	Region VII contract laboratory
Metals (As, Se, Sr, Ba, B)	Region VII contract laboratory
Major Cations (Ca, Mg, Na, K)	Region VII contract laboratory
Major Anions (Cl, NO ₃ ⁻ +NO ₂ ⁻ , SO ₄ ²⁻)	RSKERC general parameters lab

*ethanol, isopropyl alcohol, tert-butyl alcohol, naphthalene, acrylonitrile, benzene, toluene, ethylbenzene, and xylene

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

Media	July 2011 Phase I	March 2012 Phase I	July 2012 Phase I	May 2013 Phase I
Groundwater	X	X	no sampling event*	X
Surface Water	X	X	no sampling event*	X

* No event due to an inability to coordinate the sampling activity.

Table 5. 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 TSP [†] , pH>10; refrigerate 6°C ^{††}	14 days
Dissolved Metals (filtered)	EPA Methods 200.7 and 6020A	1 L plastic bottle/1	HNO ₃ , pH<2; room temperature	6 months (Hg 28 days)
Total Metals (unfiltered)	EPA Methods 200.7 and 6020A; Digestion EPA Method 200.7	1 L plastic bottle/1	HNO ₃ , pH<2; room temperature	6 months (Hg 28 days)
²²⁶ Ra	ALS SOP783v9 (EPA Method 903.1)	1 L plastic/1	HNO ₃ , pH<2; room temperature	6 months
²²⁸ Ra	ALS SOP746v9 (EPA Method 904.0)	2 L plastic/1	HNO ₃ , pH<2; room temperature	6 months
Gross Alpha/Beta	ALS SOP702v20 & 724v11 (EPA Method 900.0)	1 L plastic/1	HNO ₃ , pH<2; room temperature	6 months
SO ₄ , Cl, F, Br	RSKSOP-276v4 (EPA Method 6500)	30 mL plastic/1**	Refrigerate ≤6°C	28 days
Br	RSKSOP-288v3 (EPA Method 6500)	30 mL plastic/1**	Refrigerate ≤6°C	28 days
Br	RSKSOP-214v5 (No EPA Method)	30 mL plastic/1**	Refrigerate ≤6°C	28 days
NO ₃ + NO ₂ , NH ₄ , TKN	RSKSOP-214v5 (EPA Method 350.1, 353.1, & 351.2)	60 mL plastic/1	H ₂ SO 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 ₃ PO ₄ , pH<2; refrigerate ≤6°C	28 days
Volatile organic compounds (VOC)	EPA Method 8260B	40 mL amber glass VOA vial/4	No Headspace HCl, pH<2; 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 or RSKSOP-334 (No EPA Method)	20 mL glass VOA vial/1	Refrigerate at ≤6°C	stable

$\delta^{13}\text{C}$ of inorganic carbon	Isotech; gas stripping and IRMS (No EPA Method)	60 mL plastic bottle/1	Refrigerate $\leq 6^\circ\text{C}$	14 days
$\delta^{13}\text{C}$ and $\delta^2\text{H}$ of methane	Isotech; gas stripping and IRMS (No EPA Method)	1 L plastic bottle/1	Caplet of benzalkonium chloride; refrigerate $\leq 6^\circ\text{C}$	3 months
$^{87}\text{Sr}/^{86}\text{Sr}$ analysis	Thermal ionization mass spectrometry (No EPA Method)	500 mL plastic bottle/1	Refrigerate $\leq 6^\circ\text{C}$	6 months
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 sample, or if <10 samples collected, collect 2 more bottles for one select sample	Refrigerate $\leq 6^\circ\text{C}$	7 days until extraction, 30 days after 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 $\leq 6^\circ\text{C}$	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 $\leq 6^\circ\text{C}$	14 days
Gylcols	Region III method*** (No EPA Method)	40 mL amber glass VOA vial/2	Refrigerate $\leq 6^\circ\text{C}$	14 days
Archive	NA	1 L plastic amber	Freeze $\leq -10^\circ\text{C}$; 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.)

**Same bottle will be used for up to three different Br methods

***under development

Table 6. 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; RPD > 30 for results greater than RL. The 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 6°C. These samples will be flagged accordingly.

Table 7. RSKERC detection limits for various analytes.

Analyte	Method	MDL (µg/L)	QL or LOQ (µg/L)
Dissolved Gases**			
Methane	RSKSOP-194v4 & RSKSOP-175v5	0.08	1.5
Ethane	RSKSOP-194v4 & RSKSOP-175v5	0.20	2.9
Propane	RSKSOP-194v4 & RSKSOP-175v5	0.24	4.1
n-Butane	RSKSOP-194v4 & RSKSOP-175v5	0.22	5.2
Anions/Nutrients		MDL (mg/L)	QL or LOQ (mg/L)
Bromide	RSKSOP-276v4 or RSKSOP-288v3	0.17	1.00
Bromide	RSKSOP-214v5	0.093	0.25
Chloride	RSKSOP-276v4	0.13	1.00
Sulfate	RSKSOP-276v4	0.16	1.00
Nitrate+Nitrite	RSKSOP-214v5	0.01	0.10
Fluoride	RSKSOP-276v4	0.05	0.20
Ammonia	RSKSOP-214v5	0.01	0.10
TKN	RSKSOP-214v5	0.027	0.125
Low Molecular Weight Acids			
Lactate	RSKSOP112v6	0.02	0.10
Acetate	RSKSOP112v6	0.01	0.10
Formate	RSKSOP112v6	0.02	0.10
Butyrate	RSKSOP112v6	0.03	0.10
Isobutyrate	RSKSOP112v6	0.02	0.10
DIC/DOC			
DOC	RSKSOP330v0	0.07	0.50
DIC	RSKSOP330v0	0.02	0.50

*Current, up-to-date MDLs and QLs are provided in laboratory reports.

