GWERD QUALITY ASSURANCE PROJECT PLAN

Title: Hydraulic Fracturing Retrospective Case Study, Raton Basin, CO

TASK No. 26278

QA ID No. G-16642

QA Category: 1

HF Project #13

Original QAPP submitted: 8/30/2011

Number of Pages: 105

Revision No: 3 (submitted October 31, 2013) (see Table 1 for Revision History)

_____/s/_____ 11/5/2013_
Richard Wilkin, Principal Investigator Date

APPROVALS:

_____/s/_____ 11/5/2013_
David Jewett, Branch Chief Date

_____/s/_____ 11/5/2013_
Kelly Smith, GWERD Research Lead for Case Studies Date

_____/s/_____ 11/5/2013_
Steve Vandegrift, GWERD QA Manager Date

Distribution List:
Russell Neill, EPA/ORD/NRMRL/GWERD
Zell Peterman, U.S. Geological Survey
Tony Lee, EPA/ORD/NRMRL/GWERD
Steve Acree, EPA/ORD/NRMRL/GWERD
Randall Ross, EPA/ORD/NRMRL/GWERD
Cynthia Caporale, EPA Region 3
Gregory Oberley, EPA Region 8
Amy Wolfe, EPA/ORD/NRMRL/GWERD
Chris Ruybal, Student Contractor
Alex Kirkpatrick, Student Contractor
Cherri Adair, EPA/ORD/NRMRL/GWERD
Mark White, EPA/ORD/NRMRL/GWERD
Mark Burkhardt, EPA Region 8

Disclaimer

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). The results of the research projects will provide the foundation for EPA's 2014 study report.

This QAPP provides information concerning the Well Injection 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.

Table of Contents

1.0 Project Management 6
1.1 Project/Task Organization 6
1.2 Problem Definition/Background 9
1.3 Project/Task Description 12
1.4 Project Quality Objectives and Criteria 14
1.5 Special Training/Certification 14
1.6 Documents and Records 15
2.0 Data Generation and Acquisition 16
2.1 Sampling Process Design (Experimental Design) 16
2.1.1 Background Geologic and Hydrological Information 16
2.2 Sampling Methods 19
2.2.1 Ground-Water Sampling 19
2.2.2 Domestic Well and Surface Water Sampling 24
2.2.3 Pressure Transducers 25
2.3 Sample Handling and Custody 25
2.3.1 Water Sample Labeling 25
2.3.2 Water Sample Packing, Shipping, and Receipt at Laboratories 25
2.4 Analytical Methods 27
2.4.1 Ground and Surface Water 27
2.5 Quality Control 33
2.5.1 Quality Metrics for Aqueous Analysis 33
2.5.2 Measured and Calculated Solute Concentration Data Evaluation 37
2.5.3 Detection Limits 38
2.5.4 QA/QC Calculations 38
2.6 Instrument/Equipment Testing, Inspection, and Maintenance 39
2.7 Instrument/Equipment Calibration and Frequency 39
2.8 Inspection/Acceptance of Supplies and Consumables 41
2.9 Non-direct Measurements 41
2.10 Data Management 43
2.10.1 Data Recording 43
2.10.2 Data Storage 43
2.10.4 Analysis of Data 44
3.0 Assessment and Oversight 45

3.1 Assessments and Response Actions 45
3.1.1 Assessments 45
3.1.2 Assessment Results 46
3.2 Reports to Management 46
4.0 Data Validation and Usability 47
4.1 Data Review, Verification, and Validation 47
4.2 Verification and Validation Methods 47
4.3 Reconciliation with User Requirements 49
5.0 References 50
6.0 Tables 54
Table 1. QAPP revision history. 54
Table 2. Known constituents of hydraulic fracturing fluids used in the Raton Basin 58
Table 3. Critical analytes. 59
Table 4. Tentative schedule of field activities for the hydraulic fracturing case study in the Raton Basin, Colorado. 60
Table 5. Ground and surface water sample collection. 61
Table 6. Field QC samples for water samples. 63
Table 7. RSKERC detection limits for various analytes.* 64
Table 8. Region VII contract lab metal quantitation limits. ICP-AES uses EPA Method 200.7; ICP-MS uses EPA Method 6020A; total digestions follow EPA Method 200.7; and Hg analysis follows EPA Method 7470A. 65
Table 9. Region VII contract lab quantification limits (QLs) for VOCs 66
Table 10. 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. 67
Table 11. RSKERC QA/QC requirements summary* from SOPs. 69
Table 12. Region VIII laboratory QA/QC requirements for semivolatiles, GRO, DRO 71
Table 13. Region III detection and reporting limits for glycols. 73
Table 14. Region III laboratory QA/QC requirements for glycols. 74
Table 15. Isotech laboratory QA/QC Requirements for $\delta^{13}C$ of DIC (Dissolved Inorganic Carbon). 75
Table 16. Isotech Laboratory QA/QC Requirements for $\delta^{13}C$ of dissolved methane (and >C1) and δD of dissolved methane. 76
Table 17. Isotech Laboratory QA/QC Requirements for $\delta^{34}S$ of dissolved sulfide and sulfate and $\delta^{18}O$ of dissolved sulfate. 77
Table 18. USGS laboratory QA/QC requirements for $^{87}Sr/^{86}Sr$ analysis using TIMS*. 78

Table 19. ORD Cincinnati laboratory QA/QC requirements for molecular microbial analysis. 79
Table 20. Region VII contract laboratory QA/QC requirements for ICP-MS metals. 80
Table 21. Region VII contract laboratory QA/QC requirements for ICP-AES metals. 82
Table 22. Region VII contract laboratory QA/QC requirements for mercury by cold vapor AAS..... 83
Table 23. Region VII contract laboratory QA/QC requirements for VOCs by GC/MS..... 84
Table 24. Data qualifiers..... 85
7.0 Figures..... 86
Figure 1. Organizational chart for the Hydraulic Fracturing Retrospective Case Study in the Raton Basin, Colorado..... 86
Figure 2. Generalized geologic map of the Raton Basin near Trinidad, CO. Modified from Tweto (1979)..... 87
Figure 3. A to A' cross section and schematic stratigraphic column of the Cretaceous and Tertiary rocks in the Raton Basin (modified from Flores and Bader, 1999)..... 88
Figure 4. North Fork Ranch study area (Site 1 on Figure 2). Red symbols (diamonds) domestic wells; red symbols (circles) surface water; blue symbols (diamonds) monitoring wells; and, white symbol production wells..... 89
Figure 5. Little Creek Area (Site 2 on Figure 2). Red symbols (diamonds) domestic wells. Yellow symbols show the locations of three stimulated wells (gel fracs)..... 90
Figure 6. Durov diagram showing the distribution of major cations, major anions, as well as total dissolved solids (TDS) and pH in wells from the North Fork Ranch area (Site 1 on Figure 2)..... 91
Figure 7. Chain of Custody form for submittal of water samples to R.S. Kerr Environmental Research Center..... 92
APPENDIX A..... 93
Isotope Support for the EPA Hydraulic Fracturing Study by the U.S. Geological Survey (USGS) Denver CO..... 93

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 Raton Basin, CO. 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.

Dr. Amy Wolfe, 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. Wolfe is responsible for assisting in ground water and surface water sampling, development of the QAPP and revisions to the QAPP, assisting in the interpretation of data, and development of project reports. Her 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. 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. John Skender, 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. Skender is responsible for assisting with ground water sampling. His HAZWOPER certification is current.

Mr. Mark White, U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, 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. Jorge Santo Domingo, U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Water Supply and Water Resources Division, Cincinnati, OH 45268. Dr. Santo Domingo will be responsible for molecular microbial analysis of ground water samples for the first two sampling rounds.

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. Patrick DeArmond, U.S. Environmental Protection Agency – National Exposure Research Laboratory, Las Vegas, NV. Dr. DeArmond will analyze samples for glycols in cases where the analysis is not performed by the Region III laboratory.

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. 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.

Dr. Peter Gintautas, Colorado Gas and Oil Conservation Commission, Dr. Gintautas is the point of contact for the state of Colorado.

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

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

Mr. Gregory Oberley, U.S. Environmental Protection Agency – Region VIII. Mr. Oberley is the point of contact for the Region 8 office. Mr. Oberley is responsible for coordinating technical discussion and activities between NRMRL-Ada and EPA Region VIII, as well as coordinating data collection activities with the state and local officials in Colorado and with property owners and local stakeholders. He will also assist in ground water sampling. His HAZWOPER certification is current.

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. Ms. Mravik also assists the PIs by tracking the status of laboratory analysis of samples, data reports, ADQs, and final QA approvals of data. She is the Contracting Officer Representative for the support contract with Ecology and Environment, Inc.

Mr. Gene Florentino, Ecology and Environment, Inc., Lancaster, NY. Mr. Florentino is the point of contact for the E&E contract that provides support in drafting text, preparing graphics, collecting historical data, and carrying out statistical calculations to support the final report for this project.

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 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.

As the project PI, 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 laboratories to address issues with sample analysis, and ensuring that data reports are received.

1.2 Problem Definition/Background

The retrospective case study in the Raton Basin, Colorado will investigate the potential impacts of hydraulic fracturing and processes related to hydraulic fracturing on drinking water resources in Las Animas and Huerfano Counties, located in south-central Colorado. The location of this case study was selected in response to complaints about appearance, odors and taste associated with water in domestic wells. 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).

In July 2011, the PI, the Region VIII point of contact, and the Technical Research Lead for Case Studies visited with homeowners in the area and selected potential sites for sampling. During

that trip meetings were also held with other Region VIII staff, staff from the Colorado Oil and Gas Conservation Commission, and representatives from the primary gas producers in the area (Pioneer Natural Resources and Petroglyph Energy) to provide background on the overall HF Study Plan and specifics about the case study in the Raton Basin. This study will be conducted in conjunction with these organizations. The U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Ground Water and Ecosystems Restoration Division (GWERD) will be the lead organization for this case study.

Site Background – The Raton Basin covers an area of about 2,200 square miles in south-central Colorado and northeastern New Mexico (Figures 2 and 3). It is one of several important coal-bearing basins along the eastern margin of the Rocky Mountains. The basin extends 80 miles north and south and as much as 50 miles east and west. The basin is an elongate asymmetric syncline, with 20,000 to 25,000 feet of sedimentary rock in the deepest part. Coalbed methane resources are contained in the upper Cretaceous Vermejo Formation and the upper Cretaceous and Paleocene Raton Formation.

Over the last decade exploration for and production of coalbed methane has increased substantially in the Raton Basin. During 1999-2004, annual production of natural gas from coal in Las Animas County, Colorado increased from 28,129,515 to 80,224,130 thousand cubic feet (Watts, 2006a). In addition, ground water coproduced by coalbed methane wells increased from about 949 million gallons to about 2879 million gallons (Watts, 2006a). Individual coalbeds in the Vermejo Formation range from a few inches to about 14 feet thick, with the total coal thickness from 5 to 35 feet. The Raton Formation is thicker and contains more total coal than the Vermejo Formation, yet individual coal seams in the Raton are less continuous and generally thinner.

Hydraulic fracturing is used to enhance coalbed methane production by enabling gas and water within the rock to flow more readily to an extraction well. Coalbed methane well stimulation using hydraulic fracturing techniques is a common practice in the Raton Basin. Records show that fluids typically used are gels with water and sand proppants, 15% HCl in water, or foam fracs that use N_2. Some of the chemicals used for hydraulic fracturing in the Raton Basin are listed in Table 2. The coal seams of the Vermejo and Raton Formations, developed for methane production, also contain water that meets the water quality criteria for a USDW (underground source of drinking water). A survey of the estimated vertical separation between production intervals of coalbed-methane and water supply wells in the Raton Basin (Las Animas and Huerfano Counties) shows a wide range of separations, from less than or equal to 100 feet to 5,800 feet (Watts, 2006b). This report also suggests that in areas with less than 100 feet of vertical separation, production by coalbed-methane wells has a greater potential for interfering with nearby water supply wells.

Project Background & Objectives - Potential sources of ground-water contamination in the study area include activities associated with coal bed methane extraction (such as leaking or abandoned pits), gas well completion and enhancement techniques, coal outcrops, coal mines, residential or agricultural practices, improperly plugged and abandoned wells, and/or gas migration. Several phases of investigation for this case study are anticipated. An iterative approach is being adopted. Early in the investigation screening investigations will take place (i.e., sampling

domestic wells, surface water bodies, and monitoring wells), particularly at locations where concerns have been raised by local residents. Depending on the results of the initial screening, several different possibilities could arise. If no contamination or anomalous chemical signatures are detected, then follow-up sampling events would likely be conducted using identical methods to confirm the result. On the other hand, if contamination is detected, then confirmation sampling would be planned, but also additional studies and methods may be adopted to track the source of contamination. This iterative approach is being adopted to meet the primary objective of the study: to determine if ground-water resources in the Raton Basin have been impacted by hydraulic fracturing processes, and the related secondary objective: to determine the likely pathway(s) of contaminant migration.

In Phase I, selected domestic wells, surface water bodies, monitoring wells, and production wells will be sampled and analyzed to determine the nature of water chemistry and contamination, if it exists. The wells selected for sampling are based on a site scoping trip conducted in July 2011 that included interviews with local residents and homeowners (see Section 1.3). If evidence of ground water or surface water contamination is indicated in Phase I sampling, Phase II activities will be targeted to confirm the initial result and to identify the source or sources of contamination. If no contamination is detected in the first Phase I screening event, it is anticipated that limited follow-up sampling would take place to confirm the result. Phase II activities will likely involve additional surface water and ground-water sampling, monitoring well sampling, and may involve installation of temporary or permanent wells for hydrogeologic and geochemical characterization, core collection and analysis, and geophysical surveys (self potential and/or resistivity). Phase I sampling is expected to begin in October 2011. Version 0 of this QAPP (dated 9/20/2011) 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.

- Version 1 of this QAPP (dated 4/30/2012) includes minor revisions to sampling and analytical methodologies and additional analyses prior to the second sampling trip in May 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 May 2012 sampling event. Addendum No. 2 to Version 1 (dated 1/10/2013) was prepared to document QC acceptance criteria for the analysis of samples for metals and VOCs by a Region VII contract laboratory (Southwest Research Institute, a subcontractor to ARDL, Inc.) for the November 2012 sampling event.

- Version 2 of this QAPP describes additional quality assurance and quality control associated with water sampling and chemical analysis for the April 2013 sampling event (Table 1). The final sampling event is scheduled for April 2013 and will be carried out to verify/validate the results of the first three rounds of sampling and to better establish time trends for dissolved gases (and related constituents) in the northern field area (Huerfano County).

