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: 94

Revision No: 1 (submitted April 9, 2012) (see p. 46 for Revision History)

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1.0 Project Management

1.1 Project/Task Organization

Described below are the roles and primary responsibilities of personnel associated with the Hydraulic Fracturing Retrospective Case Study located in the 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. Dr. Jewett is the Technical Research Lead for case studies; he replaced Dr. Robert Puls in this position in January 2012.

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.

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.

Dr. Carl Miller, U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Robert S. Kerr Environmental Research Center, Ada, OK. Dr. Miller is responsible for conducting geophysical investigations. 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 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 assisting Dr. Wilkin in understanding ground water flow directions. His HAZWOPER certifications are current.

Mr. Ken Jewell, 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. Jewell is responsible for operation of the Geoprobe rig during ground water sampling. His HAZWOPER certification is current.

Mr. Russell Neill, U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Robert S. Kerr Environmental Research Center (RSKERC), Ada, OK. Mr. Neill is responsible for operation of the Geoprobe rig during ground water sampling and core collection. His HAZWOPER certification is current.

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

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

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

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

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.

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

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

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

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 and sulfur 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.

Ms. Susan Mravik, U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Robert S. Kerr Environmental Research Center (RSKERC), Ada, OK. Ms. Mravik is responsible for assisting with data management by transferring data from the PI to Shaw Environmental. Shaw then uploads the data to a secure server. Ms. Mravik also assists the PIs by tracking the status of laboratory analysis of samples, data reports, ADQs, and final QA approvals of data.

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.

Potential sources of ground-water contamination include activities associated with coal bed methane extraction (such as leaking or abandoned pits), residential or agricultural practices, gas

well completion and enhancement techniques, improperly plugged and abandoned wells, and 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 follow-up sampling event would likely be conducted using identical methods to confirm the result. On the other hand, if contamination is detected, confirmation sampling would be planned, but also additional studies and methods 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 a limited follow-up sampling would take place to confirm the result. Phase II activities will likely involve additional surface water and ground-water sampling, monitoring well sampling, and may involve installation of temporary or permanent wells for hydrogeologic and geochemical characterization, core collection and analysis, and geophysical surveys (self potential and/or resistivity). Phase I sampling is expected to take place in October 2011. Version 0 of this QAPP describes quality assurance and quality control procedures associated with Phase I studies. Subsequent revision of the QAPP, if appropriate, will occur following evaluation of Phase I results or whenever revisions are necessary. Version 1 of this QAPP includes minor revisions to sampling and analytical methodologies and additional analyses prior to a second sampling trip planned for May 2012 (Table 1).

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 (Figure 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.

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 8. The selected sampling sites meet certain criteria. A production well will be sampled in order to obtain information about the chemistry of water from the production zones (Vermejo and Raton Formations). 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 these 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. 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. Similar locations are planned for the May 2012 sampling trip. Water analysis will include a range organic and inorganic constituents, including Gasoline Range Organics (GRO), Diesel Range Organics (DRO), volatile organic compounds (VOCs), semi-volatile organic compounds (SVOCs), glycols, alcohols, 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. 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), U.S. EPA Regional laboratories located in Fort Meade (MD) and Golden (CO), EPA Office of Research and Development laboratories in Cincinnati, OH, USGS laboratories located in Denver (CO), and Isotech Laboratories located in Champaign (IL). Analytical methods are discussed in Section 2.4.

It is anticipated that data collected from this case study will be incorporated into the larger Hydraulic Fracturing report to 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.

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. The EPA GP laboratory and the Shaw 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.

1.6 Documents and Records

Data reports will be provided electronically as Excel spreadsheets. Some may be submitted as Adobe pdfs. Shaw's raw data is kept on-site at the GWERD and will be provided on CD/DVD to Rick Wilkin. 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 Rick Wilkin's office in the GWERD until they are transferred to GWERD's Records Storage Room. At some point in the future records will be transferred to a National Archive facility.

2.0 Data Generation and Acquisition

2.1 Sampling Process Design (Experimental Design)

2.1.1 Background Geologic and Hydrological Information

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. 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 1 year. 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 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.

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) will be collected, without headspace, for VOC analysis using RSKSOP-299v1. 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 Shaw, NRMRL-Ada's on-site contractor for GC-MS analysis.

    b. Duplicate 60 mL serum bottles will be collected, without headspace, for dissolved gas analysis (e.g., 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 Shaw, NRMRL-Ada's on-site contractor for analysis.

    c. Duplicate 40 mL VOA vials (clear glass) 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 Shaw, NRMRL-Ada's on-site contractor for HPLC analysis.

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

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

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

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

h. A 1L plastic bottle containing a caplet of benzalkonium chloride for preservation will be collected for carbon and hydrogen isotope analyses of dissolved methane (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.

i. A 125 mL plastic bottle will be filled for total metals analysis. Analysis of this sample will be by ICP-OES for Al, Ag, As, B, Be, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Sr, Ti, Tl, V, Zn, Si, and S and by ICP-MS for Cd, Cr, As, Cu, Pb, Ni, Se, Sb, Hg, U, Th, and Tl. This sample will be preserved by adding 5 drops of concentrated HNO_3 (Optima; pH test strips will be used as spot checks on samples to confirm that the sample pH is <2). The sample will be stored and shipped on ice to Shaw, NRMRL-Ada's on-site contractor for analysis.

j. 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.

k. 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).

l. 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 (m-u) will be collected. Prior to filling sample bottles, at least 100 mL of ground-water will be passed through the filter to waste.

m. 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 dissolved sulfide as ZnS. These bottles will be shipped on ice to Isotech Laboratories.

n. 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.

o. A 125 mL plastic bottle will be filled for dissolved metals analysis. Analysis of this sample will be by ICP-OES for Al, Ag, As, B, Be, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Sr, Ti, Tl, V, Zn, Si, and S and by ICP-MS for Cd, Cr, As, Cu, Pb, Ni, Se, Sb, Hg, U, Th, and Tl. This sample will be preserved by adding 5 drops of concentrated HNO_3 (Optima; pH test strips will be used as spot checks on samples to confirm that the sample pH is <2). The sample will be stored and shipped on ice to Shaw, NRMRL-Ada's on-site contractor for analysis.

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

q. 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.

r. 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.

s. 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.

t. 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). The sample will be stored and shipped on ice to Shaw, NRMRL-Ada's on-site contractor for analysis.

u. A 500 mL clear plastic bottle will be filled for Sr isotope analysis using thermal ionization mass spectroscopy (no acid preservation). The sample will be 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. 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 location of a surface body that will be sampled. The same set of samples will be collected as described in section 2.2.1. This surface water sample will be collected from a flowing stream that was identified during the July 2011 reconnaissance trip to the site. Depending on seasonal flow in this stream, it may not be possible to collect water from the site during all sampling visits. The stream is typically less than 0.2 m deep, but this depth is likely to change seasonally and in relation to precipitation events. This was selected as it represents a focus of surface water outflow from the North Fork Ranch sampling site (Site 1 on Figure 2). The location of the sampling site will be recorded with a handheld GPS device. The site 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 Shaw and EPA General Parameters Laboratory)

Upon receipt at RSKERC, all samples shall be logged-in and distributed to appropriate analysts by Shaw using RSKSOP-216v2, *Sample Receipt and Log-in Procedures for the On-site Analytical Contractor*. Before opening the ice chests the custody seal is checked by the sample custodian to verify it is intact. Ice chests are opened and the temperature blank is located to take the temperature and it is noted whether or not ice is still present. Chain-of-custody (COC) 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 Shaw 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 12 °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 Rick Wilkin. The samples are assigned a laboratory number and a cross list is prepared that correlates the assigned number with the field number. The samples are then transferred to their secured chemical laboratory for analysis.