** 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°C, headspace pressure of 1 atmosphere, and using the “created” headspace calculations.

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
SO ₄ , Cl, F, Br	RSKSOP-276v4 or RSKSOP-288v3	<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 , Br, TKN	RSKSOP-214v5	<½ lowest calib. std. (< lowest calib. std for TKN) (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	<MDL (Beginning and end of each sample set)	90-110% of known value (Beginning, end, and every 10 samples)	PE sample acceptance limits; 90-110% of known value (One per sample set)	RPD≤10 (every 10 samples)	80-120% Rec. (one per 20 or every set)
Low Molecular Weight Acids	RSKSOP-112v6	<MDL (Beginning of a sample set; every 10 samples; and end of sample set)	85-115% of the recovery (Prior to sample analysis; every 10 samples; end of sample set)	85-115% of recovery (Prior to sample analysis)	< 15 RPD (Every 20 samples t)	80-120 % recovery (Every 20 samples)

O, H stable isotopes of water**	RSKSOP-296v1 or RSKSOP-334v0	NA	RSKSOP-296v1: Difference of calibrated/true < 1‰ for $\delta^2\text{H}$ & < 0.2‰ for $\delta^{18}\text{O}$ (Beginning, end and every tenth sample) RSKSOP-334v0: Difference of calibrated/true $\leq 1.5\text{‰}$ for $\delta^2\text{H}$ & $\leq 0.3\text{‰}$ for $\delta^{18}\text{O}$ (Beginning, end and every twenty samples)	NA	RSKSOP296v1: Standard deviation $\leq 1\text{‰}$ for $\delta^2\text{H}$ and < 0.2‰ for $\delta^{18}\text{O}$ (every sample) RSKSOP-334v0: Difference $\leq 1.5\text{‰}$ for $\delta^2\text{H}$ and $\leq 0.3\text{‰}$ for $\delta^{18}\text{O}$ (Beginning and end of sample set and every twenty samples)	NA
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*This table only provides a summary; SOPs should be consulted for greater detail.

**Additional checks for IRMS and CRDS: internal reproducibility prior to each sample set, std dev $\leq 1\text{‰}$ for $\delta^2\text{H}$ and ≤ 0.1 for $\delta^{18}\text{O}$, and $\leq 0.5\text{‰}$ for $\delta^2\text{H}$ and ≤ 0.1 for $\delta^{18}\text{O}$, respectively

†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 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 µg/L. In June of 2012 RLs were 5 µg/L for 2-butoxyethanol; 5 µg/L for diethylene glycol, 10 µg/L for triethylene glycol, and 10 µg/L for tetraethylene glycol.

[‡] 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 10. 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 regarding the impact on sample data.

Table 11. Region VIII detection and reporting limits and LCS and MS control limits for semivolatile organic compounds (SVOC) using Method 8270 (Region VIII SOP ORGM-515 r1.1). MDLs and QLs subject to change; these values were provided in Dec. 2012.

Analyte	MDL (µg/L)	QL (µg/L)	Lab Duplicates RPD Limits (%)	Matrix Spike Recovery Limits (%)	Matrix Spike Duplicate RPD Limits (%)
(R)-(+)-Limonene	0.257	1.00	20	60-130	30
1,2,4-Trichlorobenzene	0.399	1.00	20	35-105	30
1,2-Dichlorobenzene	0.399	1.00	20	35-100	30
1,2-Dinitrobenzene	0.460	1.00	20	45-110	30
1,3-Dichlorobenzene	0.375	1.00	20	30-100	30
1,3-Dimethyl adamantane	0.277	1.00	20	60-130	30
1,3-Dinitrobenzene	0.460	1.00	20	45-110	30
1,4-Dichlorobenzene	0.377	1.00	20	30-100	30
1,4-Dichlorobenzene-d4				-	
1,4-Dinitrobenzene	0.450	1.00	20	45-110	30
1-Methylnaphthalene	0.482	1.00	20	45-105	30
2,3,4,6-Tetrachlorophenol	1.08	2.00	20	50-110	30
2,3,5,6-Tetrachlorophenol	1.05	2.00	20	50-110	30
2,4,5-Trichlorophenol	1.15	2.00	20	50-110	30
2,4,6-Trichlorophenol	1.19	2.00	20	50-115	30
2,4-Dichlorophenol	1.05	2.00	20	50-105	30
2,4-Dimethylphenol	0.937	2.00	20	30-110	30
2,4-Dinitrophenol	1.75	3.00	20	15-140	30
2,4-Dinitrotoluene	0.413	1.00	20	50-120	30