  Sampling in Las Animas County in the fourth round will include locations sampled in previous sampling: production wells, monitoring wells, domestic

wells, and streams. Cumulative results from the four sampling events will provide a seasonal measure of ground water and surface water quality over ~17 months. The first three rounds of sampling have shown few anomalies with respect to organic and/or inorganic constituents; consequently, further investigation beyond a fourth round is currently not warranted. The fourth round of data is important to characterize potential seasonal variability and to track low-level detections of certain chemicals at specific locations. Sampling in Huerfano County in the fourth round will include only domestic wells sampled in the previous sampling events. A primary focus of the sampling event will be to further document time-related changes in methane and dissolved sulfide concentrations in impacted domestic wells and wells outside the area of impact. A previous release of methane gas from the coal-bed production zone into the shallower aquifer system has led to elevated methane concentrations in the aquifer used for drinking water. Subsequently, methane in the aquifer has undergone anaerobic methane oxidation, resulting in the consumption of dissolved methane and sulfate and production of dissolved sulfide and bicarbonate. Changes in the concentrations and isotopic compositions of these reactants and products have been tracked in this retrospective study. These results are unique in showing system behavior after a methane release and provide information about biogeochemical response to methane invasion and information about attenuation rates and capacity over the 17-month window of this study.

- Version 3 of this QAPP provides additional information about the use and sources of secondary data. Additional information is also provided regarding the software and methods to be used in conducting data analysis.

1.3 Project/Task Description

Data collection in Phase I will involve sampling water from domestic wells, surface water bodies, monitoring wells, and gas production wells. Possible sampling locations were selected during a reconnaissance trip to the area conducted in July 2011. Two separate gas-producing fields were targeted for field sampling: a southern field site (North Fork Ranch Area; Las Animas County) and a northern field site (Little Creek Field; Huerfano County) as shown in Figure 2. The total number of possible sampling locations at these two sites exceeds what can realistically be sampled and delivered to the analytical laboratories in one week of sampling. A subset of sites to be sampled was selected based on discussions between GWERD and Region VIII. The selected sampling sites meet certain criteria. Two production wells will be sampled in the North Fork Ranch study area to obtain information about the chemistry of water from the production zones (Vermejo and Raton Formations). Data from these wells will be used in conjunction with data from monitoring wells, domestic wells, and surface water in the North Fork Ranch study area. These production wells will be sampled during each sampling event if access is permitted. Monitoring wells screened in the aquifer used for drinking water (Poison Canyon Formation) were selected for sampling; these are adjacent to or proximal to the deeper production wells. Domestic wells in both study areas were selected based upon reported concerns about water quality, and to achieve reasonable coverage in terms of depth and aerial distribution. One stream was targeted for sampling based on concerns of residents regarding the

nature of the stream water quality. During the second sampling trip in May 2012, two additional surface water locations were added; these surface water locations will be sampled in subsequent events. The selected sampling locations in the northern and southern sampling sites are shown in Figure 4 and Figure 5.

Additional sampling points may be included in the future and will be noted in any subsequent QAPP revisions. Figures 4 and 5 show the map location of sampling points. During the October 2011 sampling trip, 2 production wells, 5 monitoring wells, 14 domestic wells, and 1 surface water location were targeted for sampling. In the second round, samples were collected from 12 domestic wells, 2 production wells, 3 monitoring wells, and 3 surface water locations. Compared to round 1, two new domestic wells were sampled and two additional surface water sites were sampled; several monitoring wells sampled in the first round were excluded from the second round because the wells were abandoned. The third round of sampling coincided with second round in terms of sample locations, and the same sample locations are planned for the fourth round. Water analysis includes 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, low molecular weight organic acids, dissolved gases (methane, ethane, propane, n-butane), 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, S isotope composition of dissolved sulfate and dissolved sulfide, and Sr isotope ratios. Microbial analyses will also be conducted to better understand the biogeochemical cycling of carbon and sulfur (analyses conducted in round 1 and round 2).

Included in this set of measurements are a selection of components of hydraulic fracturing fluids (e.g., potassium, glycols, alcohols, and boron), potentially mobilized naturally occurring substances such as arsenic, manganese, and other trace metals, and general water quality parameters (e.g., pH, major anions and cations). Of the target analytes noted above, those that are critical analytes supporting the primary objective (i.e., to determine if ground-water resources in the Raton Basin, CO 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 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) by the EPA GP Laboratory and CB&I (formerly Shaw Environmental), U.S. EPA Regional laboratories located in Fort Meade (MD), Region III, and Golden (CO), Region VIII, EPA Office of Research and Development laboratories in Cincinnati (OH), USGS laboratories located in Denver (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 should be noted that for the November 2012 sampling event, the glycols were analyzed by the NERL-Las Vegas laboratory instead of the Region III laboratory. The Region III SOP and QA/QC requirements were used.

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.

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 are 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 expected for on-site work. HAZWOPER training and yearly refresher training is provided to GWERD personnel at an appropriate training facility chosen by the 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 are 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, the data will no longer be flagged as "screening" data. Isotech Laboratories and USGS laboratories will not provide data for critical analytes. 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.

1.6 Documents and Records

Data reports will be provided electronically as Excel spreadsheets. Some may be submitted as Adobe pdfs. 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 the PIs 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

Geology – The Raton Basin is a north-south trending sedimentary and structural depression located along the eastern edge of the Rocky Mountains, between the Sangre de Cristo Mountains to the west and the Apishapa, Las Animas, and Sierra Grande arches on the east (Watts, 2006b). It is a typical Rocky Mountain foreland basin formation formed during the Laramide Orogeny (Cooper et al., 2007). This chevron-shaped basin encompasses roughly 2200 mi^2 of southeastern Colorado and northeastern New Mexico (US EPA, 2004) and extends from southern Colfax County, New Mexico, northward into Heurfano County, Colorado (US EPA, 2004). It is the southernmost of the several major coal-bearing basins located along the eastern margin of the Rocky Mountains (Johnson and Finn, 2001). The basin is asymmetrical with the deep basin axis located along the western margin of the trough, just east of the Sangre de Cristos Mountains (Johnson and Finn, 2001). The northern part of the Raton basin is divided by a southward-plunging anticlinal extension of the Wet Mountains. The axis of the eastern basin trends northeastward between the Wet Mountains and the Las Animas arch and terminates to the north against the Apishapa arch. The structurally lowest part of the basin is north of the Spanish Peaks, as indicated by structural contours on top of the Trinidad Sandstone (Geldon, 1989).

A thick sequence of Upper Cretaceous and Tertiary coal-bearing clastic sedimentary rocks, approximately 10,000 to 25,000 ft, is preserved within the basin. The sedimentary sequence exposed within the Raton Basin was deposited in association with regression of the Cretaceous Interior Seaway and the stratigraphy reflects well-developed flow-through fluvial systems which contained peat-forming swamps (Cooper et al., 2007; Flores, 1993). Sedimentary rocks in the region, from oldest to youngest, include the Pierre Shale (Campanian to Maastrichtian), Trinidad Sandstone and Vermejo Formation (Maastrichtian), Raton Formation (Maastrichtian and Paleocene), and Poison Canyon Formation (also Maastrichtian and Paleocene) (Pillmore et al., 1984). The Pierre Shale, Trinidad Sandstone, and Vermejo, Raton and Poison Canyon Formations reflect a succession of coarsening-upward megacycles, capped by thin to thick conglomerate and sandstone dominated units (Flores and Bader, 1999). The Upper Pierre Shale, the Trinidad Sandstone and Vermejo Formations were deposited in a fluvial-deltaic environment. As the sea withdrew from the region, the Pierre shale was deposited on the shelf and the prodelta, the Trinidad Sandstone was deposited on the delta front and the Vermejo Formation accumulated on the delta plain. The Raton Formation, a continental floodplain deposit, was deposited after the shoreline had retreated from the area (Lewicki, 2001).

Numerous discontinuous and thin coal beds are located in the Vermejo Formation and Raton Formation, which lie directly above the Trinidad Sandstone. The upper Trinidad intertongues with, and is overlain by, the coal-bearing Vermejo Formation (Topper et al., 2011). This sandstone layer serves as a "marker" for the area because no coals are found below this sandstone (Lewicki, 2001). Individual coalbeds in the Vermejo Formation, located immediately below the Raton Formation, consists of interbedded shales, sandstones and coals. The formation

ranges from 150 feet thick in the southern part of the basin to 410 feet in the northern part (Lewicki, 2001). This formation contains from 3 to 14 coal beds over 14 inches thick over the entire basin and total coal thickness typically ranges from 5 to 35 feet (US EPA, 2004). The nearshore, fluvial-deltaic deposits of the Vermejo contain the best developed and most laterally extensive coal beds in the basin (Topper et al., 2011). The late Cretaceous to Paleocene Raton Formation overlies the Vermejo Formation. Syndepositional clastic sediments shed off the rising Sangre de Cristo Mountains were deposited near the mountain front as the Raton basal conglomerate and mark the erosional contact between the Raton Formation and the underlying Vermejo Formation (Topper et al., 2011). The Raton Formation is comprised of a basal conglomerate, a middle coal bearing zone, and an upper transitional zone and ranges from 0 – 2,100 ft thick; the middle coal-bearing zone is approximately 1,000 feet thick and consists of shales, sandstones and coal beds (Johnson and Finn, 2001; US EPA, 2004). This zone also contains coal seams that have been mined extensively (Lewicki, 2001); total coal thickness ranges from 10 feet to greater than 140 feet, with individual seams ranging from several inches to greater than 10 feet thick (US EPA, 2004). The sandstones are interbedded with coal beds that are currently being developed for coal-bed methane, and the coals are the likely source for gas found in the sandstones (Johnson and Finn, 2001).

Epeirogenic movements and orogenic episodes, associated with Laramide deformation, are recorded in the strata and faults and folds modify the regional structure (Geldon, 1989; Johnson et al., 1956). Laramide deformation began with epeirogenic movements west of the Raton Basin and was followed by at least seven orogenic episodes. The complex structural history is reflected by angular unconformities and lithologic changes within sedimentary rocks located in the basin: along the western edge, rocks are steeply tilted, overturned, and faulted; whereas, along the eastern edge of the basin, rocks are tilted only 1 to 5 degrees to the west (Flores and Bader, 1999; Johnson et al., 1956). Folds with small amplitude occur throughout the basin (Geldon, 1989).

Sills, dikes, plugs, stocks and laccoliths were intruded into the sedimentary rocks of the basin during the Eocene epoch and are thought to be related to the Rio Grande Rift located to the west of the basin (Cooper et al., 2007). Miocene and Pliocene igneous dikes, sills, plugs, stocks, and laccoliths – ranging in age from 6.7 to 29.5 my are common intrusions throughout the coal-bearing Vermejo and Raton Formations (Flores and Bader, 1999). The most prominent igneous features are those related to the Spanish Peaks and their associated radial dike swarm, located in the north-central portion of the basin (Cooper et al., 2007). Another system of dikes affects seams throughout the entire basin; these intrusions have a roughly east-west orientation, which varies from WSW in the northern basin, to WNW in the southern portion, always trending normal to the Sangre de Cristo Mountains to the west (Cooper et al., 2007; Flores and Bader, 1999). The dikes vary in thickness from a few inches to more than 100 ft and are presumed to be intruded into fracture systems (Flores and Bader, 1999). The formation of these intrusions altered millions of tons of coal to natural coke and may have played a minor role in generating some of the large coalbed methane resources currently being exploited in this region (Cooper et al., 2007). Coalbed methane (CBM) resources within the Raton basin are contained in both the Vermejo Formation and Raton Formations; however, expansion of CBM wells has focused on the development of the Vermejo coals because these coals are thicker and more continuous than those located in the Raton Formation (US EPA, 2004).

The selected study sites (see Figure 2) are located within the Colorado portion of the basin. Within the Colorado portion of the basin, the coal bearing region is a 1100 mi^2 area located in Las Animas and Heurfano counties (Tremain, 1980). The first study site (Site 1, Figure 2) is located north-northwest of Trinidad, CO, along the western margin of the basin. The second study site (Site 2, Figure 2), is located south-southwest of Walsenberg, CO, in the east side of the basin. While the stratigraphic sedimentary sequences are similar, the thickness of individual formations, past igneous activity and the structural history differs between the two sites.

Hydrology - The principal bedrock aquifers in the Raton Basin are the Dakota Sandstone-Purgatoire Formation, Raton Formation-Vermejo Formation-Trinidad Sandstone, Cuchara-Poison Canyon Formation, and volcanic rocks (Abbott et al., 1983). Within these units, sandstone and conglomerate layers transmit most of the water, and shale and coal layers generally retard flow. However, fracture networks in the shales and coals also transmit water. Talus and alluvium yield small to large quantities of water but are limited in aerial extent and discharges from these units fluctuate seasonally (Abbott et al., 1983).

Regional ground-water flow generally is from west to east, except where it is intercepted by valleys that cut into the rock (Watts, 2006a). Flow is generally lateral and parallel with bedding but also can be downward where fractures connect permeable rock. The depth to ground water depends mostly on topographic position. In stream valleys, ground water is usually less than 100 feet below ground surface. Some of this water discharges as springs or flows into stream alluvium. Depth to ground water is also affected by geology. Clusters of springs are often located at or near the contact between the Cuchara-Poison Canyon and Raton-Vermejo-Trinidad aquifers. Others are located along dikes and sills; these intrusive rocks are barriers to flow and can force water to the surface. Aquifer tests in the Raton-Vermejo aquifers indicate hydraulic conductivities that range from 0 to 45 ft/d (Abbott et al., 1988).

Geologic formations have somewhat distinctive ground-water chemistry. The Cuchara-Poison Canyon Formation is typically calcium-bicarbonate type with low (<500 mg/L) total dissolved solids content. The Raton-Vermejo-Trindad aquifer is typically sodium-bicarbonate with slightly higher average total dissolved solids concentrations (<1500 mg/L). Abbott et al. (1983) noted that concentrations of boron, fluoride, iron, manganese, mercury, nitrate, selenium, and zinc are increased in local areas due to geologic processes and human activities. High concentrations of fluoride occur in the Poison Canyon and Raton Formations, possibly due to dissolution of detrital fluorite. Iron and manganese concentrations can be elevated, particularly in areas where coals are present due to the dissolution of pyrite and/or siderite contained in the coal seams. Nitrate enrichment occurs most often in alluvial aquifers where fertilizers and/or animal wastes add nitrogen.

The distribution of major anions and cations in ground water from the North Fork Ranch study area is presented in Figure 6. Data to construct this diagram were obtained from homeowners who provided water quality reports from their own wells. In this area the water is sodium-bicarbonate to calcium-bicarbonate type. The more calcium-rich compositions tend to be from shallower wells. Total dissolved solids levels are below 300 mg/L and tend to increase with depth.

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. 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 production wells, monitoring wells, domestic wells, and surface water bodies to be sampled in Phase 1 of this investigation are shown in Figure 4 and Figure 5.