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. Analysis at RSKERC includes inductively coupled plasma – optical emission spectroscopy (ICP-OES; for cations), inductively coupled plasma – mass spectroscopy (ICP-MS; for trace metals), capillary electrophoresis (CE, for anions), flow injection analysis (FIA, for N-series), carbon analysis using combustion and infrared detection, gas chromatography (GC, for dissolved gas analysis), isotope ratio mass spectrometry 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), gas chromatography-mass spectroscopy (GC-MS) for VOCs, and HPLC analysis for low molecular

weight acids. Analysis by the EPA Region VIII laboratory includes GC for GRO, DRO, and GC-MS for semivolatiles with appropriate sample preparation and introduction techniques. The analytical methods to be used for water samples are presented in Table 5.

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 many of the samples submitted for methane isotopic analysis will not contain measureable concentrations of methane and

therefore no analysis will be possible. For the dissolved gas samples, the bottles will be transported so that the aqueous solution will be on top of the bottle closure, i.e., the bottles will be transported upside down. 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.

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 mm 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.

The RSKSOPs and their associated target analyte list are presented in Table 7. For these analyses, the only surrogates used are for the VOC analysis. Surrogate compounds used are p-bromofluorobenzene and 1,2-dichlorobenzene-d4, spiked at 100 ug/L.

For the semi-volatiles, the target analyte list is presented in Table 8. Surrogates used include phenol-d6, 2-fluorophenol, 2,4,6-tribromophenol, nitrobenzened5, 2-fluorobiphenyl, and p-terphenyl-d14. The concentrations used for the surrogates will 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 a tentative identification be made. Guidelines for making a tentative identification include:

- 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 due to background contamination or co-eluting peaks. Data system library reduction programs can sometimes create these discrepancies.

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

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

2.5 Quality Control

2.5.1 Quality Metrics for Aqueous Analysis

For analyses done at RSKERC, QA/QC practices (e.g., blanks, calibration checks, duplicates, second source standards, matrix spikes, and surrogates) are described in various in-house Standard Operating Procedures (RSKSOPs) and summarized in Table 9. Matrix spikes sample spiking levels are determined at the discretion of the individual analysts (based on sample concentrations) and are included with the sample results. Corrective actions are outlined in the appropriate SOPs and when corrective actions occur in laboratory analysis it will be documented and the PI will be notified as to the nature of the corrective action and the steps taken to correct

the problem. The PI will review this information and judge if the corrective action was appropriate.

For analyses done by the Region VIII laboratory, QA/QC requirements are (Table 10):

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

Semivolatiles: 7 days until extraction, 30 days after extraction

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

GRO: 14 days*

*With acid preservation

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

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

(4) Detection limits (DL) and quantitation (reporting) limits (RL) for the semi-volatiles are as provided in Table 8. The DL and RL for DRO and GRO are both at 20 µg/L.

(5) The laboratory shall be subject to an on-site QA audit (conducted July 2011) and analysis of Performance Evaluation samples. The laboratory is currently analyzing Performance Evaluation (Proficiency Testing) samples, and has provided this data.

(6) See Table 10 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 12):

(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 ug/L (Table 11).

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

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

Corrective Actions: If any samples are affected by failure of a QC sample to meet its performance criteria, the problem shall be corrected and samples will be re-analyzed. If re-analysis is not possible (such as lack of sample volume), 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 13, Table 14, and Table 15):

(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 13, 14, and 15 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 16):

(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 16 for QC types and performance criteria.

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

For analyses 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 17 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.

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 and III are discussed in Section 2.5.1. They are adequate for project objectives. For isotope measurements, detection limits do not apply. However, enough mass of the element of interest must be included in the sample. For example, 100 ng of Sr is required to determine the isotope ratio of Sr in a sample. In most cases, mass limitations are not expected for isotope measurements, except for the case of methane in samples that are low in dissolved methane.

2.5.4 QA/QC Calculations

% Recovery or Accuracy

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

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:

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

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.

2.7 Instrument/Equipment Calibration and Frequency

RSKERC calibration and calibration frequency are described in RSKSOPs (RSKERC Standard Operating Procedures). For the Region III and VIII laboratories, these requirements are identified in their SOPs and in Tables 10 and 12, and for the USGS laboratory, Table 16.

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 and should be within 10% of expected readings. 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 90-110 mg/L. Duplicates will be performed once a day or on every tenth sample. Duplicate acceptance criteria are RPD $\leq$ 15. The values obtained for each duplicate sample will be recorded in the field notebook and RPD will be calculated (section 2.5.4) and recorded in the field notebook. If the duplicate samples fail, an additional duplicate sample will be taken and reanalyzed. If the additional duplicate samples fail to meet the QC criteria, then the instruments will be checked and corrective action taken. The corrective actions will be recorded in the field notebook. Samples collected between the last valid duplicate sample and the failed duplicate sample will be flagged.

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 Medcal 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 VIII 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

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

2.10 Data Management

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

Data will be submitted to Rick Wilkin 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 Wilkin's computer or designated GWERD staff computer and will given to the PI. The PI, a technician, post-doc, or student will conduct this task. Data will be spot-checked by Rick Wilkin 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.

2.10.1 Data Recording

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

2.10.2 Data Storage

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

2.10.4 Analysis of Data

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

3.0 Assessment and Oversight

3.1 Assessments and Response Actions

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

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

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

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

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

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

3.1.1 Assessments

TSAs will be conducted on both field and laboratory activities. Detailed checklists, based on the procedures and requirements specified in this QAPP, SOPs, and EPA Methods will be prepared and used during these TSAs. One field TSA will be done. It is anticipated this will take place during the 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 will be conducted on-site at RSKERC (involves both EPA and Shaw-operated labs) and at the Region VIII laboratory

which will analyze for semi-volatile organic, DRO and GRO analyses. It is anticipated this will take place after the first sampling event. However, laboratory TSAs will not be repeated if they have been done previously for another HF case study and significant findings were not identified.

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

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 QA Manager. 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 QA Manager or the QA support contractor, Neptune and Co.. Those prepared by Neptune and Co. 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, 9, 10, 12, 13, 14, 16, and 17. In addition, sample preservation and holding times will be evaluated against requirements in Table 5.

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

4.2 Verification and Validation Methods

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

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

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

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

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

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

Data reports are reviewed by Rick Wilkin for completeness, correctness, and conformance with QAPP requirements. All sample results are verified by Rick Wilkin 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 Rick Wilkin. See Table 18 for the Data Qualifiers. The Contract Laboratory Program guidelines on organic methods data review (USEPA, 2008) is 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. Neptune and Company, a QA support contractor, will conduct data validation on a representative sample of the critical analytes with oversight by the QAM. Data summaries for the critical analytes that have been prepared by Rick Wilkin shall be provided to Steve Vandegrift, QAM, who will coordinate the data validation with Neptune. Neptune shall evaluate data against the QAPP specifications. Neptune will use NRMRL SOP #LSAS-QA-02-0, "Performing Audits of Data Quality" as a guide for conducting the data validation. The outputs from this process will include the validated data and the data validation report. The report will include a summary of any identified deficiencies and a discussion on each individual deficiency and any effect on data quality and recommended corrective action.