Analyte	MDL (µg/L)	QL (µg/L)	Lab Duplicates RPD Limits (%)	Matrix Spike Recovery Limits (%)	Matrix Spike Duplicate RPD Limits (%)
2,6-Dinitrotoluene	0.497	1.00	20	50-115	30
2-Butoxyethanol	0.698	1.00	20	60-130	30
2-Butoxyethanol phosphate	0.698	1.00	20	60-130	30
2-Chloronaphthalene	0.498	1.00	20	50-105	30
2-Chlorophenol	0.911	2.00	20	35-105	30
2-Methylnaphthalene	0.468	1.00	20	45-105	30
2-Methylphenol	0.999	2.00	20	40-110	30
2-Nitroaniline	0.556	1.00	20	50-115	30
2-Nitrophenol	0.864	2.00	20	40-115	30
3 & 4-Methylphenol	2.08	5.00	20	30-110	30
3-Nitroaniline	1.30	3.00	20	20-125	30
4,6-Dinitro-2-methylphenol	0.958	2.00	20	40-130	30
4-Bromophenyl phenyl ether	0.566	1.00	20	50-115	30
4-Chloro-3-methylphenol	1.22	2.00	20	45-110	30
4-Chloroaniline	1.05	3.00	20	15-110	30
4-Chlorophenyl phenyl ether	0.612	1.00	20	50-110	30
4-Nitroaniline	1.13	3.00	20	35-120	30
4-Nitrophenol	1.08	3.00	20	0-125	30
Acenaphthene	0.588	1.00	20	45-110	30
Acenaphthylene	0.562	1.00	20	50-105	30
Adamantane	0.280	1.00	20	60-130	30

Analyte	MDL (µg/L)	QL (µg/L)	Lab Duplicates RPD Limits (%)	Matrix Spike Recovery Limits (%)	Matrix Spike Duplicate RPD Limits (%)
Aniline	0.202	1.00	20	0-150	30
Anthracene	0.410	1.00	20	55-110	30
Azobenzene	0.596	1.00	20	50-115	30
Benzo (a) anthracene	0.377	1.00	20	55-110	30
Benzo (a) pyrene	0.475	1.00	20	55-110	30
Benzo (b) fluoranthene	0.428	1.00	20	45-120	30
Benzo (g,h,i) perylene	0.423	1.00	20	40-125	30
Benzo (k) fluoranthene	0.416	1.00	20	45-125	30
Benzoic acid	1.59	3.00	20	20-115	30
Benzyl alcohol	0.549	1.00	20	50-150	30
Bis(2-chloroethoxy)methane	0.523	1.00	20	45-105	30
Bis(2-chloroethyl)ether	0.463	1.00	20	35-110	30
Bis(2-chloroisopropyl)ether	0.480	1.00	20	25-130	30
Bis-(2-Ethylhexyl) Adipate	0.494	1.00	20	40-125	30
Bis(2-ethylhexyl)phthalate	1.12	2.00	20	40-125	30
Butyl benzyl phthalate	0.610	1.00	20	45-115	30
Carbazole	0.913	3.00	20	50-115	30
Chrysene	0.340	1.00	20	55-110	30
Dibenz (a,h) anthracene	0.425	1.00	20	40-125	30
Dibenzofuran	0.589	1.00	20	55-105	30
Diethyl phthalate	0.480	1.00	20	40-120	30

Analyte	MDL (µg/L)	QL (µg/L)	Lab Duplicates RPD Limits (%)	Matrix Spike Recovery Limits (%)	Matrix Spike Duplicate RPD Limits (%)
Dimethyl phthalate	0.516	1.00	20	25-125	30
Di-n-butyl phthalate	0.626	1.00	20	55-115	30
Di-n-octyl phthalate	0.544	1.00	20	35-135	30
Diphenylamine	0.521	1.00	20	55-115	30
Fluoranthene	0.384	1.00	20	55-115	30
Fluorene	0.626	1.00	20	50-110	30
Hexachlorobenzene	0.487	1.00	20	50-110	30
Hexachlorobutadiene	0.304	1.00	20	25-105	30
Hexachlorocyclopentadiene	0.227	1.00	20	0-95	30
Hexachloroethane	0.320	1.00	20	30-95	30
Indeno (1,2,3-cd) pyrene	0.441	1.00	20	45-125	30
Isophorone	0.578	1.00	20	50-110	30
Naphthalene	0.426	1.00	20	40-100	30
Nitrobenzene	0.453	1.00	20	45-110	30
N-Nitrosodimethylamine	0.488	1.00	20	25-110	30
N-Nitrosodi-n-propylamine	0.598	1.00	20	35-130	30
Pentachlorophenol	0.928	2.00	20	40-115	30
Phenanthrene	0.411	1.00	20	50-115	30
Phenol	0.967	2.00	20	20-115	30
Pyrene	0.386	1.00	20	50-130	30
Pyridine	0.014	1.00	20	0-150	30

Analyte	MDL (µg/L)	QL (µg/L)	Lab Duplicates RPD Limits (%)	Matrix Spike Recovery Limits (%)	Matrix Spike Duplicate RPD Limits (%)
Squalene	1.33	2.00	20	60-130	30
Terpinol	0.617	1.00	20	60-130	30

Table 12. Region VIII laboratory QA/QC requirements for semivolatiles, 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 (0.25 -12.5 ug/L) , one is at the MRL (0.50 ug/L), prior to sample analysis (not daily) RSD $\leq$ 20%, $r^2 \geq 0.990$	ICAL: 10-500 ug/L RSD $\leq$ 20% or $r^2 \geq 0.990$	ICAL: 0.25-12.5 ug/L for gasoline (different range for other compounds) RSD $\leq$ 20% or $r^2 \geq 0.990$	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	ICV1 80-120% of	ICVs 80-120% of	Each time calibration

QC Type	Semivolatiles	DRO	GRO	Frequency
	value	expected value	expected value	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 by the supplier. Otherwise 70-130% of expected value	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
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

¹Based on 1000 mL sample to 1 mL extract

²Based on a 5 mL purge

*see QAPP Table 11

Table 13. Region VII contract lab quantitation limits for metals.