Production wells and monitoring wells are maintained by Pioneer Natural Resources or Petroglyph Energy. These wells will be sampled in cooperation with these companies or their contractors using dedicated downhole pumps. Company representatives will operate all equipment around the wells. Domestic wells will be sampled using downhole pumps or via homeowner taps. It is believed that most domestic wells are screened between 50 and 800 feet below ground surface. By purging the domestic wells with down-hole pumps, the water intake location within the well casing can be controlled. When using down-hole pumps, the pump intake will be placed near the middle of the screened interval of the well. Whenever possible, drawdown of the water table will be tracked by taking water level measurements every 10 to 15 minutes during well purging. The water level measurements will follow the RSKSOP-326 standard operating procedure. Water levels will be recorded in a field notebook during purging prior to sampling. Stream samples will be collected as grab samples. It is anticipated that ground-water and surface water will be sampled by GWERD over a period of about 17 months. The timing of the ground-water sampling events is anticipated to start in the fall of 2011 and continue to the spring of 2013. The minimum number of sampling events to determine if an impact is present is estimated to be four sampling events. Updates to sampling plans and field activities 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 Ground-Water Sampling

The following methodology will be used for sampling production wells and monitoring wells equipped with dedicated pumps.

1) At each sampling site, GPS coordinates will be collected with a handheld device. Photos will be taken and stamped with the date. Pertinent information about each well will be recorded (e.g., depth, well diameter, configuration, etc.). Whenever possible, the ground-water level will be measured using a Solinst water level indicator (or equivalent) and recorded. Polyethylene tubing will be connected to the pump output; tubing will be changed in between each well. 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 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 1 to 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. 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) 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. Duplicate 40 mL VOA vials (amber glass, precleaned, certified) will be collected, without headspace, for alcohol analysis using RSKSOP-299v2. Trisodium phosphate (TSP) will be added to the VOA vial prior to shipping to the field as a preservative. Acid will not be used as a preservative due to a concern of acid hydrolysis of some analytes. The samples will be stored and shipped on ice to CB&I, NRMRL-Ada's on-site contractor for GC-MS analysis. These samples will not be collected during the fourth round because VOCs will be analyzed under the Region VII contract.

    b. 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 collection to obtain a pH < 2 for sample preservation. The samples will be stored and shipped on ice to a lab designated under the EPA Region VII contract with ARDL, Inc. for GC-MS analysis.

    c. 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 April 2013), an additional 2 samples will be collected at each site 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 for 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.

d. Duplicate 40 mL VOA vials (clear glass, precleaned) will be collected for low molecular weight organic acid analysis using RSKSOP-112v6. 1 M sodium hydroxide will be added to the VOA vial prior to shipping to the field as a preservative. The samples will be stored and shipped on ice to CB&I, NRMRL-Ada's on-site contractor for HPLC analysis.

e. 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. Samples will be packed in coolers with ice and shipped overnight to the Region VIII laboratory for analysis.

f. Duplicate 1L 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.

g. 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.

h. 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.

i. A 1L plastic bottle containing a caplet of benzalkonium chloride for preservation will be collected for carbon and hydrogen isotope analyses of dissolved methane (and C2 through C4 if concentrations are high enough to allow isotopic measurements). 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.

j. A1 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 HNO_3 (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.

k. Duplicate 1 L water samples will be collected (unfiltered) in amber plastic bottles previously sterilized using autoclaving, with no preservative added. Samples will be collected leaving some headspace (up to the neck of the bottle). No preservatives will be added to these samples. Sealed bottles will be placed in coolers and shipped on ice to the processing laboratory for microbial analyses (RSKERC). Samples will be shipped overnight to NRMRL-Ada for biomass concentration (via membrane filtration; 0.40-micron, 47-mm polycarbonate filters). Following filtration, the filters will be sent to the ORD Cincinnati laboratory for analysis. Samples for microbial analysis were collected during the October 2011 and May 2012 sampling events; samples will not be collected in subsequent events.

l. 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 H_2SO_4 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-S^{2-} D for wastewater).

m. Next a high-capacity ground-water filter (0.45-micron) will be attached to the end of the tubing and a series of filtered samples (n-u) will be collected. Prior to filling sample bottles, at least 100 mL of ground water will be passed through the filter to waste.

n. Two 1 liter clear plastic bottles will be filled for analysis of $\delta^{34}S$ and $\delta^{18}O$ of dissolved sulfate and $\delta^{34}S$ of dissolved sulfide. The bottles will contain Zn-acetate to fix any dissolved sulfide present as ZnS (zinc sulfide). These bottles will be shipped on ice to the GWERD laboratory in Ada, OK and stored in a walk-in refrigerator. Within one month of sample collection the contents of these bottles will be filtered through 47-mm diameter membrane filters (polycarbonate; 0.4-micron). Samples containing dissolved sulfide will yield a zinc sulfide precipitate upon filtration. These solids will be dried in an oven at 60°C (24 hours), gently ground into a fine powder using an agate mortar and pestle, and placed into plastic cryotubes with screwtop seals. The tubes will be shipped to Isotech Laboratories for measurement of $\delta^{34}S$ of dissolved sulfide. Solutions passing through the 47-mm diameter membrane filters will be collected into 1 L clear plastic bottles and sent to Isotech Laboratories for analysis of $\delta^{34}S$ and $\delta^{18}O$ of dissolved sulfate.

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

p. A1 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 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.

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

r. One 30 mL clear plastic bottle for nitrate + nitrite and ammonium (FIA analysis). This sample will be preserved with 2 drops of 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 stored and shipped on ice to the RSKERC general parameters lab.

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

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

u. A 20 mL glass VOA will be collected for analysis of $\delta^{18}O$ and $\delta^{2}H$ of water using isotope ratio mass spectroscopy (IRMS) 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.

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

See Tables 5 and 6 for numbers of sample bottles needed for each sample type and field QC samples for ground and surface water sampling.

2.2.2 Domestic Well and Surface 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 can be controlled. In this way domestic well sampling can be comparable to monitoring well sampling. 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.

The following is the preferred methodology that will be used for 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, i.e. a water softener). The pump (Proactive Monsoon or equivalent) will be lowered down the well casing to a level selected in the field and powered on. The pump intake will be positioned approximately in the middle of the screened interval of the well. In most cases well construction details will not be available. The goal in domestic well sampling is 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 variables such as water volume pumped, water level drawdown, and stabilization of geochemical parameters will be considered. Once the geochemical parameters, recorded with a YSI probe have stabilized, a series of samples will collected as described above in section 2.2.1.

Figure 4 shows the locations of surface waters that will be sampled. The same set of samples will be collected as described in section 2.2.1. Surface water samples will be collected from flowing streams that were identified during the July 2011 reconnaissance trip to the site and during subsequent visits to the site. Depending on seasonal flow in the streams, it may not be possible to collect surface water during all sampling visits. The streams are typically less than 0.2 m deep, but this depth is likely to change seasonally and in relation to precipitation events. Site 1 was selected as it represents a focus of surface water outflow from the North Fork Ranch sampling site (Site 1 on Figure 2). Site 3 represents a collection/discharge point of produced water in the North Fork Ranch area. The locations of the sampling sites will be recorded with a handheld GPS device. The sites will be photographed. Sample bottles will be submerged into the surface water just below the surface and filled as grab samples for unfiltered samples. The sampling will be performed as to minimize capture of sediment into the sampling bottles. General observations about the flow and the stream depth will be recorded in a field notebook. Filtered samples will be collected by pumping water from the stream through a 0.45-micron high-capacity filter (for filtered metals, all isotope analyses except methane, anions, nutrients, and inorganic/organic carbon). Clean tubing will be used prior to any sampling and filtration. The readings from the YSI will be recorded by inserting the probe with protective cover attached 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.

2.2.3 Pressure Transducers

Pressure transducers will be used to measure water pressure changes correlated with changes in water levels within wells. The transducers are coupled with data loggers to electronically record the pressure changes and the time the measurement was obtained. The device used in this study is the Model 3001 Levelogger manufactured by Solinst Canada, Ltd. It consists of a small, self-contained pressure sensor, temperature sensor, battery, and non-volatile memory. The measurement frequency is programmable. The typical accuracy of the pressure transducer, as reported by the manufacturer, is 0.05% full scale with a resolution of 0.001% full scale. These data will be used to help evaluate possible relationships between hydraulic stresses (e.g., pumping, injection, natural recharge, etc.) and changes in water levels in wells. These data may aid in evaluations of hydrostratigraphy and hydraulic communication within the aquifer. The pressure transducer/data loggers will be deployed according to RSKSOP 331 - Standard Operating Procedure for Water Level Monitoring Using Automated Pressure Transducer/Data Loggers. Pressure transducers were installed in 4 domestic wells during the October 2011 sampling trip and in two of these domestic wells barometric pressure loggers were installed; data were first downloaded from these devices in March 2012.

2.3 Sample Handling and Custody

2.3.1 Water Sample Labeling

Each well will be uniquely labeled. Samples collected from each well will include the unique label, the date, the initials of the sampler, and designation of the sample type, e.g., “metals” and preservation technique (when applicable). This information will be recorded onto labeling tape, using water-insoluble ink, affixed to each sample bottle. Samples will be labeled as follows. Production wells will be labeled RBPWxx-mmyy. The xx will move in sequence (i.e., 01, 02, etc.). The mmyy will record the month and year (i.e., 1011 for October 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., RBPW05d-1011). Labeling of monitoring wells, domestic wells, and surface water samples will follow the same approach, except instead of PW, MW, DW, and SW, respectively, will be used in the identification (i.e., RBSW01-1011). Equipment Blanks will be labeled RBEqBlkxx-1011, where the xx will move in sequence (i.e., 01, 02, etc.). Field Blanks will be labeled RBFBlkxx-1011. Trip Blanks will be labeled RBTripBlkxx-1011.

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 7) and custody seal.

R.S. Kerr Environmental Research Center
919 Kerr Research Drive
Ada, OK 74820
1-580-436-8942

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

EPA Region 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 3 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, methane, sulfate, and sulfide 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 the PI. 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 to be shipped to the EPA Region VII contract with ARDL, Inc. will be delivered overnight via UPS or Fedex, to the contract laboratory awarded the work, with appropriate chain of custody forms (see Figure 7) and the cooler will be sealed with custody seals. Sample receipt and log-in will be conducted per contract lab SOPs.

Polycarbonate membranes (i.e., filtered samples) that will be used in nucleic analyses will be packed in an ice chest with dry ice and sent to:

Jorge W. Santo Domingo
US Environmental Protection Agency
NRMRL/WSWRD/MCCB
26 W. Martin Luther King Dr.
MS 387
Cincinnati, OH 45268
513-569-7085

Upon receipt, the lab will sign the chain-of-custody form and inventory samples. Signed chain-of-custody forms will be returned to Rick Wilkin.

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 second and subsequent sampling events for $\delta^{18}O$ and $\delta^{2}H$ 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. For these analyses, the only surrogates used are for the alcohol analysis. Surrogate compounds used are p-bromofluorobenzene and 1,2-dichlorobenzene-d4, spiked at 100 µg/L.

Samples will be submitted to Isotech Laboratories for analysis of stable isotope ratios of dissolved inorganic carbon ($\delta^{13}C$) by gas stripping and isotope ratio mass spectrometry (IRMS) and $\delta^{13}C$ of methane (C1 and >C1 if concentrations permit isotopic measurement), $\delta^{2}H$ of methane, $\delta^{34}S$ of dissolved sulfide, and $\delta^{34}S/\delta^{18}O$ of dissolved sulfate. Isotech Laboratories will follow their own in-house Standard Operating Procedures, including: Isotech, SOP112v2, $^{13}C/^{12}C$ Determination of DIC, 05/26/2011; Isotech, SOP100v0, Offline Hydrocarbon Gas Preparation System, Gamma Bench, 12/27/2010; Isotech SOP101v0, Offline Gas Preparation System, Alpha Bench, 10/21/2003; Isotech SOP103v0, Delta Plus Mass Spectrometer, Dual Inlet Analysis of δD, 2/22/2010; Isotech SOP104, Delta S Mass Spectrometer, Dual Inlet Analysis of $\delta^{13}C$, (in preparation); Isotech, SOP119v0, Elementar Vario EL Continuous Flow Determination of ^{34}S; and, Isotech SOP120v0, Thermo Quest Finnegan TCEA Continuous Flow Determination of ^{18}O and δD. 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), methane, sulfate, and sulfide. The vendor shall not be required to determine the concentration of inorganic carbon, dissolved sulfur, or dissolved gases in the samples. The isotope analyses are intended to provide information on the carbon and sulfur cycles in the system. The measurements will be for $\delta^{13}C$ of dissolved inorganic carbon, $\delta^{13}C$ value of C1-C4 (if concentrations permit), $\delta^{2}H$ of hydrogen in methane, $\delta^{34}S$ of dissolved sulfide, and $\delta^{34}S/\ \delta^{18}O$ of dissolved sulfate. These analyses will support the Hydraulic Fracturing Case Study in the Raton Basin. This project is being conducted under a Category 1 QAPP ("Hydraulic Fracturing Retrospective Case Study, Raton Basin, CO; QA ID no. G-16642).
>
> Samples will be provided from domestic wells and surface water bodies located in Las Animas and Huerfano Counties in Colorado. 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. A total of up to 25 samples will be submitted for $\delta^{13}C$ of dissolved inorganic carbon, up to 25 samples are planned for methane gas analysis, and up to 15 samples are planned for sulfur isotope analyses. 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 some 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. For sulfur isotopes analyses, duplicate 1 L plastic bottles will be filled with filtered ground water. The bottles will contain sufficient Zn-acetate to fix all dissolved sulfide as ZnS. All samples will be transported on ice. ZnS will be provided to the vendor in filtered form, as a dried solid.

The vendor shall determine the stable isotope ratios of C, S, and H in the water samples as described above using isotope ratio mass spectrometry. Isotech Laboratories will follow their own in-house Standard Operating Procedures, including: Isotech, SOP112v2, $^{13}C/^{12}C$ Determination of DIC, 05/26/2011; Isotech, SOP100v0, Offline Hydrocarbon Gas Preparation System, Gamma Bench, 12/27/2010; Isotech SOP101v0, Offline Gas Preparation System, Alpha Bench, 10/21/2003; Isotech SOP103v0, Delta Plus Mass Spectrometer, Dual Inlet Analysis of δ D, 2/22/2010; Isotech SOP104, Delta S Mass Spectrometer, Dual Inlet Analysis of $\delta^{13}C$, (in preparation); Isotech, SOP119v0, Elementar Vario EL Continuous Flow Determination of ^{34}S; and, Isotech SOP120v0, Thermo Quest Finnegan TCEA Continuous Flow Determination of ^{18}O and δD. .

Analyses of the laboratory duplicates shall agree within 1 permil $\delta^{13}C$ and within 3 permil $\delta^{2}H$, 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. Analysis of laboratory duplicates for sulfur isotopes shall be within 0.5 permil. QA/QC requirements are summarized in the attached tables (13-15).

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.

Region III's LC-MS-MS method for glycols is under development with the intent to eventually have a validated, documented method. Aqueous samples are injected directly into the HPLC

after tuning the 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). The HPLC gradient is with H_2O and CH_3CN with 0.1% formic acid. The 3 glycols are run on a separate gradient than the 2-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 step in sample preparation, extraction efficiency calculations using a surrogate are not applicable. If a suitable surrogate is found, it will be used to evaluate matrix effects. Custom standard mix from Ultra Scientific, (Kingstown RI) is used for the instrument calibration. The working, linear range varies for each compound, but is about 10-1000 µg/L and could 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).