Rick Wilkin will use the information from these data verification/validation activities to assist in making a final determination of data usability. As part of the data validation process, the synthesis of data and conclusions drawn from the data will be reviewed by the RSKERC Case Study Team (minimally will include case study PIs, Technical Research Lead for case studies, and GWERD Division Director) prior to release of this information or data to entities outside of RSKERC. Once reviewed by the RSKERC Case Study Team in coordination with the GWERD Division Director, the GWERD Division Director will approve its release.

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

The types of statistical analyses that 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.

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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.

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RSKSOP-213v4. Standard operating procedure for operation of Perkin Elmer Optima 3300 DV ICP-OES. 22 p.

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RSKSOP-216v2. Sample receipt and log-in procedures for the on-site analytical contractor. 5 p.

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RSKSOP-276v3. Determination of major anions in aqueous samples using capillary ion electrophoresis with indirect UV detection and Empower 2 Software. 11 p.

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

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.

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6.0 Tables

Table 1. QAPP revision history.

Revision Number	Date Approved	Revision
0	8/30/2011	New document
1	4/xx/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 Shaw 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

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 (VOC)*	Shaw Environmental
Semivolatile Organic Compounds (SVOC)	EPA Region VIII Laboratory
Metals (As, Se, Sr, Ba)	Shaw Environmental
Major Cations (Ca, Mg, Na, K)	Shaw Environmental
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 8 that have DL, RL, and Control Limits listed may be used as critical analytes; all others will be used only as screening data.
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	October 2012 Phase	April 2013 Phase
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
Metals (filtered)	RSKSOP-213v4 &-257v3 or 332v0 (EPA Methods 200.7 and 6020)	125 mL plastic bottle/1	HNO_3, pH<2; room temperature	6 months (Hg 28 days)
Metals (unfiltered)	RSKSOP179v2; RSKSOP-213v4 &-257v3 or 332v0 (EPA Methods 200.7 and 6020)	125 mL plastic bottle/1	HNO_3, pH<2; room temperature	6 months (Hg 28 days)
SO_4, Cl, F, Br	RSKSOP-276v3 (EPA Method 6500)	30 mL plastic/1	Refrigerate ≤6°C	28 days
$NO_3 + NO_2$, NH_4	RSKSOP-214v5 (EPA Method 350.1 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)	RSKSOP-299v1 (EPA Method 5021A plus 8260C)	40 mL amber glass VOA vial/2	No Headspace TSP†, pH>10; refrigerate ≤6°C	14 days
Low Molecular Weight Acids	RSKSOP-112V6 (No EPA Method)	40 mL glass VOA vial/2	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 at ≤6°C	stable
$\delta^{13}C$ of inorganic carbon	Isotech: gas stripping and IRMS (No EPA Method)	60 mL plastic bottle/1	Refrigerate ≤6°C	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	ORGM-515 r1.1, EPA Method 8270D	1L Amber glass bottle/2 and for every 10 samples of ground water need 2 more bottles for one selected	Refrigerate ≤6°C	7 days until extraction, 30 days after 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 VOA and dissolved gas samples.	<RL*; if >RL, PI will determine if significant relative to sample data.
Equipment Blanks	Assess contamination from field equipment, sampling procedures, decon procedures, sample container, preservative, and shipping.	Apply only to samples collected via equipment, such as filtered samples: Reagent water is filtered and collected into bottles and preserved same as filtered samples.	One per day of sampling.	<RL; if >RL, PI will determine if significant relative to sample data.
Field Duplicates	Represent precision of field sampling, analysis, and site heterogeneity.	One or more samples collected immediately after original sample.	One in every 10 samples, or if <10 samples collected for a water type (ground or surface), collect a duplicate for one sample.	Report duplicate data; if RPD >30 for results greater than 5xRL, then affected data will be flagged as needed.
Temperature Blanks	Measure temperature of samples in the cooler.	Water sample that is transported in cooler to lab.	One per cooler.	Record temperature; condition noted on COC form***
Field Blanks**	Assess contamination introduced from sample container with applicable preservative.	In the field, reagent water is collected into sample containers with preservatives.	One per day of sampling.	<RL*; if >RL, PI will determine if significant relative to sample data.

*- Reporting limit or Quantitation Limit
** - Blank samples will not be collected for isotope measurements, including O, H, C, 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 12 °C. These samples will be flagged accordingly.

Table 7. RSKERC detection limits for various analytes.*

Analyte	Method	MDL (µg/L)	QL or LOQ (µg/L)
VOCs			
Vinyl chloride	RSKSOP-299v1	0.18	0.50
Ethanol	RSKSOP-299v1	18.0	100
1,1-Dichloroethene	RSKSOP-299v1	0.12	0.50
Acetone	RSKSOP-299v1	3.45	10.0
Isopropyl alcohol	RSKSOP-299v1	2.37	10.0
Carbon disulfide	RSKSOP-299v1	0.21	0.50
Methylene chloride	RSKSOP-299v1	0.21	1.00
t-Butyl alcohol	RSKSOP-299v1	2.41	10
Methyl t-butyl ether	RSKSOP-299v1	0.09	1.00
t-1,2-Dichloroethene	RSKSOP-299v1	0.10	0.50
1,1-Dichloroethane	RSKSOP-299v1	0.13	0.50
Diisopropyl ether	RSKSOP-299v1	0.11	1.00
Ethyl t-butyl ether	RSKSOP-299v1	0.08	1.00
c-1,2-Dichloroethene	RSKSOP-299v1	0.14	0.50
Chloroform	RSKSOP-299v1	0.13	0.50
1,1,1-Trichloroethane	RSKSOP-299v1	0.13	0.50
Carbon tetrachloride	RSKSOP-299v1	0.12	0.50
Benzene	RSKSOP-299v1	0.06	0.50
1,2-Dichloroethane	RSKSOP-299v1	0.21	0.50
t-Amyl methyl ether	RSKSOP-299v1	0.09	1.00
Trichloroethene	RSKSOP-299v1	0.09	0.50
Toluene	RSKSOP-299v1	0.08	0.50
1,1,2-Trichloroethane	RSKSOP-299v1	0.21	0.50
Tetrachloroethene	RSKSOP-299v1	0.13	0.50
Chlorobenzene	RSKSOP-299v1	0.08	0.50
Ethyl benzene	RSKSOP-299v1	0.06	0.50
m/p-Xylene	RSKSOP-299v1	0.09	1.00
o-Xylene	RSKSOP-299v1	0.08	0.50
Isopropyl benzene	RSKSOP-299v1	0.05	0.50
1,3,5-Trimethylbenzene	RSKSOP-299v1	0.05	0.50
1,2,4-Trimethylbenzene	RSKSOP-299v1	0.05	0.50
1,3-Dichlorobenzene	RSKSOP-299v1	0.16	0.50
1,4-Dichlorobenzene	RSKSOP-299v1	0.17	0.50

Analyte	Method	MDL (µg/L)	QL or LOQ (µg/L)
VOCs, *cont'd*			
1,2,3-Trimethylbenzene	RSKSOP-299v1	0.07	0.50
1,2-Dichlorobenzene	RSKSOP-299v1	0.10	0.50
Naphthalene	RSKSOP-299v1	0.31	1.00