Analyte	ICP-AES ¹		ICP-MS ²	
	MDL	QL	MDL (µg/L)	QL (µg/L)
Ag (Silver)	3 µg/L	10 µg/L		
Al (Aluminum)			0.5	4
As (Arsenic)			0.1	0.1
B (Boron)	5.3 µg/L	40 µg/L		
Ba (Barium)	0.4 µg/L	5 µg/L		
Be (Beryllium)	0.2 µg/L	5 µg/L		
Ca (Calcium)	0.0154 mg/L	0.100 mg/L		
Cd (Cadmium)			0.04	0.04
Co (Cobalt)	1.8 µg/L	5 µg/L		
Cr (Chromium)			0.05	0.4
Cu (Copper)			0.02	0.1
Fe (Iron)	39.7 µg/L	100 µg/L		
Hg (Mercury)			0.01	0.2
K (Potassium)	0.0481 mg/L	0.500 mg/L		
Li (Lithium)	0.8 µg/L	10 µg/L		
Mg (Magnesium)	0.0103 mg/L	0.050 mg/L		
Mn (Manganese)	0.3 µg/L	5 µg/L		
Mo (Molybdenum)			0.01	0.1
Na (Sodium)	0.0126 mg/L	0.250 mg/L		
Ni (Nickel)			0.02	0.04
P (Phosphorous)	0.0114 mg/L	0.050 mg/L		
Pb (Lead)			0.01	0.04
Sb (Antimony)			0.02	0.04
Se (Selenium)			0.3	1
Si (Silicon)	0.0087 mg/L	0.100 mg/L		
Sr (Strontium)	0.2 µg/L	5 µg/L	0.04	0.4
Th (Thorium)			0.01	0.04
Ti (Titanium)	0.5 µg/L	5 µg/L		
Tl (Thallium)			0.01	0.04
U (Uranium)			0.03	0.04
V (Vanadium)			0.01	0.1
Zn (Zinc)	0.6 µg/L	5 µg/L		

¹AES: Atomic Emission Spectroscopy, equivalent to OES. ICP-AES uses EPA Method 200.7. ICP-MS uses EPA Method 6020A; total digestions follow EPA Method 200.7.

²For Hg the method is cold vapor atomic absorption spectroscopy. Hg analysis follows EPA Method 7470A.

Table 14. Region VII contract lab quantification limits for VOCs.

Analyte	MDL (µg/L)	QL (µg/L)
1,1,1-Trichloroethane	0.087	0.5
1,1,2-Trichloroethane	0.066	0.5
1,1-Dichloroethane	0.063	0.5
1,1-Dichloroethene	0.088	0.5
1,3,5-Trimethylbenzene	0.147	0.5
1,2,4-Trimethylbenzene	0.034	0.5
1,2-Dichlorobenzene	0.047	0.5
1,2-Dichloroethane	0.042	0.5
1,2,3-Trimethylbenzene	0.083	0.5
1,3-Dichlorobenzene	0.091	0.5
1,4-Dichlorobenzene	0.073	0.5
Acetone	0.284	1.0
Benzene	0.052	0.5
c-1,2-Dichloroethene	0.100	0.5
Carbon disulfide	0.098	0.5
Carbon tetrachloride	0.088	0.5
Chlorobenzene	0.080	0.5
Chloroform	0.052	0.5
Diisopropyl ether	0.107	0.5
Ethanol	63.0	100
Ethyl benzene	0.059	0.5
Ethyl t-butyl ether	0.092	0.5
Isopropyl alcohol	7.42	10
Isopropyl benzene	0.066	0.5
m/p-Xylene	0.149	1.0
Methyl t-butyl ether	0.071	0.5
Methylene chloride	0.100	0.5
Naphthalene	0.081	0.5
o-Xylene	0.061	0.5
t-1,2-Dichloroethene	0.067	0.5
t-Amyl methyl ether	0.147	0.5
t-Butyl alcohol	4.89	10
Tetrachloroethene	0.132	0.5
Toluene	0.067	0.5
Trichloroethene	0.117	0.5
Vinyl chloride	0.139	0.5
Acrylonitrile	0.074	1.0

Table 15. Isotech laboratory QA/QC Requirements for $\delta^{13}\text{C}$ of DIC (Dissolved Inorganic Carbon).

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

*Working standards calibrated against IAEA (International Atomic Energy Agency) standard LSVEC and NBS-19; referenced to $\delta^{13}\text{C}$ 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 16. Isotech Laboratory QA/QC Requirements for $\delta^{13}\text{C}$ of dissolved methane and δD of dissolved methane.

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

*Working standards calibrated against IAEA (International Atomic Energy Agency) standard LSVEC and NBS-19; referenced to $\delta^{13}\text{C}$ 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 about the impact on the sample data.

Table 17. USGS laboratory QA/QC requirements for $^{87}\text{Sr}/^{86}\text{Sr}$ 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 $^{87}\text{Sr}/^{86}\text{Sr}$.	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 about the impact on the sample data.

Table 18. ALS Environmental detection limits for various analytes.

Analyte	Method	RL	DL (MDC*)
²²⁶ Ra	EPA 903.1	NA	1 pCi/L
²²⁸ Ra	EPA 904.0	NA	1 pCi/L
Gross alpha	EPA 900.0	NA	3 pCi/L
Gross beta	EPA 900.0	NA	4 pCi/L

*Minimum Detectable Concentration

Table 19. ALS Environmental QA/QC requirements.