Microbial analysis will be conducted at the ORD, Cincinnati laboratory. As soon as possible upon arrival to the laboratory (within 10 days) in Ada, water samples (1 L) will be filtered onto polycarbonate membranes (0.4 µm pore size, 47-mm diameter) (GE Water and Process Technologies, Trevose, PA). Membranes will be folded with sterile forceps, placed into autoclaved microcentrifuge tubes, and placed in a freezer (-15°C). These samples will then be shipped to the ORD-Cincinnati lab on dry ice.

Total nucleic acid will be extracted from the membranes using Mo Bio PowerSoil kits (MO BIO Laboratories, Carlsbad, CA) according to the manufacturer's protocol. DNA concentration will be estimated using a NanoDrop ND-1000 UV spectrophotometer (NanoDrop Technologies, Wilmington, DE). DNA extracts will be stored at -20°C until further processing. Total community DNA will be used in PCR studies to develop 16S rRNA gene clone libraries.

Eubacterial (8F and 787R) and archaeal (25F and 958R) primers will be used to amplify 16S rRNA genes of each corresponding microbial group. Amplification reactions contain 5 U of Ex TaqTM DNA polymerase (Takara Bio USA, Madison, WI), 5 µL of 10X concentrated Ex TaqTM Buffer, 4µL of a 2.5 mM mixture of dNTPs, 3 µL each of forward and reverse primers (2.0 µM stock concentration), and 2 µL of template DNA (50 µL total volume). Amplification conditions for the bacterial assay include an initial denaturation step (4 min at 94°C), followed by 35 cycles of 30s at 94°C, 30s at 56°C, and 1 min at 72°C, with a final extension step of 7 min at 72°C. For assay targeting Archaea the conditions are an initial denaturation step (4 min at 94°C), followed by 35 cycles of 90 s at 94°C, 90 s at 58°C, and 2 min at 72°C, with a final extension step of 12 min at 72°C. PCR products will be visualized in 1.5% agarose gels using GelStar Nucleic Acid gel stain (Lonza, Rockland, ME, USA).

Mixed community PCR products will be cloned into the pCR4.1 TOPO TA vector following the manufacturer's instructions (InvitrogenTM, Carlsbad, CA). Transformed cells are grown on Luria-Bertani agar plates containing the antibiotic ampicillin (100 mg/ml) and random colonies are screened for the presence of inserts of right size using M13 primers and gel electrophoresis. Selected clones will be sequenced using the BigDye® Terminator sequencing chemistry (Applied Biosystems, Foster City, CA) using forward and reverse M13 primers on an ABI 3730xl DNA Analyzer in the DNA Core Facility at the Cincinnati Children's Hospital. Sequencing will be used to identify the phylogenetic affiliation of the amplification products and as a result to describe the composition of microbial communities associated with each water sample. Raw sequences will be processed using Sequencher 4.9 software (Gene Codes, Ann Arbor, MI). Chimeric sequences will be detected using Bellerophon and identified chimeras will not be included in further analyses. Sequences will be submitted to Greengenes for alignment using the Nearest Alignment Space Termination algorithm and clone libraries will be compared using Naive Bayesian rRNA Classifier version 2.0 of Ribosomal Database Project (RDP) with 95% confidence threshold. The distance matrix and phylogenetic tree will be generated using ARB software. Trees will be inferred from 650 sequence positions using neighbor-joining (using a Kimura correction) and maximum parsimony (using the Phylip DNAPARS tool). To statistically evaluate branching confidence, bootstrap values will be obtained from a consensus of 100 parsimonious trees using MEGA software (http://www.megasoftware.net). Depending on the sequences generated in each sample different rRNA 16S gene sequences will be used as outgroups. Sequences generated in this study will be submitted to the GenBank database.

Molecular diversity analyses and assemblage comparison of clone libraries will be performed using Mothur software. A distance matrix will be calculated using uncorrected pair-wise distances between aligned sequences, which will be then assigned to operational taxonomic units (OTUs) using the furthest-neighbor algorithm. Chao 1, Abundance-based Coverage Estimator (ACE), and Good's coverage will be calculated for each clone library at OTU0.03 distance. Sample rarefaction curves will be calculated using resampling without replacement with 1,000 randomizations. A rectangular phylogram will be generated to describe similarity between libraries. Clustering will be performed using the UPGMA algorithm with the distance between communities calculated using the Yue and Clayton theta (www.mothur.org/wiki/Tree.shared). The Yue and Clayton measure of similarity between the structures of any two Bacteroidales assemblages (OTU distance=0.03) will be used to create a heat map of pair-wise similarities. The statistical significance of these pair-wise similarities will be tested using the Cramer von

Mises statistic (www.mothur.org/wiki/Libshuff). Heat maps of bacterial and archaeal populations (OTU0.03) from each environmental library will be created and the abundance of each OTU will be transformed using log10 scale and scaled to the largest log10 abundance value. Mothur software will be used to retrieve sequences shared by multiple libraries at the OTU0.03 definition.

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 10. 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 are made. Guidelines for making tentative identification are:

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

A commercial standard for DRO calibration is locally procured DF #2 (source: Texaco station). Surrogates used in DRO include o-terphenyl at spiking concentrations 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 (November 2012 and April 2013 sampling events. These analyses for the November 2012 sampling event were addressed in the Addendum No.2 to Version 1 of the QAPP). 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 8 and 9.

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 11. 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.

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), then the PI will 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 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 DRO and GRO are both at 20 µg/L. The Detection limits (DL) and quantitation (reporting) limits (RL) for the semivolatiles are provided in Table 10.

(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), then the PI will 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 Table 14):

(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 being determined, but most will be between 10 and 50 µg/L (Table 13).

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

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

Corrective Actions: If any samples are affected by failure of a QC sample to meet its performance criteria, the problem shall be corrected and samples will be re-analyzed. If re-analysis is not possible (such as lack of sample volume), then the PI will 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, Table 16, and Table 17):

(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, 16, and 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), then the PI will 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 18):

(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 18 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 completed at the ORD-Cincinnati laboratory, QA/QC practices (e.g., blanks, calibration checks, duplicates) are described in an approved QAPP (EPA/ORD/NRMRL/WSWRD, e.g., WSWRD-QAPP, 2010; QA Log # W-15689-QP-1-0). See Table 19 for QC types and performance criteria.

(1) Samples shall be filtered within the holding time of 10 days. Filters shall be kept frozen using dry ice or in freezers at least -15 °C until analysis. Filters can be held frozen for up to 45 days.

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

(3) 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.

Specifically, the Cincinnati laboratory will use several non-template blanks (negative controls) in each PCR plates used in PCR assays to determine potential nucleic acid contamination during the amplification process. Since universal bacterial primers will be used for the proposed work each sample is expected to produce a PCR product given that enough DNA is recovered from each sample extract. In the event that samples are negative, PCR inhibition will be assessed by spiking bacterial DNA from known pure cultures (e.g., *Escherichia coli* and *Enterococcus faecalis*). Different concentrations of nucleic acid from pure cultures (0.1 pg to 10 ng) will be used in matrix spiking experiments and results will be compared to assays conducted using nucleic acid spiked into DNA-free molecular grade water. Additionally, inhibition will be handled by diluting the samples 2, 5, and 10 fold and repeating the PCR assays. The first dilution that tests positive will be used in cloning experiments.

Corrective Actions: Corrective actions are outlined in WSWRD-QAPPs and when corrective actions occur in laboratory analysis, they will be documented.

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 2:00pm CST on the 21st 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 8 and 9.

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, and the Region VII contract with ARDL, Inc. 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

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

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

Precision

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

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

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.

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

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 11. 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 12 and 14, and for the USGS laboratory, Table 18.
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 ±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 ±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 RPD ≤15. The values obtained for each duplicate sample will be recorded in the field notebook and RPD will be calculated (section 2.5.4) and recorded in the field notebook. If the duplicate samples fail, an additional duplicate sample will be taken and reanalyzed. If the additional duplicate samples fail to meet the QC criteria, then the instruments will be checked and corrective action taken. The corrective actions will be recorded in the field notebook. Samples collected between the last valid duplicate sample and the failed duplicate sample will be flagged.

The microbial analyses rely on a limited number of instruments that require frequent calibration and/or performance evaluation tests. These instruments are pipetters, PCR thermal cyclers, and a DNA sequencer. Pipetters are calibrated at least once a year as required by ORD/NRMRL-Cincinnati Laboratory Quality Assurance Policy. Calibration is performed by certified personnel

in the AWBERC facility. PCR thermal cyclers are under service maintenance agreements and are serviced once a year, or when problems are noted by the laboratory staff. Instrument maintenance includes performance analysis of the instrument based on a wide spectrum of temperatures for each amplification well under different cycling profiles. Performance tests are performed by the manufacturer (BioRad) engineering support staff. The sequencing electrophoresis is done on an ABI 3730xl with a 50cm array producing a high quality sequence with Phred20 past the 700bp mark. The system is located at the Cincinnati Children's Hospital Medical Center (CCHMC). Plate records are linked to the sequencing process via a barcode system in order to minimize errors in sample identification. Depending on the specification of the batch by the EPA (long or short clones) we will use T3, T7, M13(-21) or M13rev in order to maximize the sequencing of the cloned insert while sequencing a minimal amount of the vector sequence. Sequencing reactions are cleaned up by EDTA/Ethanol precipitation in 384 well format. The latter is done in a completely automated fashion and without transferring the sample into a new plate in order to eliminate sample mixup. The CCHMC DNA Sequencing facility is a CLIA accredited laboratory (CLIA # 36D0996734) with 9 years of activity in support of over 400 customers in the greater Cincinnati area and beyond. Quality control pipeline includes several control samples that are run every day and examined for reproducibility. Positive controls, back a year, for every day of operation are publically available on the facility's website at http://dna.chmcc.org/sequence_controls/ and are evaluated all the way to 800bp for clear peak distinction. Reagents (e.g., enzymes) and other miscellaneous consumables (e.g., PCR plates and extraction kits) are obtained from reputable companies that in all cases follow established QA-QC protocols.

2.8 Inspection/Acceptance of Supplies and Consumables

RSKSOPs, Region III and VIII SOPs, Region VII contract laboratory SOPs, Isotech SOPs as well as the strontium isotope procedure for USGS 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

Non-direct measurements (also known as existing data or secondary data) are data from sources other than those collected directly for this case study (primary data). Existing data are needed for background evaluation of the local ground-water quality to compare with the case study data and to determine if there are significant differences. Such differences may indicate an impact to water quality at the case study location. Sources of existing data could include federal and state databases, peer reviewed literature, and homeowner data.

As described elsewhere in the QAPP, primary data have criteria that must be met in order to be usable for this project. Likewise, existing data must also be evaluated to ensure that project requirements are met. Whether or not these data are acceptable for use in this case study is dependent upon these evaluation criteria: (1) the organization that collected the data has a quality system in place, (2) data were collected under an approved Quality Assurance Project

Plan or other similar planning document, (3) analytical methods used are comparable to those used for the primary data, (4) the laboratory has demonstrated competency (such as through accreditation) for the analysis they performed, (5) the data accuracy and precision is within limits similar to that for the primary data, (6) the MDLs and QLs are comparable to those associated with the primary data or at least adequate to allow for comparisons, and (7) sampling methods are comparable to those used for the primary data.

To be able to evaluate these criteria, metadata (data or information about the data) associated with the data sources will be reviewed by the PI and results described in documents prepared for this project. Examples would include the final report, journal articles, and working documents, such as Excel spreadsheets and/or Origin projects. If the data do not meet project requirements, or metadata are not available to provide for a complete evaluation of data quality based on the criteria above, the data would need to be qualified or rejected. If this action removes much of the background data needed to make comparisons, it will not be possible to determine if there have been significant changes to water quality. Instead of taking this action, these data will be used with the understanding that they are of an indeterminable quality relative to the project requirements. The final report will use a disclaimer to identify these data.

The USGS and the State of Colorado have published reports and databases including ground water and surface water data for the Raton Basin. There is variability in the parameters contained in these databases. The USGS databases are the National Uranium Evaluation (NURE) database (USGS, 2012) and the National Water Information System (NWIS) database (USGS, 2013). Data from these resources may be used for assisting in the delineation of background water quality conditions at the study locations or in assisting with the understanding of the source of formation water from the oil and gas activities in the area. The data will be assessed for duplication between the databases so that duplicate data do not bias the results of the study.

An additional QA check, when possible, will be an analysis of the major anion-cation balances. Sample data for which the major anion-cation balances are greater than 15% for the net positive and negative charges may be removed from the data set. However, this is problematic for the NURE database, because most of the samples do not contain all of the major anions and cations. This is because water quality analysis was not the intended purpose of the NURE data collection. Therefore, major anion-cation balances cannot be made. This fact will be brought out in the final report/publications if the NURE data are used. Finally, some of the data in these databases could represent contaminated wells. If a sample can be related to a potential source of contamination it will be removed from the background dataset used for analysis. Examples could be wells in urban areas or near industrial complexes. Data that are removed from the analysis because of potential contamination will be acknowledged in any use of the data.

Data were made available in some cases from individual homeowners. Homeowner data were used as background information for the PI to assist with project planning. Homeowner data could be used as part of the reporting process in delineating background water quality conditions. Other data sources such as data from published peer reviewed literature could also be used. The data quality issues will most likely be unknown for these types of data. However, since the data

have gone through a peer review process, it could still be used. Data from homeowner's and peer reviewed sources will be evaluated in the same manner as described above.

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 the Raton Basin, CO. 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 for compiling all data and records.

2.10.4 Analysis of Data

All data collected associated with ground water and surface water sampling will be summarized in Microsoft Excel and/or Origin spreadsheets and project files. 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. The AqQA program will be used for preparing water quality diagrams, such as Piper or Durov diagrams, to visualize multi-parameter data collected in this study, and for aiding in comparisons with secondary historical data. Statistical calculations, such as determinations of the mean, median, and standard deviation, and data population tests, such as analysis of variance and other non-parametric tests will be carried out using MS Excel or the SYSTAT software package. For this study, some of these calculations will be conducted by Ecology and Environment, Inc. through a contractual mechanism. For concentration data below the MDL, a value of ½ the MDL will be used. However, this approach should only be followed in cases where detections above the MDL are available for 50% or more of the concentration values in a data series to be used for calculating statistical parameters (USEPA, 2000). This guideline will be followed and any exceptions will be noted. Analysis of primary and secondary data will also be carried out using the Geochemist's Workbench software package. Geochemical calculations will be performed to estimate the saturation state of ground water and surface water with respect to naturally occurring minerals (e.g., calcite, gypsum). The software is analogous to other packages (e.g., MinteqA2 and Phreeq-C). Major ion data (e.g., Ca, Mg, Na, K, Cl, SO_4, HCO_3, pH) and temperature are entered into a user interface. The software uses the Debye-Hückel equation to estimate ion activity coefficients and a selectable thermodynamic database in order to calculate mineral saturation indices for minerals that may be undersaturated, at equilibrium, or oversaturated in the prescribed system (Bethke, 1996). The Lawrence Livermore National Laboratory database (thermo.com.v8.r6) will be used for calculating aqueous speciation and mineral saturation. This software may also be used to construct activity-activity diagrams, such as Eh-pH diagrams. Such diagrams can be helpful in describing processes that impact the concentration of redox-sensitive elements, like iron and manganese.