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

Cu	RSKSOP-213v4	0.002	0.007
Sb	RSKSOP-213v4	0.008	0.027
Cr	RSKSOP-213v4	0.001	0.004
Ni	RSKSOP-213v4	0.001	0.004
Zn	RSKSOP-213v4	0.005	0.017

Analyte	Method	MDL (mg/L)	QL or LOQ (mg/L)
Metals ICP-OES, cont'd			
Ag	RSKSOP-213v4	0.003	0.010
Tl	RSKSOP-213v4	0.009	0.030
Pb	RSKSOP-213v4	0.003	0.010
Sr	RSKSOP-213v4	0.001	0.004
V	RSKSOP-213v4	0.002	0.007
Ba	RSKSOP-213v4	0.001	0.004
B	RSKSOP-213v4	0.005	0.017
Ti	RSKSOP-213v4	0.001	0.004
Si	RSKSOP-213v4	0.019	0.064
P	RSKSOP-213v4	0.011	0.037
S	RSKSOP-213v4	0.026	0.087
U	RSKSOP-213v4	0.009	0.030
Dissolved Gases**		**MDL (µg/L)**	**QL or LOQ (µg/L)**
Methane	RSKSOP-194v4 & RSKSOP-175v5	0.08	1.5
Ethane	RSKSOP-194v4& RSKSOP-175v5	0.20	2.91
Propane	RSKSOP-194v4& RSKSOP-175v5	0.24	4.1
n-Butane	RSKSOP-194v4& RSKSOP-175v5	0.22	5.22
Anions/Nutrients		**MDL (mg/L)**	**QL or LOQ (mg/L)**
Br^-	RSKSOP-276v3	0.248	1.00
Cl^-	RSKSOP-276v3	0.118	1.00
SO_4^{2-}	RSKSOP-276v3	0.226	1.00
$NO_3^- + NO_2^-$	RSKSOP-214v5	0.014	0.10
F^-	RSKSOP-276v3	0.052	0.20
NH_4^+	RSKSOP-214v5	0.012	0.05
Low Molecular Weight Acids		**MDL (mg/L)**	**QL (mg/L)**
Lactate	RSKSOP-112v6	0.020	0.100
Isobutyrate	RSKSOP-112v6	0.018	0.100

Analyte	Method	MDL (mg/L)	QL or LOQ (mg/L)
Low Molecular Weight Acids, cont'd			
Acetate	RSKSOP-112v6	0.011	0.100
Propionate	RSKSOP-112v6	0.022	0.100
Formate	RSKSOP-112v6	0.015	0.100
Butyrate	RSKSOP-112v6	0.025	0.100
DIC/DOC			
DOC	RSKSOP-330v0	0.067	0.50
DIC	RSKSOP-330v0	0.017	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 degrees, headspace pressure of 1 atmosphere, and using the "created" headspace calculations.

Table 8. Region VIII detection and reporting limits and LCS and MS control limits for semi-volatile organic compounds (SVOC) using Method 8270.

Analyte	Detection Limits		Control Limits			
	DL[1] (µg L^{-1})	RL (µg L^{-1})	Mean	Standard Deviation	Lower Control Limit	Upper Control Limit
1,2-Dichlorobenzene	0.335	0.500	67.3	11.4	33	102
1,2-Dinitrobenzene	0.098	0.500				
1,2,4-Trichlorobenzene	0.349	0.500	71.7	11.6	37	107
1,3-Dichlorobenzene	0.396	0.500	64.8	10.9	32	98
1,3-Dinitrobenzene	0.092	0.500				
1,4-Dichlorobenzene	0.382	0.500	64.8	10.9	32	98
1,4-Dinitrobenzene	0.072	0.500				
1-Methylnaphthalene	0.174	0.500				
2-Chloronaphthalene	0.166	0.500	76.5	9.3	49	104
2-Chlorophenol	0.108	0.500	71.3	11.4	37	106
2-Methylnaphthalene	0.202	0.500	75.0	9.5	46	104
2-Methylphenol	0.103	0.500	73.3	11.7	38	109
2-Nitroaniline	0.112	0.500	81.8	11.2	48	115
2-Nitrophenol	0.121	0.500	75.8	12.4	39	113
2,3,4,6-Tetrachlorophenol	0.173	0.500				
2,3,5,6-Tetrachorophenol	0.202	0.500				
2,4-Dichlorophenol	0.171	0.500	76.3	9.6	48	105
2,4-Dimethylphenol	0.213	0.500	68.8	13.5	28	109
2,4-Dinitrophenol		5.00	75.8	20.6	14	138
2,4-Dinitrotoluene	0.092	0.500	84.3	11.2	51	118
2,4,5-Trichlorophenol	0..176	0.500	79.7	10.3	49	111
2,4,6-Trichlorophenol	0.154	0.500	80.7	10.7	49	113
2,6-Dinitrotoluene	0.101	0.500	82.7	11.3	49	117
3-Nitroaniline	0.135	0.500	72.6	17.7	19	126
3&4-Methylphenol	0.221	0.500	71.3	13.0	32	110
3,3'-Dichlorobenzidine	0.558	1.00	65.2	15.3	19	111
4-Bromophenyl phenyl ether	0.106	0.500	82.9	10.2	52	113
4-Chloroaniline	0.357	1.00	62.2	15.6	15	109
4-Chloro-3-methylphenol	0.164	0.500	78.6	10.7	47	111
4-Chlorophenyl phenyl ether	0.131	0500	80.6	10.3	50	111
4-Nitroaniline	0.158	0.500	77.2	13.7	36	118
4-Nitrophenol		2.50				
4,6-Dinitro-2-methylphenol	0.175	0.500	84.9	15.0	40	130
Acenaphthene	0.112	0.500	77.6	10.1	47	108
Acenaphthylene	0.095	0.500	78.5	9.4	40	107
Aniline	0.310	1.00				
Anthracene	0.089	0.500	83.0	9.7	54	112
Azobenzene	0.085	0.500				
Benzoic acid		5.00				
Benz(a)anthracene	0.102	0.500	82.7	8.9	56	109