QC Type	Radium-226 (frequency; performance criteria)	Radium-228 (frequency, performance criteria)	Gross Alpha/Beta (frequency, performance criteria)
Method Blanks	1 per batch of 20 (or 5% frequency); <MDC	1 per batch of 20 (or 5% frequency); <MDC	5% with minimum of 1 per batch of samples; <MDC
Blank Spikes (LCS)	1 per batch of 20 (or 5% frequency); 67-120% Recovery	1 per batch of 20 (or 5% frequency); 70-130% Recovery	5% with minimum of 1 per batch; 70-130% Recovery
Duplicates	Minimum frequency of 10%; DER**<2.13	Minimum frequency of 10%. (Duplicate samples with activity levels <5X RL will not be assessed with RPD); DER**<2.13	10% with minimum of 1 per batch; DER**<2.13
Matrix Spikes	NA	NA	5% with minimum of 1 per batch; 70-130% Recovery
Calibration	NIST-traceable ²²⁶ Ra solution; calibration performed at least annually	Calibration with NIST-traceable ⁸⁹ Sr, i.e., comparable to the beta activity of ²²⁸ Ac.	Calibration NIST-traceable ²⁴¹ Am for gross alpha and ⁹⁰ Sr for beta
Tracer/Carrier Limits	40-110% Recovery	40-110% Recovery	NA

Table 20. Region VII contract laboratory QA/QC requirements for ICP-MS.

QC Type or Operation	Acceptance Criterion	Frequency
Instrument Calibration	The acceptance criterion for the initial calibration correlation coefficient is $r \geq 0.998$.	Daily. Each time instrument is turned on or set up, after ICV or CCV failure, and after major instrument adjustment. The lowest non-blank standard shall be set at the RL for all analytes.
Initial Calibration Verification	90-110% Recovery	Following instrument calibration for each mass used.
Initial Calibration Blank	$\leq$ RL	Following each instrument calibration, immediately after the ICV.
Continuing Calibration Verification	90-110% Recovery	For each mass used, at a frequency of at least after every 10 analytical runs, and at the end of each run.
Low Level Initial Calibration Verification (LLICV) and Low Level Continuing Calibration Verification (LLCCV) at the RL (identified by lab as CRDL)	70-130% Recovery	LLICV, following each instrument calibration., and LLCCV analyzed at the end of each run.
Continuing Calibration Blank	$\leq$ RL	At a frequency of at least after every 10 analytical runs, and at the end of each run. Performed immediately after the last CCV.
Interference Check Sample	For solution AB, $\pm 20\%$ of the analyte's true value; for solution A ± 5 ppb or ± 2 times the RL of the analyte's true value, whichever is greater.	At the beginning of the run after the ICB but before the CCV.

Serial Dilution	If the analyte concentration is sufficiently high (minimally a factor of 50 above the RL in the original sample), the serial dilution (a five-fold dilution) shall then agree within 10% of the original determination after correction for dilution.	Every 20 samples.
Preparation or Method Blank	$\leq$ RL	Every 20 samples.
Laboratory Control Sample	80-120% Recovery	Every 20 samples.
Matrix Spike	75-125% Recovery (Recovery calculations are not required if sample concentration $>4\times$ spike added.)	Every 20 samples.
Post-Digestion Spike	80-120% Recovery per 6020A (Note that the lab SOP uses 75-125% Recovery)	Each time Matrix Spike Recovery is outside QC limits.
Duplicate Sample	RPD $<20\%$ for sample values $>5\times$ RL; for samples $<5\times$ RL, control limit = RL	Every 20 samples.
ICP-MS Tune	Mass calibration must be within 0.1 amu of the true value in the mass regions of interest. The resolution must also be verified to be less than 0.9 amu full width at 10% peak height.	Prior to calibration.
Internal Standards	The absolute response of any one internal standard in a sample must not be $<70\%$ from the response in the calibration standard.	Internal standards shall be present in all samples, standards, and blanks (except the tuning solution) at identical levels.
Determination of Method Detection Limits		Annually and after major instrument adjustment.

Table 21. Region VII contract laboratory QA/QC requirements for ICP-AES metals.

QC Type	Acceptance Criteria	Frequency
Instrument Calibration	Criteria not given in 200.7.	Daily. Each time instrument is turned on or set up, after ICV or CCV failure, and after major instrument adjustment.
Initial Calibration Verification (QCS or Quality Control Standard)	95-105% Recovery	Immediately after calibration.
Initial Calibration Blank	$\leq$ RL	Analyzed after the analytical standards, but not before analysis of the Initial Calibration Verification (ICV) during the initial calibration of the instrument.
Continuing Calibration Verification (IPC or Instrument Performance Check)	90-110% Recovery	At beginning and end of run; every 10 samples during analytical run.
Continuing Calibration Blank	$\leq$ RL	Analyzed immediately after every Continuing Calibration Verification (CCV); at beginning and end of run and every 10 samples during an analytical run.
Interference Check Sample (SIC or Spectral Interference Check)	For solution AB, $\pm 20\%$ of the analyte's true value; for solution A $\pm 20\%$ of the interferent's true value, for all other analytes ± 5 ppb or within ± 2 times the RL of the analyte's true value, whichever is greater.	At the beginning of the run after the ICB but before the CCV and at the end of the run.
Serial Dilution	If the analyte concentration is sufficiently high (minimally a factor of 50 above the MDL in the original sample), the serial dilution (a five-fold dilution) shall then agree within 10% of the original determination after correction for dilution.	Every 20 samples.
Preparation Blank (LRB or Laboratory Reagent Blank)	$\leq$ RL	Every 20 samples.