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 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 QAM, 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 QA Manager 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 first sampling event in October 2011. 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 analyzes PE samples routinely, on a quarterly basis. The Region VIII laboratory is currently analyzing Performance Evaluation (aka Proficiency Testing) samples twice a year and data from the past two studies have been provided to the QAM. Glycols analyzed by Region III are not critical, but even if they become critical, PE samples are not available commercially, so PEs will not be done by their laboratory for glycols. Strontium isotopes analyzed by the USGS laboratory are not critical, and as such, PEs will not be done. Isotech will not be expected to perform PE sample analysis (which are not available commercially) as their analyses are 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 6, 11, 12, and 14-23. 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 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 Batschelet, 2010). Results are reported to the client electronically, unless requested otherwise. Electronic test results reported to the client include the following: data release memo from the analysts, LQAO, and Laboratory Director (or their Designees) authorizing release of the data from the Laboratory, and a case narrative prepared by the analysts summarizing the samples received, test methods, QC notes with identification of noncompliance issues and their impact on data quality, and an explanation of any data qualifiers applied to the data.

The Region III laboratory data verification and validation procedure is described in detail in their Laboratory Quality Manual (Metzger et al., 2011). Briefly, the procedure is as follows. The actual numeric results of all quality control procedures performed must be included in the case file. The data report and narrative must describe any limitations of the data based on a comprehensive review of all quality control data produced. A written procedure or reference must be available for the method being performed and referenced in the narrative. If the method to be performed is unique, the procedures must be fully documented and a copy included in the case file. Results must be within the method, procedure, client or in-house limits. The data report must document the accuracy and precision of the reported data by applying qualifier codes, if applicable, and include a summary of the quality control in the case file.

For the samples analyzed under the Region VII contract with ARDL, Inc., metals and VOCs, initial data validation shall be conducted by the laboratory according to the SOW and documented in the laboratory report narrative. ARDL, Inc. shall perform a data assessment on the laboratory's hardcopy and electronic deliverable based on the requirements of the SOW and methods used. The laboratories shall contact the PI upon detection of any data quality issues which significantly affect sample data. They shall also report any issues identified in the data report, corrective actions, and their determination of impact on data quality.

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.

Molecular assays and data analyses will be conducted by experienced personnel in NRMRL's Microbial Contaminants Control Branch (NRMRL/WSWRD). Data verification will consist of the use of bioinformatic analysis to determine the phylogenetic affiliation of clone sequences. These procedures have been evaluated by the WSWRD QAM and certified in the form of approved QAPPs. Data is reported as sequences and products associated with bioinformtic analyses such as phylogenetic trees, Venn Diagrams, rarefaction analysis, among others. Additionally, these procedures have been used in peer-reviewed manuscripts published in the top journals in the general field of environmental microbiology. Jorge Santo Domingo will verify that the analyses are conducted following the established procedures. Any amendments to proposed analyses will be revised by the branch chief and other experts and prior to final approval by the division's QAM. Dedicated laboratory notebooks will be used to record all data generated for this project and to record any steps associated with chain of custody and sample processing. Data will be used in the development of reports and publications in consultation with those designated by the project leader (Rick Wilkin).

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 Raton Basin sites showing well locations and concentrations of analytes.

5.0 References

Abbott, P.O., Geldon, A.L., Cain, D., Hall, A.P., and Edelmann, P., 1983. Hydrology of area 61, Northern Great Plains and Rocky Mountain coal provinces, Colorado and New Mexico. U.S. Geological Survey Water-Resources Investigations Open-File Report 83-132.

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.

American Public Health Association; American Water Works Association; Water Environment Federation. 1998. Method 4500-S2- D. Methylene Blue Method. 2p 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.

Bade, M., 2011. Sample receipt and control procedure. SOP No. GENLP-808 rev 1.0. EPA Region 8 Laboratory.

Bethke, C.M. (1996). *Geochemical Reaction Modeling*. Oxford University Press, New York.

Burkhardt, M. and Batschelet, W., 2010. U.S. EPA Region 8 Environmental Laboratory Quality Assurance Manual. SOP No. QSP-001 rev 1.0. EPA Region 8 Laboratory.

Cooper, J.R., Crelling, J.C., Rimmer, S.M. and Whittington, A.G., 2007. Coal metamorphism by igneous intrusion in the Raton Basin, CO and NM: Implications for generation of volatiles. International Journal of Coal Geology, 71(1): 15-27.

Flores, R.M., 1993. Geologic and geomorphic controls of coal developments in some Tertiary Rocky-Mountain Basins, USA. International Journal of Coal Geology, 23(1-4): 43-73.

Flores, R.M. and Bader, L.R., 1999. A Summary of Tertiary coal resources of the Raton Basin, Colorado and New Mexico. In: Resource Assessment of Tertiary Coal Beds and Zones in the Northern Rocky Mountains and Great Plains Region. U.S. Geological Survey Professional Paper 1625-A, 35 pp.

Geldon, A.L., 1989. Ground-water hydrology of the central Raton Basin, Colorado and New Mexico. U.S. Geological Survey Water-Supply Paper 2288.

Isotech SOP112v2. $^{13}C/^{12}C$ Determination of DIC, 05/26/2011.

Isotech SOP100v0. Offline hydrocarbon gas preparation system, Gamma Bench, 12/27/2010.

Isotech SOP101v0. Offline gas preparation system, Alpha Bench, 10/21/2003.

Isotech SOP103v0. Delta Plus mass spectrometer, dual inlet analysis of δD, 2/22/2010.

Isotech SOP104. Delta S mass spectrometer, dual inlet analysis of $\delta^{13}C$, in preparation.

Isotech SOP119v0. Elementar Vario EL continuous flow determination of ^{34}S.

Isotech SOP120v0, Thermo Quest Finnegan TCEA continuous flow determination of ^{18}O and δD.

Johnson, R.B., Dixon, G.H. and Wanek, A.A. (Editors), 1956. Late Cretaceous and Tertiary Stratigraphy of the Raton Basin of New Mexico and Colorado. In: New Mexico Geological Society Fall Field Conference Guidebook # 7: Southeastern Sangre de Cristo Mountains. New Mexico Geological Society, 151 pp.

Johnson, R.C. and Finn, T.M., 2001. Potential for a basin-centered gas accumulation in the Raton Basin, Colorado and New Mexico. U.S. Geological Survey Bulletin 2184-B, pp. 18.

Kiernan, J., 2010a. Determination of BTEX, MTBE, naphthalene and TPH/GRO using EPA Method 8021B and 8015D Modified. SOP No. ORGM-506 rev. 1.0. EPA Region 8 Laboratory.

Kiernan, J., 2010b. Determination of diesel range organics using EPA Method 5015D Modified. SOP No. ORGM-508 rev. 1.0. EPA Region 8 Laboratory.

Lewicki, G., 2001. Raton Basin coal mine feature inventory, Greg Lewicki & Associates, Highlands Ranch, CO.

Marti, V., 2011. Determination of semivolatile organic compounds using Method 8270D. SOP No. ORGM-515 rev. 1.1. EPA Region 8 Laboratory.

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.

Pillmore, C.L., Tschudy, R.H., Orth, C.J., Gilmore, J.S. and Knight, J.D., 1984. Geologic framework of nonmarine Cretaceous-Tertiary boundary sites, Raton Basin, New Mexico and Colorado. Science, 223(4641): 1180-1183.

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-259v1. Determination of volatile organic compounds (fuel oxygenates, aromatic and chlorinated hydrocarbons) in water using automated Headspace gas chromatography/mass spectrometry (TEKMAR 7000 HS-Varian 2100T GC/MS System-ION Trap Detector). 28p.

RSKSOP-276v4. Determination of major anions in aqueous samples using capillary ion electrophoresis with indirect UV detection and Empower 2 Software. 12 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-299v2. 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.

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-331v0. Standard operating procedure for water level monitoring using automated pressure transducer/data loggers. 9 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). 30 p.

Topper, R., Scott, K. and Watterson, N., 2011. Geologic model of the Purgatoire River watershed within the Raton Basin, Colorado. Colorado Geological Survey.

Tremain, C.M., 1980. The coal bed methane potential of the Raton Basin, Colorado., SPE Unconventional Gas Recovery Symposium, Pittsburgh, Pennsylvania.

Tweto, O., 1979. Geologic map of Colorado. U. S. Geological Survey, scale 1:500,000.

USEPA, Office of Pesticide Programs, 2000. Assigning values to non-detected/non-quantified pesticide residues in human health food exposure assessments. (http://www.epa.gov/oppfead1/trac/science/trac3b012.pdf).

USEPA, Office of Water, 2004. The Raton Basin. In: Evaluation of Impacts to Underground Sources of Drinking Water by Hydraulic Fracturing of Coalbed Methane Reservoirs. Environmental Protection Agency, pp. A9 - A9-19.

USEPA, Office of Superfund Remediation and Technology Innovation, 2008. USEPA Contract Laboratory Program: National Functional Guidelines for Superfund Organic Methods Data Review. EPA/540/R-08/01 (http://www.epa.gov/superfund/programs/clp/download/somnfg.pdf).

USEPA, Office of Superfund Remediation and Technology Innovation, 2010. USEPA Contract Laboratory Program: National Functional Guidelines for Inorganic Superfund Data Review. EPA/540/R-10/11 (http://www.epa.gov/superfund/programs/clp/download/ism/ism1nfg.pdf).

USEPA, Office of Research and Development, 2011. Plan to Study the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources. EPA/600/R-11/122 (http://www.epa.gov/hydraulicfracturing).

USEPA Method 180.1. Determination of Turbidity by Nephelometry, 10 p.

USEPA Method 310.1. Alkalinity (Titrimetric), pH 4.5, 3 p.
WSWRD-QAPP (2010). W-15689-QP-1-0, Identification of groundwater microbial communities using molecular methods.

U.S. Geological Survey. 2013. National Water Information System, http://waterdata.usgs.gov/nwis/

Watts, K.R., 2006a. Hydrostratigraphic framework of the Raton, Vermejo, and Trinidad aquifers in the Raton Basin, Las Animas County, Colorado. U.S. Geological Survey Scientific Investigations Report 2006-5129 (http://pubs.usgs.gov/sir/2006/5129/).

Watts, K.R., 2006b. A preliminary evaluation of vertical separation between production intervals of coalbed-methane wells and water-supply wells in the Raton Basin, Huerfano and Las Animas Counties, Colorado, 1999-2004. U.S. Geological Survey Scientific Investigations Report 2006-5109 (http://pubs.usgs.gov/sir/2006/5109/).

6.0 Tables

Table 1. QAPP revision history.

Revision Number	Date Approved	Revision
0	8/30/2011	New document
1	4/30/2012	Section 1: • Updated project organization (Jewett replaced Puls, added ALS Environmental contact, added Mravik with new duties) • Updated accreditation information in 1.5 to provide clarification Section 2: • Sampling timing has changed (also see Table 4) and been extended until spring of 2013 • Revised dissolved gas/methane isotope sample collection method to allow for more effective collection of samples and removed hydrogen and carbon dioxide as target analytes because of their limited value to the study • Changed preservative for low molecular weight acids from TSP to sodium hydroxide here and in Table 5 because TSP was identified as a source of acetate contamination • Replaced Standard Methods with EPA Methods for turbidity as it more appropriately reflects the method used as well as the preference for EPA Methods • Replaced CB&I lab sample contact with current personnel • CRDS will be used in the second and subsequent sampling events for H and O stable isotopes of water instead of IRMS, as CRDS is replacing the IRMS for analysis of water isotopes at RSKERC using RSKSOP-334, also added to Table 5 • Add sample collection for dissolved sulfate and dissolved sulfide for stable isotope analyses of sulfur; also added to Table 5. Needed to understand links between C and S cycling in groundwater • Added updated SOW for Isotech for the stable isotope analysis of sulfur • Updated information on Region VIII QA/QC regarding on-site QA audit and PEs • Added RSKSOP-334 for water isotopes (CRDS is replacing IRMS); also add to References and Table 5 • Added RPD/Blank sample data analysis • Provided clarification on sulfide and turbidity calibration checks • Duplicate acceptance criteria was changed from RPD<15 to RPD≤15, which was the original intent • Deleted 2.10.1 as information is redundant Section 3: Provided clarification on ADQ and PE requirements and to whom audit reports are provided

		Section4: • Added text on data report review and data usability to reflect actual practice Section 5: • Updated references, replaced alkalinity method with correct one and added CLP guidelines on data review Section 6: • Added this table on QAPP revision history • B and NO_3+NO_2 were removed from Table 3 as critical analytes due to the fact that they are not critical • Benzene, toluene, ethylbenzene, and xylenes were add to Table 3 as critical analytes • Table 5: Replaced EPA Method 220.7 with correct one, 200.7; deleted RSKSOP-259 as only RSKSOP-299 is used; replaced holding times of "No Information" with specific times for stable C and H isotopes based on info from lab • MDLs and QLs in Table 7 for RSKSOP-299v1 were changed to those listed in the SOP; footnote added to indicate that current MDLs and QLs are included in the laboratory reports • In Table 7 deleted gases that are not analyzed due to limited value to study (ethylene, acetylene, carbon dioxide, hydrogen) • Replaced Table 8 with update (removed compounds not analyzed and replaced limits with more recent ones determined by lab) • Provided corrections to QC requirements for DIC/DOC and added requirements for RSKSOP-334 for O, H stable isotopes of water in Table 9 • Replaced Table 10 with one the lab actually uses as discovered during the lab TSA July 2011 • Addition of tables 15; Isotech S/O isotope QA/QC • Added Table 18 of Data Qualifiers developed by PIs for data review/qualification
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, Mo, Ni, Pb, Sb, Se, Th, Tl, and U by ICP-MS.
1, Addendum No. 2	1/10/2013	• Title changed to reflect the focus of this addendum • Scope of addendum is limited to the SwRI analysis of samples for metals, mercury, and VOC analysis
2	4/12/2013	• Added EPA disclaimer and information about the EPA Quality System Section 1: • Updated staff assignments, including QA staff, NRMRL management, communications staff, and technical support staff • Section 1.2: re-organized the section, added reference to the EPA HF study plan, added other potential sources of

		contamination to ground and surface water, added a summary of the QAPP history, provided rationale for the future direction of the project • Section 1.3: added information about sampling points, added information about sampling locations in the various field events, added information about surface water sampling locations; added a note that the NERL-LV laboratory performed the glycol analysis for the November 2012 sampling event using the same SOP and QA requirements as the Region III laboratory • 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 laboratory Section 2: • Section 2.1.2: added information about the placement of down-hole pumps • Section 2.2.1: updated sample collection information, added details about glass bottles (certified, pre-cleaned), added dissolved gas sampling test for final round, added new metals sample information, updated information about S isotope sample preparation • 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 analyses, provide QA/QC information for 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 3.1.1: specified when the field and laboratory TSAs occurred Section 4: • Section 4.1: specified the role NRMRL management regarding data release to the public • Section 4.2: specified Region VII contract lab data validation procedures, clarified data validation process, specified 100% data transcription checks, added information on development of a database • Section 4.3: clarified conflict resolution process Section 5: • Added references to the EPA HF Study Plan and EPA CLP guidance Section 6: • Updated this Table on the QAPP revision history • Table 3, added dissolved gases to the critical analyte list • Table 4, updated the schedule • Table 5, updated the metals (dissolved and totals) samples • Table 6, acceptance criteria language revised to be consistent with data qualifier Table 24; in footnote changed 12^{o}C to 6^{o}C to be consistent with requirement in Table 5 • Table 7, revised the RSKERC MDLs and QLs and updated

		RSKSOP-299v1 to v2 and RSKSOP-276v3 to v4 • Table 8, added this table on the Region VII contract lab MDLs and QLs for metals • Table 9, added this table on the Region VII contract lab MDLs and QLs for VOCs • Table 10, updated the Region VIII MDLs and QLs • Table 13, provided glycol QLs from a recent data report • Table 20, added this table on the Region VII contract lab QA/QC requirements for ICP-MS • Table 21, added this table on the Region VII contract lab QA/QC requirements for ICP-AES • Table 22, added this table on the Region VII contract lab QA/QC requirements for Hg by cold vapor • Table 23, added this table on the Region VII contract lab QA/QC requirements for VOCs • Table 24, added this table on the data qualifiers
3		• Updated project organization, including Figure 1, added technical staff for review and contract support for report preparation • Updated Section 2.9 on use of secondary data, QA requirements, data sources, and evaluation • Updated Section 2.10 on data analysis, software packages and analysis methods • Updated references section

Table 2. Known constituents of hydraulic fracturing fluids used in the Raton Basin.