Benzo(b)fluoranthene	0.096	0.500	81.8	12.1	45	118
Benzo(k)fluoranthene	0.099	0.500	84.6	13.2	45	124
Benzo(g,h,i)perylene	0.091	0.500	80.5	14.1	38	123
Benzo(a)pyrene	0.083	0.500	81.3	9.5	53	110
Benzyl alcohol	0.148	0.500	71.0	13.8	30	112
Bis(2-chloroethoxy)methane	0.092	0.500	76.2	10.2	46	107
Bis(2-chloroethyl) ether	0.122	0.500	73.3	12.3	37	110
Bis(2-chloroisopropyl) ether	0.104	0.500	78.2	17.5	26	131
Bis(2-Ethylhexyl) adipate	0.422	1.00				
Bis(2-ethylhexyl) phthalate	0.370	1.00	84.2	14.0	42	126
Butyl benzyl phthalate	0.199	0.500	81.1	11.7	46	116
Carbazole	0.131	0.500	82.5	11.4	48	117
Chrysene	0.087	0.500	82.1	8.9	55	109
Dibenz(a,h)anthracene	0.106	0.500	84.7	14.1	42	127
Dibenzofuran	0.100	0.500	80.3	8.8	54	107
Diethyl phthalate	0.085	0.500	79.2	12.9	41	118
Dimethyl phthalate	0.094	0.500	75.9	16.9	25	127
Diphenylamine	0.144	0.500				
Di-n-butyl phthalate	0.199	0.500	84.8	10.3	54	116
Di-n-octyl phthalate	0.105	0.500	87.4	16.6	37	137
Fluoranthene	0.087	0.500	85.2	10.4	54	116
Fluorene	0.099	0.500	80.6	10.3	50	112
Hexachlorobenzene	0.099	0.500				
Hexachlorobutadiene	0.482	1.00	65.2	12.6	27	103
Hexachlorocyclopentadiene	0.205	0.500				
Hexachloroethane	0.452	1.00	60.9	11.1	28	94
Indeno(1,2,3-cd)pyrene	0.096	0.500	84.3	13.6	43	125
Isophorone	0.104	0.500	81.0	10.5	50	112
Naphthalene	0.181	0.500	70.8	10.5	39	102
Nitrobenzene	0.140	0.500	76.8	10.8	44	109
N-Nitrosodimethylamine		0.500	67.9	41.1	26	110
N-Nitrosodi-n-propylamine	0.113	0.500	80.9	15.7	34	128
Pentachlorophenol	0.538	1.00	77.6	13.3	38	117
Phenanthrene	0.088	0.500	84.0	11.0	51	117
Phenol	0.102	0.500				
Pyrene	0.072	0.500	88.6	13.2	49	128
Pyridine		0.500				
R-(+)-Limonene	0.260	0.500				
1,3-Dimethyl adamantine	0.278	0.500				
2-Butoxyethanol	0.101	0.500				
Adamantane	0.258	0.500				
Squalene	0.256	1.00				
Terpiniol	0.057	0.500				
Tri(2-butoxyethyl)phosphate	0.226	1.00				

Table 9. RSKERC QA/QC requirements summary* from SOPs.

Measurement	Analysis Method	Blanks (Frequency)	Calibration Checks (Frequency)	Second Source (Frequency)	Duplicates (Frequency)	Matrix Spikes (Frequency)
Dissolved gases	RSKSOP-194v4 &-175v5*	≤MDL (He/Ar blank, first and last in sample queue; water blank before samples)	85-115% of known value (After helium/Ar blank at first of analysis queue, before helium/Ar blank at end of sample set, and every 15 samples)	85-115% of known value (After first calibration check)	RPD≤20 (Every 15 samples)	NA
Metals (filtered & undigested)	RSKSOP-213v4	<QL for 80% of metals; (Beginning and end of each sample queue, 10-15 samples)	90-110% of known value (Beginning and end of each sample queue, 10-15 samples)	PE sample acceptance limits or 90-110% of known value (Immediately after first calibration check)	RPD<10 for 80% of metals; for results <5x QL, difference of ≤QL(Every 15 samples)	90-110% Rec. for 80% of metals w/ no individual exceeding 50-150% Rec. (one per sample set, 10-15 samples)
Metals (unfiltered & digested)	RSKSOP-213v4	<10xMDL	See "undigested"	See "undigested"	RPD<20 for 80% of metals; for results <5x QL, difference of ≤QL (Every 15 samples)	80-120% Rec. for 80% of metals w/ no individual exceeding 50-150% Rec. (one per sample set, 10-15 samples)

Measurement	Analysis Method	Blanks (Frequency)	Calibration Checks (Frequency)	Second Source (Frequency)	Duplicates (Frequency)	Matrix Spikes (Frequency)
Metals (filtered & undigested)	RSKSOP-257v3 and -332v0	<QL for 80% of metals; none>10xMDL (Beginning and end of each sample queue, 10-15 samples)	90-110% of known value (Beginning and end of each sample queue, 10-15 samples)	PE sample acceptance limits or 90-110% of known value (Immediately after first calibration check)	RPD<10 for 80% of metals; for results <5xQL, difference of <QL (Every 15 samples)	90-110% Rec. for 80% of metals w/ no individual exceeding 70-130% (one per sample set, 10-15 samples)
Metals (unfiltered & digested)	RSKSOP-257v3 and -332v0	<ICP MDL for RSKSOP-213v4	See "undigested"	See "undigested"	RPD<20* for 80% of metals above 5xQL; for results <5x QL, difference of ≤QL (Every 15 samples) *35 for solids	80-120% average rec. with at least 50% of individuals within 50-150% rec. for pre-digestions and 70-130% rec. for all results for post-digestions (one per sample set, 10-15 samples)
SO_4, Cl, F, Br	RSKSOP-276v3	<MDL (Beginning and end of each sample queue)	90-110% Rec. (Beginning, end, and every 10 samples)	PE sample acceptance limits (One per sample set)	RPD<10 (every 15 samples)	80-120% Rec. (one per every 20 samples)
$NO_3 + NO_2$, NH_4	RSKSOP-214v5	<½ lowest calib. std. (Beginning and end of each sample queue)	90-110% Rec. (Beginning, end, and every 10 samples)	PE sample acceptance limits (One per sample set)	RPD<10 (every 10 samples)	80-120% Rec. (one per every 20 samples)

Measurement	Analysis Method	Blanks (Frequency)	Calibration Checks (Frequency)	Second Source (Frequency)	Duplicates (Frequency)	Matrix Spikes (Frequency)
DIC/DOC	RSKSOP-330v0	<½QL (after initial calib., every 10-15 samples, and at end)	80-120% of known value (after initial calib., every 10-15 samples, and at end)	80-120% of known value (Immediately after calibration)	RPD<10 (every 15 samples)	80-120% Rec. (one per 20 or every set
Volatile organic compounds (VOC)**	RSKSOP-299v1	<MDL (Beginning and end of each sample set)	80-120% Rec. (Beginning, end, and every 20 samples)	80-120% of known value Once at beginning (and at end for -259v1)	-299v1 RPD<20 -259v1 RPD<25 (every 20 samples)	70-130% Rec. (every 20 samples)
Low Molecular Weight Acids	RSKSOP-112v6	<MDL (Beginning of a sample queue; every 10 samples; and end of sample queue)	85-115% of the recovery (Prior to sample analysis; every 10 samples; end of sample queue)	85-115% of recovery (Prior to sample analysis)	< 15 RPD (Every 20 samples through a sample queue)	80-120 % recovery (Every 20 samples through a sample queue)
O, H stable isotopes of water***	RSKSOP-296v1 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/t	NA	RSKSOP296v1: 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	NA

			rue ≤ 1.5‰ for δ^2H & ≤ 0.3‰ for $\delta^{18}O$ (Beginning, end, and every twenty samples)		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 10. Region VIII laboratory QA/QC requirements for semi-volatiles, GRO, DRO.

QC Type	Semivolatiles	DRO	GRO	Frequency
Method Blanks	<RL Preparation or Method Blank, one with each set of extraction groups. Calibration Blanks are also analyzed	<RL Preparation or Method Blank	<RL Preparation or Method Blank and IBL	At least one per sample set
Surrogate Spikes	Limits based upon DoD statistical study (rounded to 0 or 5) for the target compound analyses.	60-140% of expected value	70-130% of expected value	Every field and QC sample
Internal Standards Verification	Every sample, EICP area within -50% to +100% of last ICV or first CCV.	NA	NA	Every field and QC sample
Initial multilevel calibration	ICAL: minimum of 6 levels (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: .25-12.5 ug/L for gasoline (different range for other compounds) RSD<=20% or r2>=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	Use and SRM: Values of all analytes in the LCS should be within the limits determined by the supplier.	One per analytical batch or every 20 samples, whichever is greater

		limits determined by the supplier. Otherwise 70-130% of expected value	Otherwise 70-130% of expected value	
Matrix Spikes (MS)	Same as LCS	Same as LCS	70-130% of expected value	One per sample set or every 20 samples, whichever is more frequent
MS/MSD	% Recovery same as MS RPD $\leq$ 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 7

Table 11. Region III detection and reporting limits for glycols.