QC Type	Acceptance Criteria	Frequency
Laboratory Control Sample (LFB or Laboratory Fortified Blank)	85-115% recovery	Every 20 samples.
Matrix Spike (LFM or Laboratory Fortified Matrix)	75-125% Recovery (Recovery calculations are not required if sample concentration >4x spike added.)	Every 20 samples.
Post-Digestion Spike	85-115% Recovery	Each time Matrix Spike Recovery is outside QC limits .
Duplicate Sample	RPD<20% for sample values >5x RL; for sample values <5xRL, control limit = RL	Every 20 samples.
Determination of Method Detection Limits		Annually and after major instrument adjustment.

Table 22. Region VII contract laboratory QA/QC requirements for mercury by cold vapor AAS.

QC Type	Acceptance Criteria	Frequency
Instrument Calibration	The acceptance criterion for the initial calibration correlation coefficient is $r \geq 0.995$.	Daily. Each time instrument is turned on or set up, after ICV or CCV failure, and after major instrument adjustment. The lowest non-blank standard shall be set at the RL.
Initial Calibration Verification (ICV, second source)	90-110% Recovery	Immediately after calibration.
Initial Calibration Blank (ICB)	$\leq$ RL	Analyzed after the analytical standards, but not before analysis of the Initial Calibration Verification (ICV) during the initial calibration of the instrument.
Continuing Calibration Verification (CCV)	90-110% Recovery	Every 10 samples and at the end of the run.
Lower Limit of Quantitation Check (LLQC) (identified by lab as either CRI or CRA)	70-130% Recovery	Analyzed at beginning and the end of each run.
Continuing Calibration Blank (CCB)	$\leq$ RL	Analyzed immediately after every Continuing Calibration Verification (CCV); every 10 samples and at the end of the run.
Method or Preparation Blank	$\leq$ RL	Every 20 samples.
Laboratory Control Sample	80-120% recovery	Every 20 samples.
Matrix Spike	75-125% Recovery (Recovery calculations are not required if the sample concentration is $>4x$ the spike added.)	Every 20 samples.

QC Type	Acceptance Criteria	Frequency
Post-Digestion Spike	80-120% Recovery per Method 7000B as reference in 7470A (Note the lab sop uses 75-125% Recovery)	If a MS and/or MSD are out of control.
Duplicate Sample	$RPD \leq 20\%$ for sample values $\geq 5 \times RL$; for sample values $< 5 \times RL$, control limit = RL	Every 20 samples.
Determination of Method Detection Limits		Annually and after major instrument adjustment.

Table 23. Region VII contract laboratory QA/QC requirements for VOCs by GC/MS.

QC Type	Acceptance Criteria	Frequency
Instrument Calibration	The acceptance criterion for the initial calibration requires RSD <15% or for alternate curve fits the correlation coefficient $r \geq 0.990$.	Each time instrument is turned on or set up, after ICV or CCV failure, and after major instrument adjustment. The lowest non-blank standard shall be set at the RL.
System Performance Check	BFB Tune must meet tuning criteria in Table 4 of 8260B. Minimum average response factors for the SPC compounds* must meet criteria	Prior to sample analysis; beginning of each 12 hour shift.
Initial Calibration Verification (second source)	75-125% Recovery	Immediately after calibration.
Continuing Calibration Verification (CCV)	%D $\leq 20\%$ for analytes using RF; 80-120% Recovery for analytes using curve fitting	Every 12 hours.
Surrogates	70-130% Recovery	All blanks, QC samples, and samples.
Internal Standards	EICP area must not vary by more than a factor of 2 (-50 to +100%) of the mid-point calibration standard. Retention time must not vary by more than 0.50 min of those in the mid-point calibration standard.	All blanks, QC samples, and samples.
Method Blank	<RL <2xRL for methylene chloride, acetone, and 2-butanone	After calibration standards. Every 12 hours.
Laboratory Control Sample	70-130% Recovery 60-140% Recovery for t-butyl alcohol, isopropyl alcohol, and	Every 20 samples. Evaluated only when MS is outside control limit.

QC Type	Acceptance Criteria	Frequency
	ethanol	
Matrix Spike	70-130% Recovery 60-140% Recovery for t-butyl alcohol, isopropyl alcohol, and ethanol	Every 20 samples.
Duplicate Sample (MS/MSD)	RPD<30%	Every 20 samples.
Determination of Method Detection Limits		Annually and after major instrument adjustment.

*SPC compounds minimum response factors (RF):

Chloromethane, min. RF = 0.10

1,1-Dichloroethane, min. RF = 0.10

Bromoform, min. RF = 0.10

1,1,2,2-Tetrachloroethane, min. RF = 0.30

Chlorobenzene, min. RF = 0.30

Table 24. Data qualifiers.

Qualifier	Definition
U	The analyte was analyzed for, but was not detected above the reported quantitation limit (QL).
J	The analyte was positively identified. The associated numerical value is the approximate concentration of the analyte in the sample (due either to the quality of the data generated because certain quality control criteria were not met, or the concentration of the analyte was below the QL).
J+	The result is an estimated quantity, but the result may be biased high.
J-	For both detected and non-detected results, there may be a low bias due to low spike recoveries or sample preservation issues.
B	The analyte is found in a blank sample above the QL and the concentration found in the sample is less than 10 times the concentration found in the blank.
H	The sample was prepared or analyzed beyond the specified holding time. Sample results may be biased low.
*	Relative percent difference of a field or lab duplicate is outside acceptance criteria.
R	The data are unusable. The sample results are rejected due to serious deficiencies in the ability to analyze the sample and/or meet quality control criteria. Sample results are not reported. The analyte may or may not be present in the sample.