Component	Purpose	Chemical Abstract Service Number (CAS#)
N2-Foam Frac		
Quartz	Proppant	--
Guar Gum	Gelling Agent	68130-15-4
Methanol	Foaming Agent	67-56-1
2-Butoxyethanol	Foaming Agent	111-76-2
Ethylene Glycol	Foaming Agent	107-21-1
Nitrogen	Nitrogen Foam	7727-37-9
Sodium Chloride	High pH Enzyme Breaker	7647-14-5
Sucrose	Enzyme Breaker	57-50-1
Ethylene Glycol	Enzyme Breaker	107-21-1
Hydrochloric Acid	Utility Chemical	7647-01-0
Gel-Frac		
Quartz	Proppant	--
Guar Gum	Slurry Guar	9000-30-0
Petroleum Distillate	Slurry Guar	64742-47-8
Clay	Slurry Guar	14808-60-7
Surfactant	Slurry Guar	68439-51-0
Guar Gum	Gelling Agent	9000-30-0
Petroleum Distillate	Gelling Agent	64742-47-8
Clay	Gelling Agent	14808-60-7
Surfactant	Gelling Agent	68439-51-0
Ethylene Glycol	Crosslinker	107-21-1
Potassium Hydroxide	Crosslinker	1310-58-3
Boric Acid	Crosslinker	10043-35-3
Ammonium Persulfate	Breaker	7727-54-0
Sodium Bromate	Breaker	7789-38-0
Branched Alcohol Oxyalkylate	Surfactant	NA
Tetramethylammonium Chloride	Surfactant	75-57-0
Organic Acid	Scale Inhibitor	67-56-1
Tetrasodium Ethylenediaminetetraacetate	Scale Inhibitor	64-02-8
Methanol	Foaming Agent	67-56-1
2-Butoxyethanol	Foaming Agent	111-76-2
Erythorbic Acid	Iron Control	6381-77-7
Sodium Chloride	High pH Enzyme Breaker	7647-14-5
Sucrose	Enzyme Breaker	57-50-1
Acetic Acid	Utility Chemical	64-19-7
Hydrochloric Acid	Utility Chemical	7647-01-0

From the Frac Focus Chemical Disclosure Registry, http://fracfocus.org/ (accessed August 23, 2011) . Constituents represent typical fluids used in the Raton Basin for Nitrogen foam and Gel fracturing.

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 and Alcohols (VOC)*	ARDL, Inc.
Dissolved Gases**	CB&I
Metals (As, Se, Sr, Ba)	ARDL, Inc.
Major Cations (Ca, Mg, Na, K)	ARDL Inc.
Major Anions (Cl^-, SO_4^{2-})	RSKERC general parameters lab

*Ethanol, isopropyl alcohol, tert-butyl alcohol, naphthalene, benzene, toluene, ethylbenzene, and xylenes.
Only those SVOC compounds in Table 10 that have DL, RL, and Control Limits listed may be used as critical analytes; all others will be used only as screening data.
**Methane and ethane are considered to be critical analytes based on previous sampling and analysis.
Both VOC and SVOC have many target analytes and initially all are considered critical (with exception for SVOC noted above). A tiered approach will be used to further refine the identification of specific compounds as critical. Data from the first sampling events will be evaluated by the PI to determine if there are specific compounds that are identified in these samples which would warrant their specific identification as critical to narrow the list. These will be identified in a subsequent QAPP revision.
GRO analysis provides data for not only TPH as gasoline, but several other compounds. Only TPH as gasoline will be considered critical from this analysis.

Table 4. Tentative schedule of field activities for the hydraulic fracturing case study in the Raton Basin, Colorado.

Media	October 2011 Phase I	May 2012 Phase I	November 2012 Phase I	April 2013 Phase I
Groundwater	X	X	X	X
Surface Water	X	X	X	X

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)
SO_4, Cl, F, Br	RSKSOP-276v4 (EPA Method 6500)	30 mL plastic/1	Refrigerate ≤ 6°C	28 days
$NO_3 + NO_2$, NH_4	RSKSOP-214v5 (EPA Method 350.1 and 353.1)	30 mL plastic/1	H_2SO_4, pH<2; refrigerate ≤ 6°C	28 days
DIC	RSKSOP-330v0 (EPA Method 9060A)	40 mL clear glass VOA vial/2	refrigerate ≤ 6°C	14 days
DOC	RSKSOP-330v0 (EPA Method 9060A)	40 mL clear glass VOA vial/2	H_3PO_4, pH<2; refrigerate ≤ 6°C	28 days
Volatile organic compounds (VOC)	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	1M NaOH, 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 ≤ 6°C	stable
$\delta^{13}C$ of inorganic carbon	Isotech: gas stripping and IRMS (No EPA Method)	60 mL plastic bottle/1	Refrigerate ≤ 6°C	14 days
$\delta^{13}C$ and $\delta^{2}H$ of methane	Isotech: gas stripping and IRMS (No EPA Method)	1 L plastic bottle/1	Caplet of benzalkonium chloride; refrigerate ≤ 6°C	3 months
$^{87}Sr/^{86}Sr$ analysis	Thermal ionization mass spectrometry (No EPA Method)	500 mL plastic bottle/1; 2 for every 10 samples	Refrigerate ≤6°C	6 months
$\delta^{34}S$ of dissolved sulfide	Elemental analysis coupled to isotope ratio mass spectrometer	1 L plastic bottle/1	Zn-acetate to fix H_2S(aq) as ZnS; refrigerate ≤ 6°C	6 months
$\delta^{34}S/\delta^{18}O$ of dissolved sulfate	Elemental analysis coupled to isotope ratio mass spectrometer	1 L plastic bottle/1	Zn-acetate to fix H_2S(aq) as ZnS; refrigerate ≤ 6°C	6 months
Semi-volatile organic compounds	EPA Method 8270D, (ORGM-515 r1.1)	1L amber glass bottle/2 and for every 10 samples of ground water need 2 more bottles for one selected	Refrigerate ≤ 6ºC	7 days until extraction, 30 days after extraction

		sample, or if <10 samples collected, collect 2 more bottles for one select sample		
DRO	ORGM-508 r1.0, EPA Method 8015D	1L amber glass bottle/2 and for every 10 samples of ground water need 2 more bottles for one selected sample, or if <10 samples collected, collect 2 more bottles for one select sample	HCl, pH<2; refrigerate ≤ 6°C	7 days until extraction, 40 days after extraction
GRO	ORGM-506 r1.0, EPA Method 8015D	40 mL amber glass VOA vial/2 and for every 10 samples of ground water need 2 more bottles for one selected sample, or if <10 samples collected, collect 2 more bottles for one select sample	No headspace; HCl, pH<2; refrigerate ≤ 6°C	14 days
Glycols	Region III method** (No EPA Method)	40 mL amber glass VOA vial/2	Refrigerate ≤ 6ºC	14 days
Microbial	PCR Assays	1 L plastic amber/2 Autoclaved	Water: Refrigerate ≤ 6ºC Filters: dry ice or -15°C	Water: 10 days until filtered Filters: 45 days

† Trisodium phosphate

†† Above freezing point of water

*Spare bottles made available for laboratory QC samples and for replacement of compromised samples (broken bottle, QC failures, etc.).

** Under development

Table 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 VOC and dissolved gas samples.	<QL: Sample will be flagged if >QL and analyte concentration <10x concentration in blank.
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.	<QL: Sample will be flagged if >QL and analyte concentration <10x concentration in blank.
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 5xQL. 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.	<QL: Sample will be flagged if >QL and analyte concentration <10x concentration in blank.

*- Reporting Limit or Quantitation Limit
** - Blank samples will not be collected for isotope measurements, including O, H, C, S, 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 as needed.

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	0.17	1.00
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
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. Region VII contract lab metal quantitation limits. ICP-AES uses EPA Method 200.7; ICP-MS uses EPA Method 6020A; total digestions follow EPA Method 200.7; and Hg analysis follows EPA Method 7470A.

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 (Thalium)			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		

[1]AES: Atomic Emission Spectroscopy, equivalent to OES.
[2]For Hg the method is cold vapor atomic absorption spectroscopy.

Table 9. Region VII contract lab quantification limits (QLs) 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 10. 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
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
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
Squalene	1.33	2.00	20	60-130	30
Terpiniol	0.617	1.00	20	60-130	30

Table 11. 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	No EPA Method 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	EPA Method 6500 (RSKSOP-276v4)	<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	EPA Method 350.1 (RSKSOP-214v5)	<½ lowest calib. std. (Beginning and end of each sample queue)	90-110% Rec. (Beginning, end, and every 10 samples)	PE sample acceptance limits (One per sample set)	RPD<10 (every 10 samples)	80-120% Rec. (one per every 20 samples)
DIC/DOC	EPA Method (RSKSOP-330v0)	<½QL (after initial calib., every 10-15 samples, and at end)	80-120% of known value (after initial calib., every 10-15 samples, and at end)	80-120% of known value (Immediately after calibration)	RPD<10 (every 15 samples)	80-120% Rec. (one per 20 or every set

Measurement	Analysis Method	Blanks (Frequency)	Calibration Checks (Frequency)	Second Source (Frequency)	Duplicates (Frequency)	Matrix Spikes (Frequency)
Low Molecular Weight Acids	No EPA Method (RSKSOP-112v6)	<QL (Beginning of a sample queue; every 10 samples; and end of sample queue)	85-115% of the recovery (Prior to sample analysis; every 10 samples; end of sample queue)	85-115% of recovery (Prior to sample analysis)	<15 RPD (Every 20 samples through a sample queue)	80-120 % recovery (Every 20 samples through a sample queue)
O, H stable isotopes of water* **	RSKSOP-296v1 or RSKSOP-334v0	NA	RSKSOP-296v1: Difference of calibrated/ true <1‰ for δ^2H & <0.2‰ for $\delta^{18}O$ (Beginning, end and every tenth sample) RSKSOP-334v0: Difference of calibrated/ true ≤ 1.5‰ for δ^2H & ≤ 0.3‰ for $\delta^{18}O$ (Beginning, end, and every twenty samples)	NA	RSKSOP296 v1: Standard deviation ≤ 1‰ for δ^2H and < 0.2‰ for $\delta^{18}O$ (every sample) RSKSOP-334v0: Difference ≤ 1.5‰ for δ^2H and ≤ 0.3‰ for $\delta^{18}O$ (Beginning and end of sample set and every twenty samples)	

*This table only provides a summary; SOPs should be consulted for greater detail.
**Surrogate compounds spiked at 100 ug/L: p-bromofluorobenzene and 1,2-dichlorobenzene-d4, 85-115% recovery.
***Additional checks for IRMS and CRDS: internal reproducibility prior to each sample set, std dev <1‰ for δ^2H and ≤ 0.1‰ for $\delta^{18}O$, and ≤ 0.5‰ for δ^2H and ≤ 0.1‰ for $\delta^{18}O$, 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 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 ≤ 20%, r^2≥0.990	ICAL: 10-500 ug/L RSD ≤ 20% or r^2≥0.990	ICAL: 0.25-12.5 ug/L for gasoline (different range for other compounds) RSD ≤ 20% or r^2≥0.990	As required (not daily if pass ICV)
Initial and Continuing Calibration Checks	80-120% of expected value	80-120% of expected value	80-120% of expected value	At beginning of sample set, every tenth sample, and end of sample set
Second Source Standards	ICV1 70-130% of expected value	ICV1 80-120% of expected value	ICVs 80-120% of expected value	Each time calibration performed
Laboratory Control Samples (LCS)	Statistical Limits from DoD LCS Study (rounded to 0 or 5) or if SRM is used based on those certified limits	Use an SRM: Values of all analytes in the LCS should be within the limits determined 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 $\leq$ 30	% Recovery same as MS RPD $\leq$ 25	% Recovery same as MS RPD $\leq$ 25	One per sample set or every 20 samples, whichever is more frequent
Reporting Limits*	0.1 µg/L (generally)[1] for target compounds HF special compounds are higher	20 µg/L[1]	20 µg/L[2]	NA

[1]Based on 1000 mL sample to 1 mL extract
[2]Based on a 5 mL purge
*see QAPP Table 10

Table 13. 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 5 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 14. 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 ≤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 15. Isotech laboratory QA/QC Requirements for $\delta^{13}C$ of DIC (Dissolved Inorganic Carbon).

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

*Working standards calibrated against IAEA (International Atomic Energy Agency) standard LSVEC and NBS-19; referenced to $\delta^{13}C$ of the Peedee belemnite (NIST material).
**If <5 samples are submitted, run a duplicate regardless of total number.
Corrective Actions: If any samples are affected by failure of a QC sample to meet its performance criteria, the problem shall be corrected and samples will be re-analyzed. If re-analysis is not possible (such as lack of sample volume), the data will be qualified with a determination about the impact on the sample data.