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

† Detection and reporting limits are still being determined, most will be between 10 and 50 pbb.
‡ The samples are analyzed according to OASQA On Demand Procedures- See the QA manual for procedures. See Section 13.1.4.2 Procedure for Demonstration of Capability for "On-Demand" Data (Metzger et al., 2011)

Table 12. Region III laboratory QA/QC requirements for glycols.

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

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

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

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

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

Table 14. 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 $\leq$ 0.5‰ for $\delta^{13}C$ and $\leq$ 3‰ for δD	One @ beginning of day and after samples are analyzed for $\delta^{13}C$*; one @ beginning of day and every tenth sample for δD**
Mass Spec Zero Enrichment Check	0 +/- 0.1 ‰ for $\delta^{13}C$ and 0 +/- 1 ‰ for δD	Once a day for $\delta^{13}C$ and every tenth sample for δD
Lab Duplicates	$\leq$ 1 ‰ for $\delta^{13}C$ and $\leq$ 3‰ for δD	1 per every 10 samples***
Preparation System Check/Reference Standards	$\leq$ 1 ‰ for $\delta^{13}C$ and $\leq$ 3‰ for δD	One per every 10 samples

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

Table 15. 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 $\leq$ 0.5‰ for $\delta^{34}S$ and $\leq$ 0.5‰ for $\delta^{18}O$	One at beginning of sequence and after samples are analyzed*
Lab Duplicates	$\leq$ 0.5 ‰ for $\delta^{34}S$ and $\leq$ 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 16. 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 17. 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 about the impact on the sample data.

Table 18. Data qualifiers

Qualifier	Definition
U	The analyte was analyzed for but not detected above the reported method detection limit.
U1	The analyte was analyzed for but not detected above the quantification or reporting limit
LB	Analyte is found in an associated laboratory blank above QL or RL.
TB	Analyte is found in an associated trip blank above QL or RL.
FB	Analyte is found in an associated field blank above QL or RL.
EB	Analyte is found in an associated equipment blank above QL or RL .
*	Duplicate not within control limits (field or lab duplicates).
D	The reported value is from a dilution.
R	The sample results are rejected due to serious deficiencies in the ability to analyze the sample and meet quality control criteria.
K	Samples may be biased high because of high % recoveries in some BS and MS/MSD samples.
J	Estimated value.
J1	Estimated value, laboratory calibration criteria not met.
J2	Estimated value, laboratory QA/QC acceptance criteria not met.
J3	Samples bottles received from the field were not intact.
J4	Problem with sample extraction.
J5	Holding time exceeded.

7.0 Figures

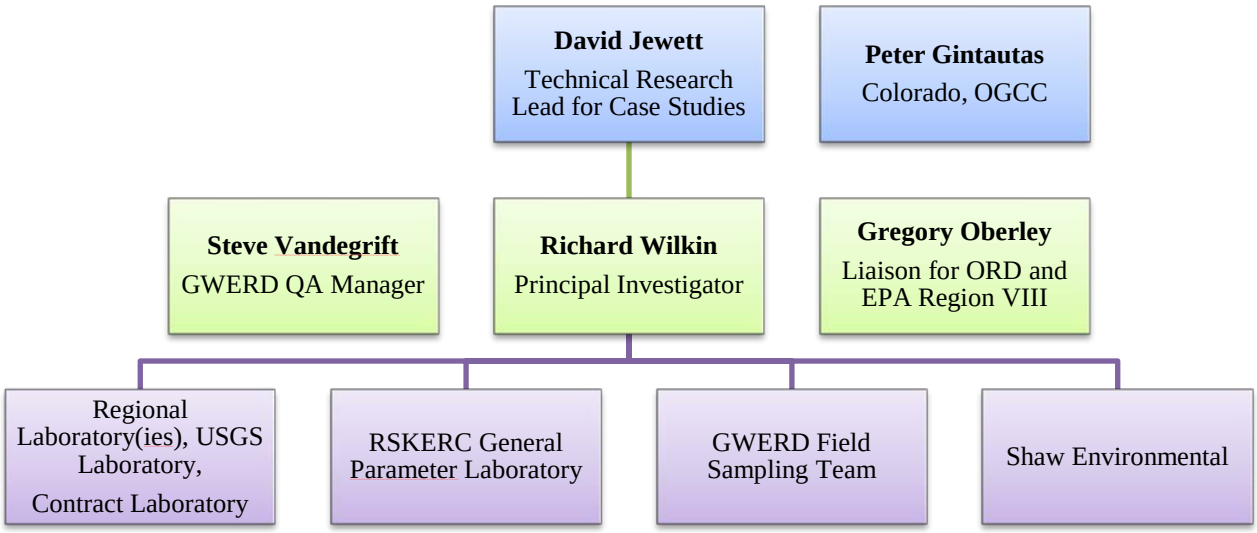


Figure 1. Organizational chart for the Hydraulic Fracturing Retrospective Case Study in the Raton Basin, Colorado.