Data Descriptors

Definition
Not Applicable (See QAPP)
Not Reported by Laboratory or Field Sampling Team
Not Detected
Not Sampled

If the analyte concentration was less than the Quantitation Limit (<QL), then the B qualifier was not applied.
If both an analyte and an associated blank concentration are between the MDL and QL, then the sample results are reported as <QL and qualified with U.
For samples associated with high Matrix Spike recoveries, the J+ qualifier was not applied if the analyte was less than the Quantitation Limit (<QL).
For samples associated with low Matrix Spike recoveries, the J- qualifier was applied to the analyte with low recovery regardless of analyte concentration (< or > QL).

7.0 Figures

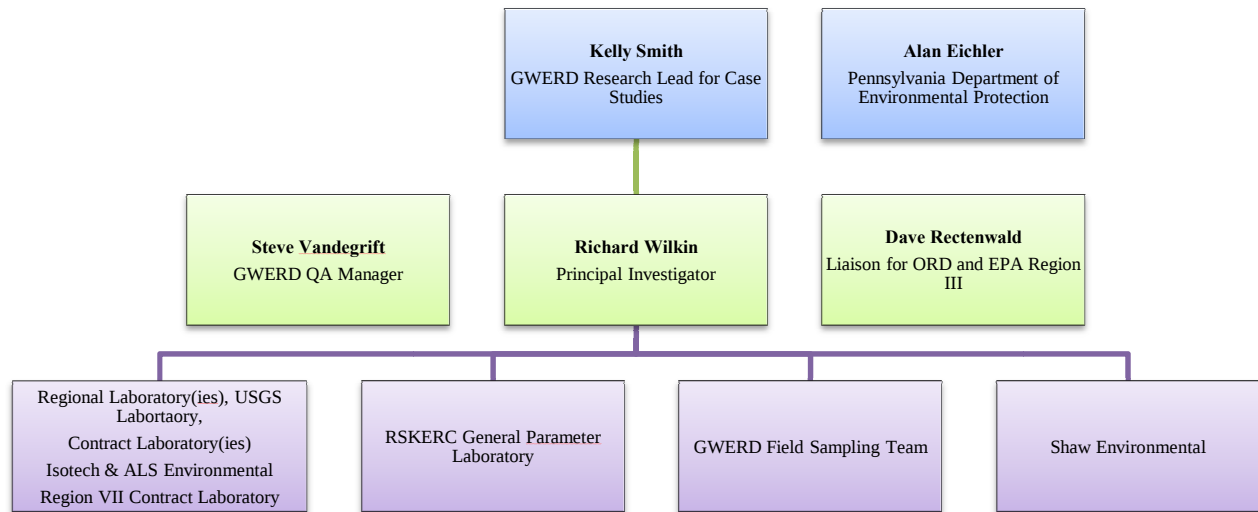


Figure 1. Organizational chart for the Hydraulic Fracturing Retrospective Case Study, Marcellus Shale, Washington County, PA.