Table 16. Isotech Laboratory QA/QC Requirements for $\delta^{13}C$ of dissolved methane (and >C1) and δD of dissolved methane.

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

*Working standards calibrated against IAEA (International Atomic Energy Agency) standard LSVEC and NBS-19; referenced to $\delta^{13}C$ of the PeeDee belemnite (NIST material).
**Working standards calibrated against VSMOW, SLAP, and GISP; referenced to VSMOW.
***If < 10 samples are submitted, run a duplicate regardless of total number.
Corrective Actions: If any samples are affected by failure of a QC sample to meet its performance criteria, the problem shall be corrected and samples will be re-analyzed. If re-analysis is not possible (such as lack of sample volume), the data will be qualified with a determination about the impact on the sample data.

Table 17. Isotech Laboratory QA/QC Requirements for $\delta^{34}S$ of dissolved sulfide and sulfate and $\delta^{18}O$ of dissolved sulfate.

QC Type	Performance Criteria	Frequency
Mass Spec Calibration Check	Difference of calibrated/true ≤ 0.5‰ for $\delta^{34}S$ and ≤ 0.5‰ for $\delta^{18}O$	One at beginning of sequence and after samples are analyzed*
Lab Duplicates	≤ 0.5 ‰ for $\delta^{34}S$ and ≤ 0.5‰ for $\delta^{18}O$	1 per every 10 samples**
Preparation System Check/Reference Standards	System maintains pressure of at least 1.25 bar	Reference gas pressure and peak shape evaluation done daily

*Calibration standards are NBS123 (sphalerite, $\delta^{34}S$ = +17.4 permil versus Vienna-Canyon Diablo Troilite (VCDT)) and NBS127 (barium sulfate, $\delta^{34}S$ = +20.3 permil versus VCDT, $\delta^{18}O$ = +9.3 permil versus Vienna-Standard Mean Ocean Water (VSMOW)); Working standard with $\delta^{34}S$ = +16.1 permil versus VCDT, and IAEA (International Atomic Energy Agency) Nitrate with $\delta^{18}O$ = +25.6 permil versus VSMOM.

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

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

*Thermal Ionization Mass Spectrometry

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

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

Table 19. ORD Cincinnati laboratory QA/QC requirements for molecular microbial analysis.

QC Type	Performance Criteria	Frequency
Lab Duplicates	Positive amplification signals in agarose gel	1 per sample
Negative Controls (Blank Water)	No amplification signals in agarose gel	5 per plate (5%)
Pure Culture Positive Controls	Positive control, positive amplification signals in the agarose gel; confirmation of signal via species-specific PCR	5 per plate (5%)

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

QC Type or Operation	Acceptance Criterion	Frequency
Instrument Calibration	The acceptance criterion for the initial calibration correlation coefficient is r≥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	≤ 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	≤ 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, ±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	≤ 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 >4x 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 >5x RL; for samples <5xRL, 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	≤ 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	≤ 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, ±20% of the analyte's true value; for solution A ±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)	≤ RL	Every 20 samples.
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≥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)	≤ 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)	≤ RL	Analyzed immediately after every Continuing Calibration Verification (CCV); every 10 samples and at the end of the run.
Method or Preparation Blank	≤ 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.
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 ≤ 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 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≥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≤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 ethanol	Every 20 samples.
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

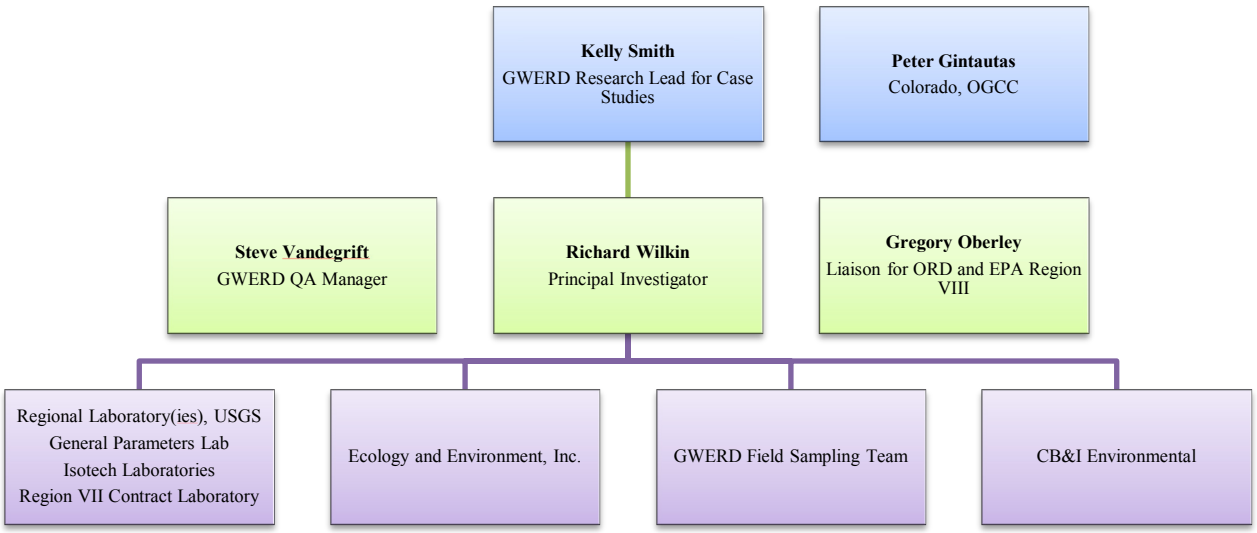


Figure 1. Organizational chart for the Hydraulic Fracturing Retrospective Case Study in the Raton Basin, Colorado.

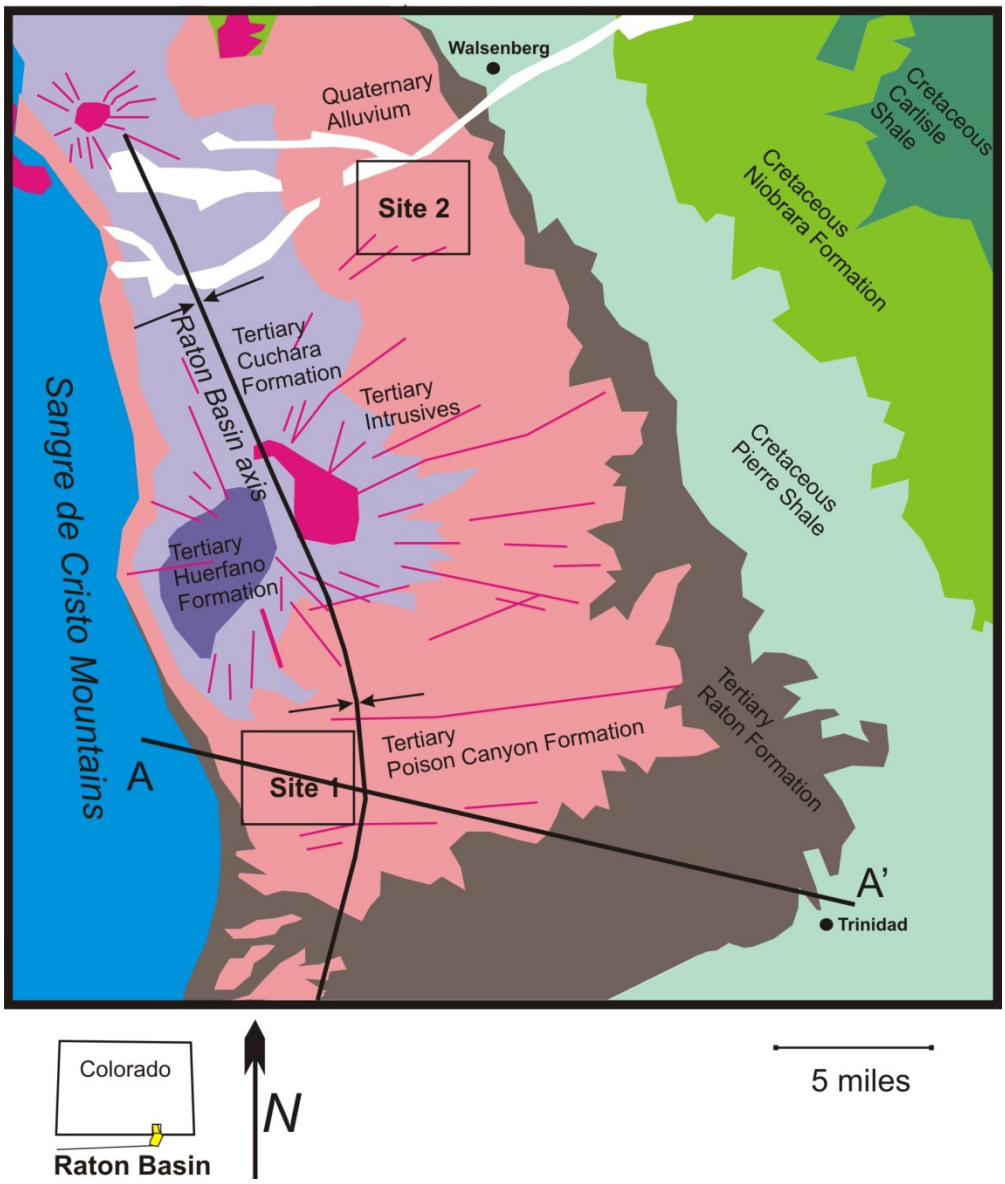
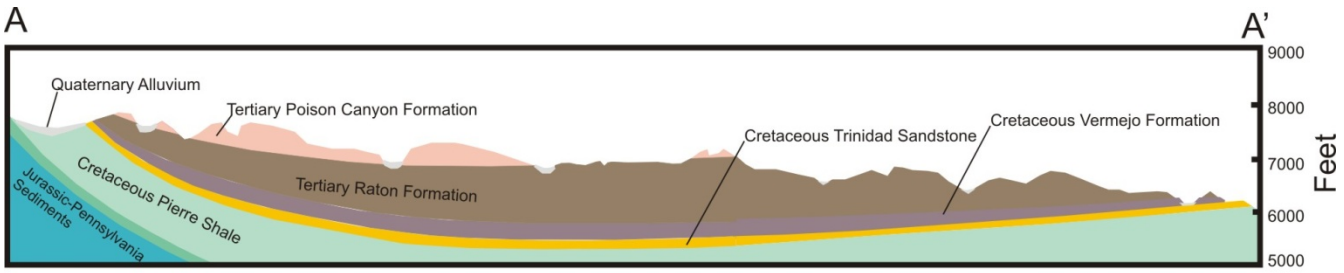


Figure 2. Generalized geologic map of the Raton Basin near Trinidad, CO. Modified from Tweto (1979).



Age	Formation Name	Description	Lithology	Thickness approximate, ft
Tertiary	Poison Canyon Formation	Sandstone: coarse-sand to conglomerate; beds 10-50 feet thick, yellow siltstones and shales.		0-2500
	Raton Formation	Upper coal zone: very fine-grained sandstone,siltstone, and mudstone with cabonaceous shale and coal beds. Barren series: fine-grained sandstone and mudstone with cabonaceous shale and thin coal beds. Lower coal zone: same as upper coal zone; thin coal beds and discontinuous		0-2000
Cretaceous	Vermejo Formation	Sandstone: fine- to medium-grained, with mudstone; thick coal beds.		0-380
	Trinidad Sandstone	Sandstone: fine- to medium-grained.		0-260
	Pierre Shale	Shale: contains limestone concretions.		1300-2300

Figure 3. A to A' cross section and schematic stratigraphic column of the Cretaceous and Tertiary rocks in the Raton Basin (modified from Flores and Bader, 1999).

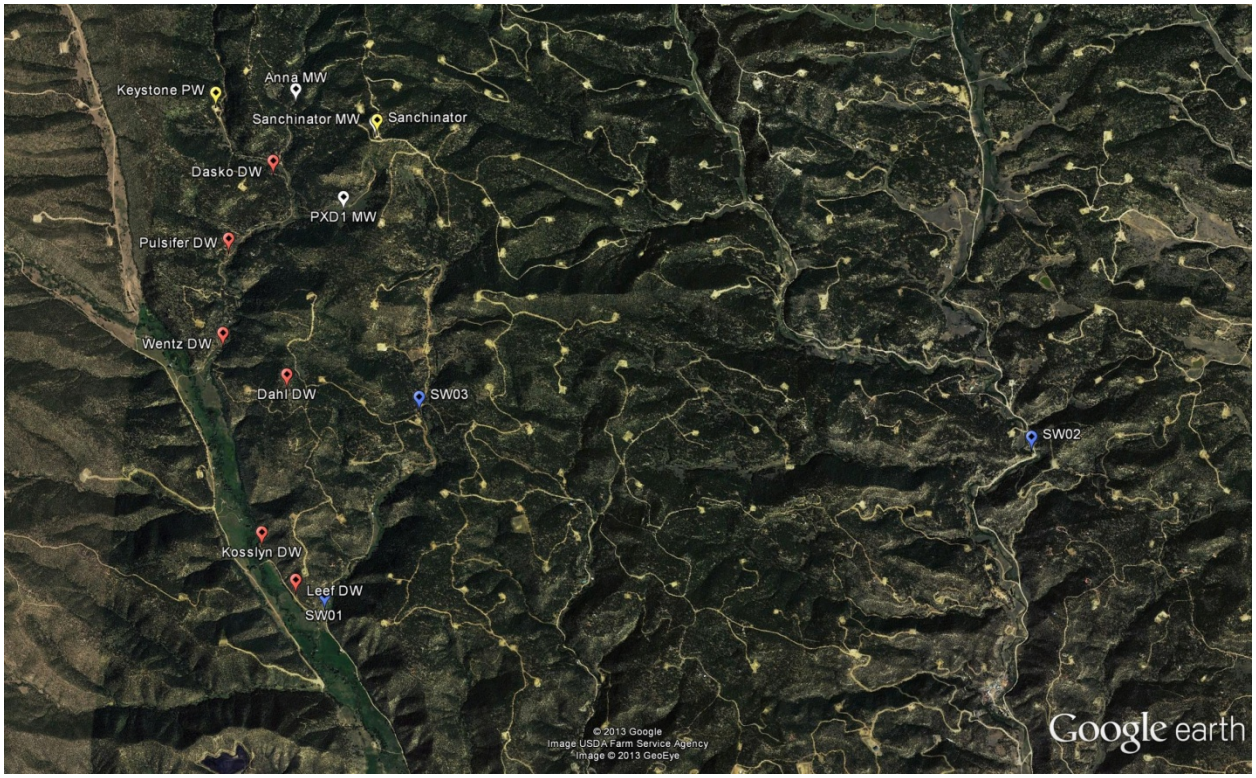


Figure 4. North Fork Ranch study area (Site 1 on Figure 2). Red symbols (diamonds) domestic wells; red symbols (circles) surface water; blue symbols (diamonds) monitoring wells; and, white symbol production wells.