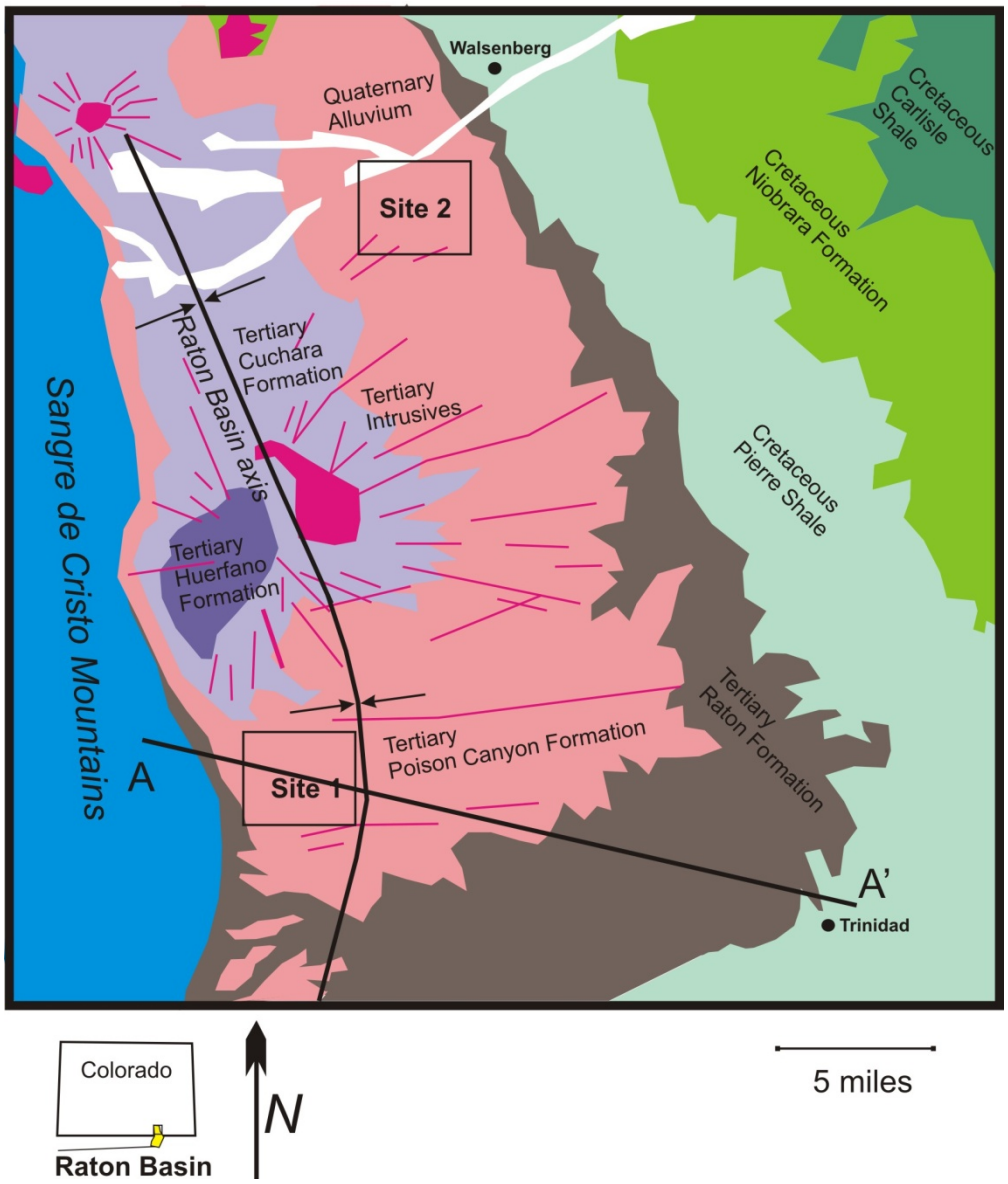
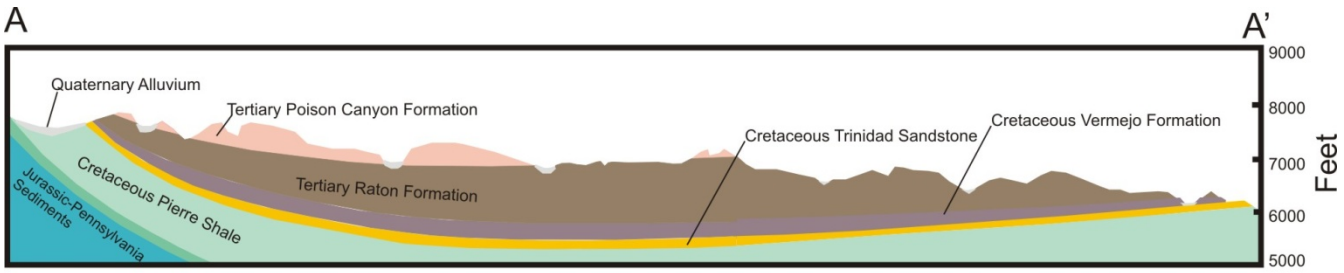


Figure 2. Generalized geologic map of the Raton Basin near Trinidad, CO. Modified from Tweto (1979).



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).

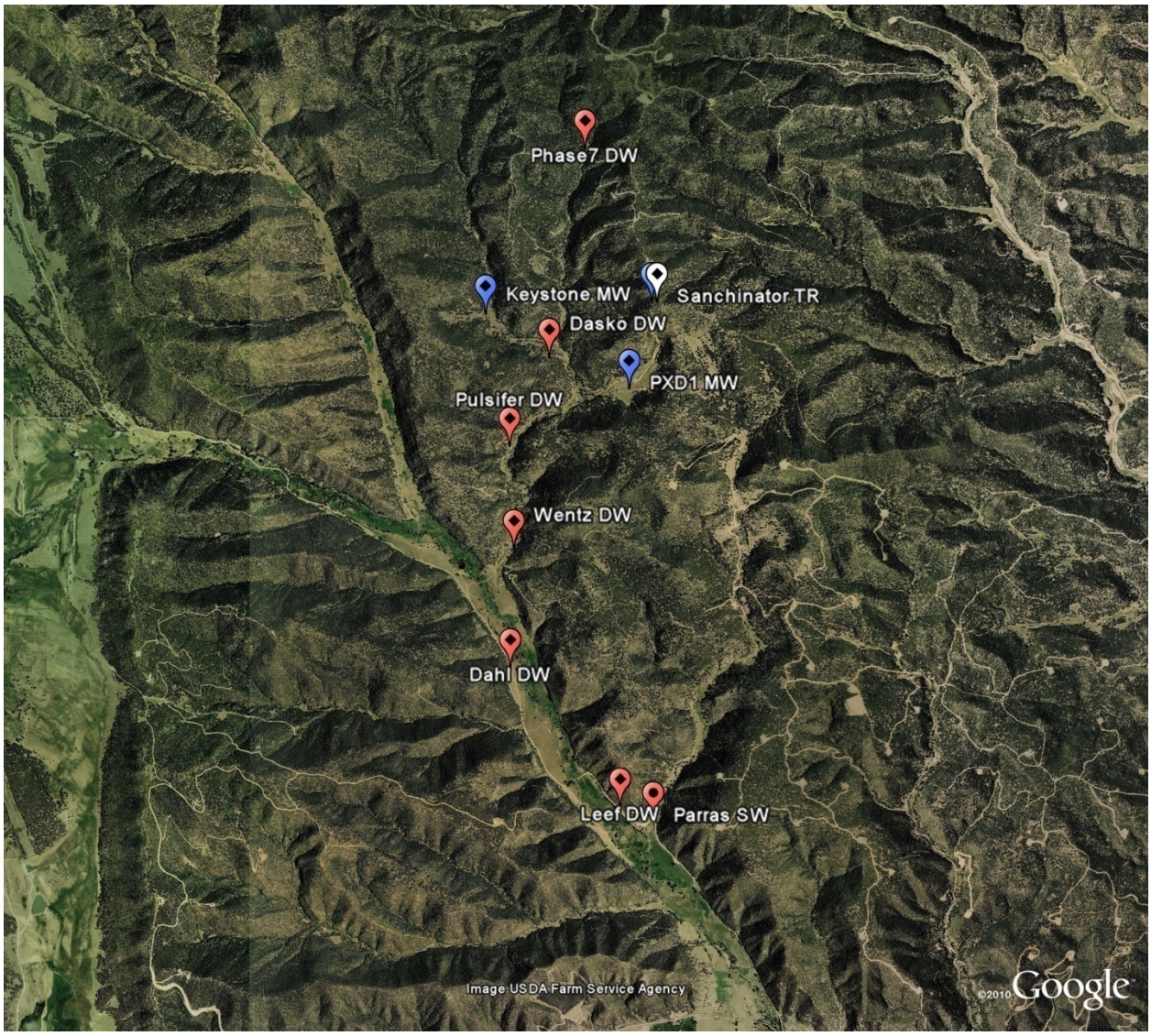


Figure 4. North Fork Ranch study area (Site 1 on Figure 2). Red symbols (diamonds) domestic wells; red symbols (circles) surface water; blue symbols (diamonds) monitoring wells; and, white symbol production wells.