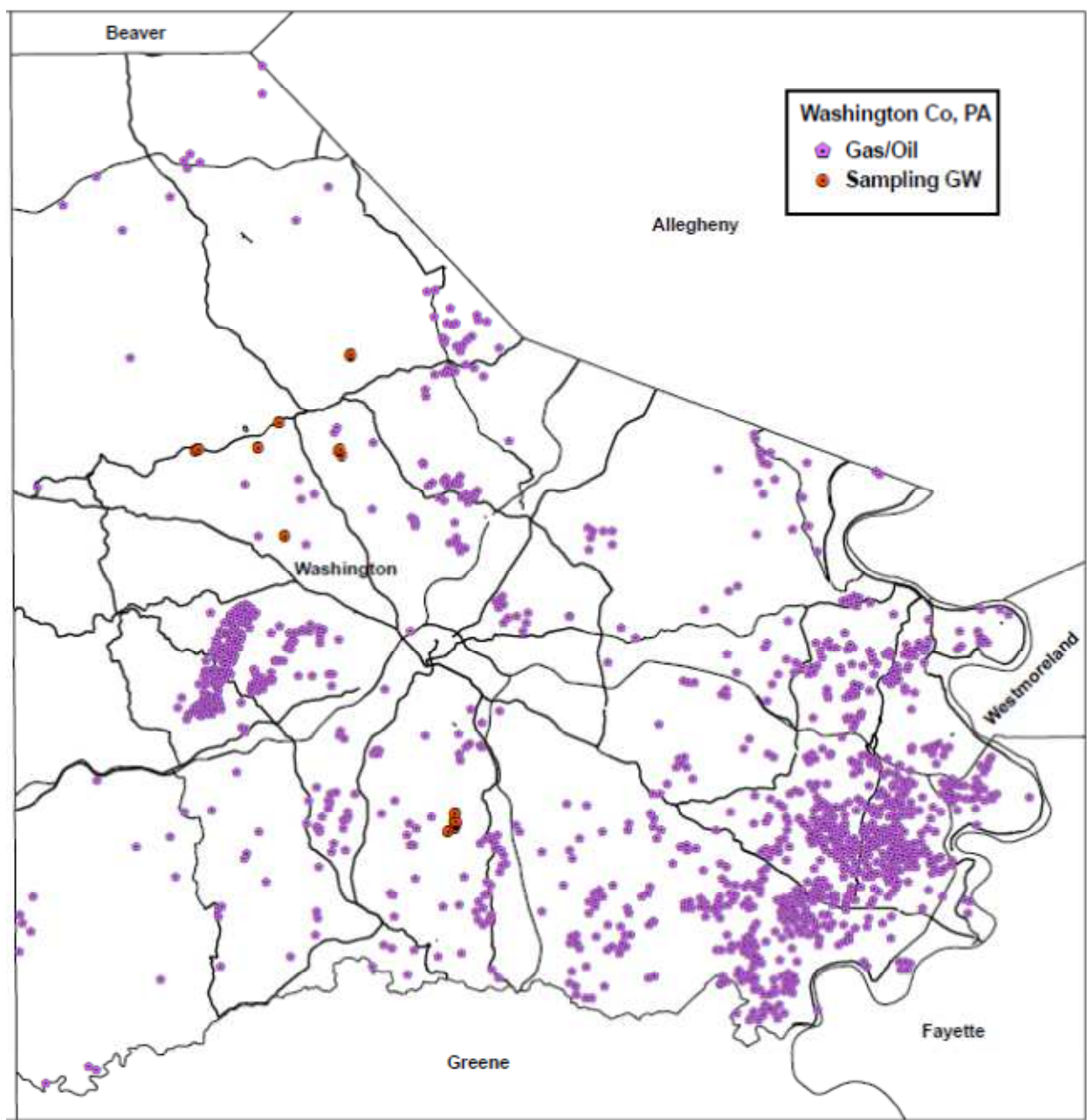


Figure 2. Map of SW Pennsylvania study area, sampling locations and gas/oil production wells.

[illegible]

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 $^{87}\text{Sr}/^{86}\text{Sr}$ 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) hydrofracing 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 $^{87}\text{Sr}/^{86}\text{Sr}$ 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 $^{87}\text{Sr}/^{86}\text{Sr}$ 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.

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Prepared by:

Zell E. Peterman, PhD, PE (emeritus)

U.S. Geological Survey MS 963 Box 25046 DFC; Denver CO 80225; Email: Peterman@usgs.gov; Phone: 303-324-0458; FAX: 303-236-4930

YMPB USGS TECHNICAL PROCEDURE

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 $^{87}\text{Sr}/^{86}\text{Sr}$ where ^{86}Sr is a nonradiogenic isotope) is a function of the time-integrated $^{87}\text{Rb}/^{86}\text{Sr}$ 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:

$$\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}} \right)_p = \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}} \right)_i + \left(\frac{^{87}\text{Rb}}{^{86}\text{Sr}} \right)_p (e^{\lambda t} - 1)$$

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 ($1.42 \times 10^{-11} \text{ yr}^{-1}$).

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 $\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}} \right)_i$ 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 $\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}} \right)_i$ 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 $\left(\frac{^{87}\text{Rb}}{^{86}\text{Sr}} \right)_p$ must be known so that $\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}} \right)_p$ 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 calcretes, 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 ⁸⁴Sr and ⁸⁷Rb. Sample dissolution is accomplished through a combination of small amounts of concentrated H₂SO₄, HCl, HClO₄, or HNO₃ with concentrated HF. After refluxing on a hot plate to dryness the resultant precipitate is brought into solution with HCl or HNO₃ and centrifuged. The supernatant solution is pipetted in small volumes onto an ion-exchange resin column pretreated with HCl or HNO₃. After washing with a measured volume of HCl or HNO₃ 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 HNO₃ leaving admixed silicates intact. Other methods of leaching include, but are not limited to 10 percent CH₃COOH (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 insoluble 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 HNO₃ acid. To estimate the proportion of carbonate in the original sample, the acid-leached residue is washed with ultra high purity (UHP) H₂O, 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 HNO₃ 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 $^{87}\text{Sr}/^{86}\text{Sr}$ 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 $^{86}\text{Sr}/^{88}\text{Sr}$ 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 $^{87}\text{Rb}/^{86}\text{Sr}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ 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

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6.2.2 Chemical Dissolution:

- Ultra-high purity (UPH) H₂O (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: H₂SO₄ (concentrated) HF (concentrated) HClO₄ (concentrated) HNO₃ (concentrated) HCl (concentrated) CH₃COOH (acetic acid) Disodium EDTA (ethylenedinitrilotetraacetate)
- Platinum dishes
- Teflon covers, jars, beakers, tubes and other equipment
- Electronic analytical balance
- NIST traceable weights
- ⁸⁷Rb spike solution
- NIST SRM-607 Rb standard
- ⁸⁴Sr 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 laboratory 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 $^{87}\text{Rb}/^{85}\text{Rb}$ 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 $^{87}\text{Sr}/^{88}\text{Sr}$ 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 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 5 years or as necessary by an OCRWM OQA approved/accepted supplier.

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

12. CONSUMABLE STANDARDS/MATERIALS. Consumable materials will be 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 $^{87}\text{Sr}/^{86}\text{Sr}$ 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.

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- 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*
- Faure, Gunter, 1986, *Principles of Isotope Geology*: John Wiley and Sons, New York, 589 p.
- Peterman, Z.E., Sims, P.K., Zartman, R.E., and Schulz, K.J., 1985, Middle Proterozoic uplift events in the Dunbar Dome of northeastern Wisconsin, USA: *Contributions to Mineralogy and Petrology*, v. 91, p. 138-150

17. ATTACHMENTS. None.

18. HISTORY OF CHANGES.

<u>Revision/Modification No.</u>	<u>Effective Date</u>	<u>Description of Changes</u>
R0	5/14/2007	Initial issue.