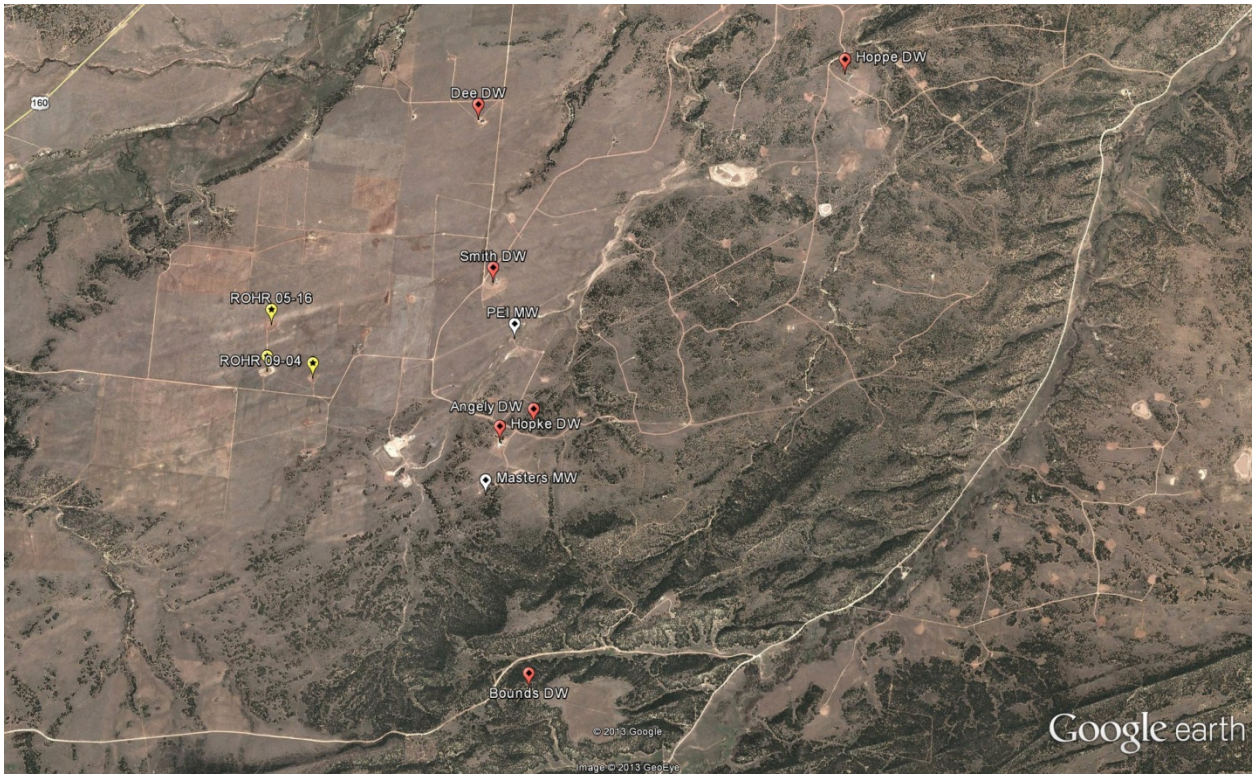


Figure 5. Little Creek Area (Site 2 on Figure 2). Red symbols (diamonds) domestic wells. Yellow symbols show the locations of three stimulated wells (gel fracs).

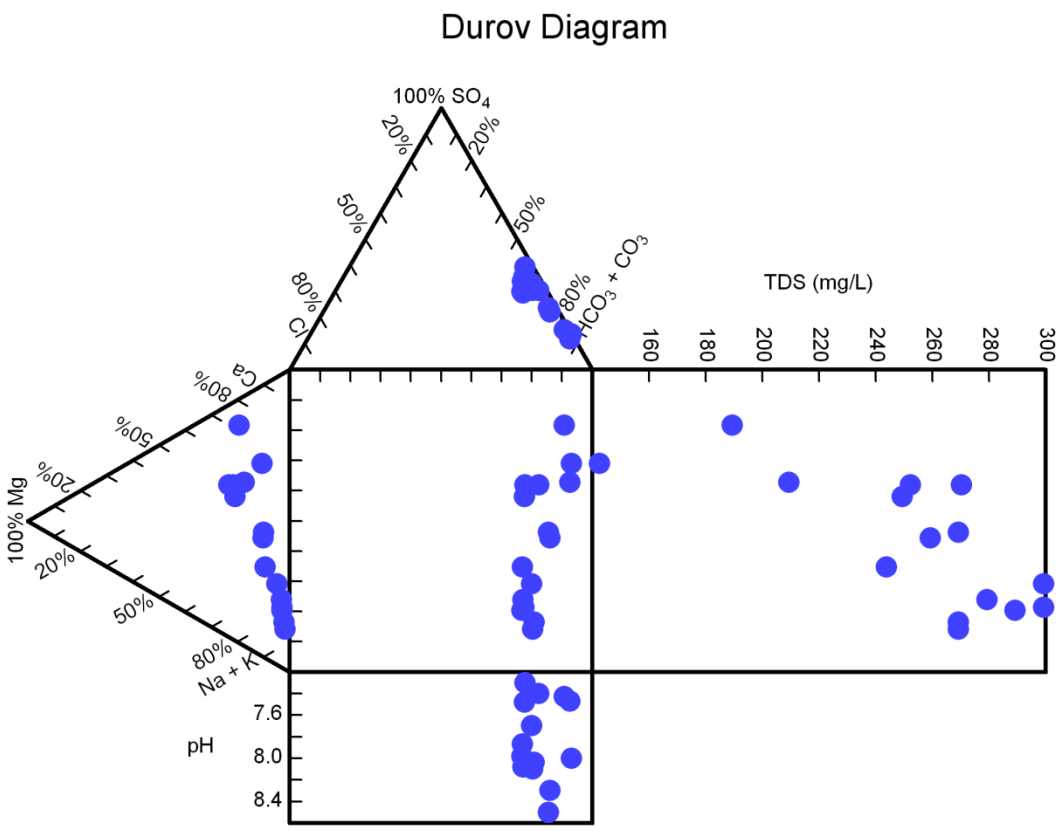


Figure 6. Durov diagram showing the distribution of major cations, major anions, as well as total dissolved solids (TDS) and pH in wells from the North Fork Ranch area (Site 1 on Figure 2).

USEPA, ORD, NRMRL

Sample Analysis Request and Chain of Custody (COC) Record

Page ____ of ____

Project:

Location:

Project Manager/Phone:

Lab Name:

Address:

Contact Name/Phone:

Shipping Method:

Shipping Tracking Number:

Shipping Date:

Total Number of Shipping Containers:

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

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

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

Comments:

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

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

Comments:

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

EPA-442 (CIN) (09/08)

Figure 7. Chain of Custody form for submittal of water samples to R.S. Kerr Environmental Research Center.

APPENDIX A

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

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

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

Application to Hydraulic Fracturing Study: Formation water is typically many times more saline than fresh water and commonly more saline than ocean water. When hydraulic fracturing fluids are injected into rock units, it mixes with the formation water, and the flowback water typically has a high salinity. Potential contamination of groundwater can occur from the injection water which commonly contains a number of proprietary chemical compounds and flowback water which is a mixture of injection water and formation water. Use of Sr isotopes to detect contamination associated with the hydraulic fracturing process requires samples of (1) uncontaminated groundwater, (2) 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 $^{87}Sr/^{86}Sr$ analysis with a 2-sigma uncertainty of ±0.00002.
2. ICPMS analysis of Sr concentration (coefficient of variation of ±5 percent).
3. Sr isotope measurements of USGS standard EN-1 which is analyzed every six samples. The $^{87}Sr/^{86}Sr$ values for EN-1 allow precise interlaboratory comparisons of analyses. These data will be compiled and included in the report.
4. For each study site, a report describing the isotopic results and their implications can be prepared.
5. Other isotopes (O, H, C, U, Pb) and other dissolved ions and trace metal concentrations can be determined by the USGS laboratories in Denver if needed.
6. USGS personnel can participate or advise in the specific site studies and sample collection if needed by the EPA.

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

Brinck, E. L., and C. D. Frost, 2007a, Detecting infiltration and impacts of introduced water using strontium isotopes: Ground Water, v. 45, p. 554– 568.

Frost, C.D., and Toner, R.N., 2004, Strontium isotopic identification of water-rock interaction and groundwater mixing: Ground Water, v. 42, p. 418–432.

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

Moller, P., Seise, S.M., Tesmer, M., Dulski, P., Pekdeger, A., Bayer, U., and Magri, F. 2008, Salinization of groundwater in the North German Basin: Results from conjoint investigation of major, trace element and multi-isotope distribution: International Journal of Earth Science (Geol Rundsch), v. 97, p. 1057-1073.

Naftz, D.L., Peterman, Z.E., Spangler, L.E. 1997, Using δ^{87}Sr to identify sources of salinity to a freshwater aquifer, Greater Aneth Oil Field, Utah, USA: Chemical Geology, v. 141, p. 195-209.

Peterman, Zell E., and Wallin, Bill, 1999, Synopsis of strontium isotope variations in groundwater at Äspö, southern Sweden: Applied Geochemistry, v. 14, p. 939-951.

Quattrocchi, F., Barbieri, M., Bencini, R., Cinti, D., Durocher,K., Galli, G., Pizzino, L., Shevalier, M., and Volttorni, N., 2006, Strontium isotope ($^{87}Sr/^{86}Sr$) chemistry in produced oil field waters: The IEA CO2 monitoring and storage project: Advance in the Geological Storage of Carbon Dioxide, Springer, The Netherlands, p. 243-259.

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

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

Prepared by:

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

Rb-Sr Isotope Geochemistry

1. INTRODUCTION.

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

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

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

One form of the basic decay equation follows:

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

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

For geochronologic applications, the above equation is solved for "t" which is the interval of time since the rock or mineral system formed with an initial Sr isotopic composition of $(^{87}Sr/^{86}Sr)i$ assuming closed system evolution (i.e. no loss or gain of parent or daughter isotopes other than by radioactive decay). For tracer studies, the above decay equation may or may not be relevant. Initial Sr isotope values $(^{87}Sr/^{86}Sr)i$ values for igneous rock are valuable for characterizing the sources of magmas from which the rocks formed including possible assimilation of crustal rocks during ascent of the magmas. For this usage, the age of the system and the $(^{87}Rb/^{86}Sr)p$ must be known so that $(^{87}Sr/^{86}Sr)p$ can be corrected for the ingrowth of radiogenic ^{87}Sr. Other materials for which Sr isotopes can be effectively used as tracers or for characterization include calcite deposits such as in veins or 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 ^{84}Sr and ^{87}Rb. Sample dissolution is accomplished through a combination of small amounts of concentrated H_2SO_4, HCl, $HClO_4$, or HNO_3 with concentrated HF. After refluxing on a hot plate to dryness the resultant precipitate is brought into solution with HCl or HNO_3 and centrifuged. The supernatant solution is pipetted in small volumes onto an ion-exchange resin column pretreated with HCl or HNO_3. After washing with a measured volume of HCl or HNO_3 acid, the final solution containing the purified Sr is collected in a Teflon beaker and dried on low heat. The sample is transferred to the mass spectrometer laboratory for isotopic analysis.

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

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

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

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

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

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

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

6.2.1 Sample Preparation:

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

6.2.2 Chemical Dissolution:

- Ultra-high purity (UPH) H_2O (18.2×10^6 ohms resistivity)
- Ultrex, Baker Analyzed, C Star Suprapur (EM Science) and/or
- Reagents of equivalent or higher purity of the following: H_2SO_4 (concentrated), HF concentrated), $HClO_4$ (concentrated), HNO_3 (concentrated), HCl (concentrated), CH_3COOH (acetic acid), Disodium EDTA (ethylenedinitrilotetraacetate)
- Platinum dishes
- Teflon covers, jars, beakers, tubes and other equipment
- Electronic analytical balance
- NIST traceable weights
- ^{87}Rb spike solution
- NIST SRM-607 Rb standard
- ^{84}Sr spike solution
- NIST SRM-610 or 611 Sr standard
- Hot plate
- Centrifuge
- Ion-exchange resins and columns
- Parafilm
- Environmental hood or laminaire flow hoods
- Appropriate standard laboratory equipment including, but not limited to: quartz, Teflon, and Pyrex beakers; graduated cylinders; and glass and plastic centrifuge tubes (accuracies in all ranges to $\pm$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 (where) and designated EN-1. Sr in the clam shell represents the isotopic composition of modern sea water. Because the $^{87}Rb/^{85}Rb$ ratio is constant in nature, rubidium isotopic measurements are checked by analyzing Rb from an unspiked biotite or K-feldspar. These operational checks of the chemistry and mass spectrometry laboratories shall incorporate components that measure and/or regulate volume, vacuum, filament current/temperature, accelerating voltage, and ion-beam current. If the results of these operational checks are not within acceptable limits per Para. 11 of this procedure, mass spectrometer and/or laboratory operations are suspended until the problem(s) is (are) identified and rectified. If elemental concentrations of the standards indicate a significant change in the spike solution concentration then the affected spikes are re-determined with NIST standards. These checks will be documented in the mass spectrometer logbook.

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

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

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

7.2 Limits: Mass spectrometers are complex systems composed of a number of sensitive electronic components. Any electronic problem will commonly manifest itself as beam instability during the course of an analysis. This is identified immediately by the operator on the basis of an unstable signal. The instruments will be shut down until the

problem is rectified. There are no unconstrained assumptions in the laboratory procedures that have not been experimentally tested during the long-term operation of the facility.

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

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

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

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

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

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

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

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

9.4 Nonconforming Samples: Nonconforming samples will be documented in

accordance with YMPB-USGS-QMP-SII.01.

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

11. MEASURING AND TEST EQUIPMENT.

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

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

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

11.1.3 Analytical Balance: The laboratory scales and analytical balances 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 ^{87}Rb and shelf life is not applicable.

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

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

15. RECORDS. The following QA:QA records are submitted by the PI, or delegate, to the Records Processing Center through the Records Management Specialist in accordance with YMPB-USGS-QMP-17.01, *Quality Assurance Records Management*:

15.1 Records Packages: The following may be submitted as part of a records package:

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

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

15.1.2 Supporting Information:

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

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

15.2 Individual Records: None

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

- YMPB-USGS-QMP-5.01, *Preparation of Technical Procedures*
- YMPB-USGS-QMP-12.01, *Control of Measuring and Test Equipment*
- YMPB-USGS-QMP-17.01, *Quality Assurance Records Management*
- YMPB-USGS-QMP-SI.01, *Software Management*
- YMPB-USGS-QMP-SII.01, *Identification and Control of Samples*
- YMPB-USGS-GCP-25, *Determination of Chemical Composition by Energy Dispersive X-Ray Fluorescence Spectrometry*
- YMPB-USGS-GCP-38, *Determination of Chemical Composition by Inductively Coupled Plasma Mass Spectrometry*
- YMPB-USGS-GCP-42, *Calibration of Laboratory Scales and Analytical Balances*
- 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.

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