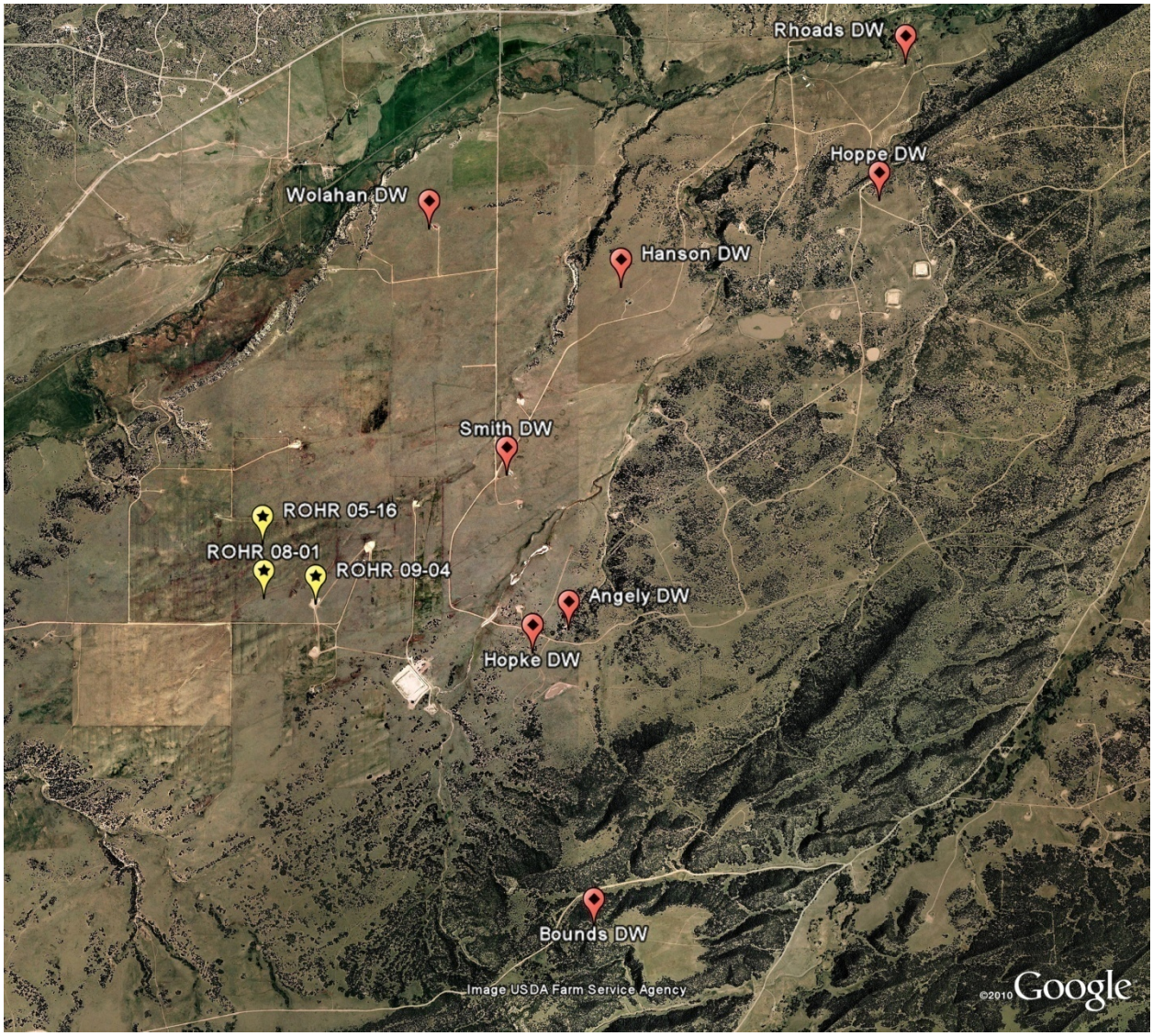


Figure 5. Little Creek Area (Site 2 on Figure 2). Red symbols (diamonds) domestic wells. Yellow symbols show the locations of three stimulated wells (gel fracs).

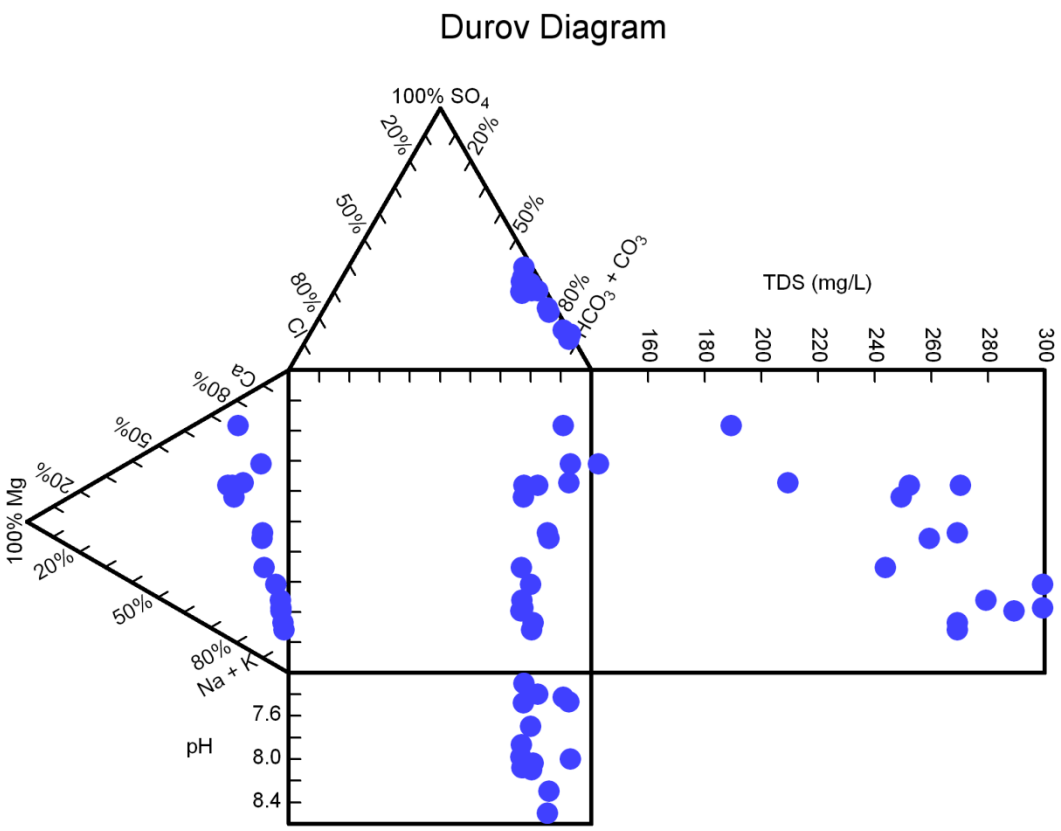


Figure 6. Durov diagram showing the distribution of major cations, major anions, as well as total dissolved solids (TDS) and pH in wells from the North Fork Ranch area (Site 1 on Figure 2).

Sample Analysis Request and Chain of Custody (COC) Record

USEPA, ORD, NRMRL

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.

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

Prepared by:

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Rb-Sr Isotope Geochemistry

1. INTRODUCTION.

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

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

The utility of the Rb-Sr decay system in geochronology and isotope tracer studies is described by Faure (1986). ^{87}Rb decays to ^{87}Sr with a half-life of 48.8 billion years, and the change in isotopic composition of Sr (measured as $^{87}Sr/^{86}Sr$ where ^{86}Sr is a 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:

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

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

For geochronologic applications, the above equation is solved for “t” which is the interval of time since the rock or mineral system formed with an initial Sr isotopic composition of $(^{87}Sr/^{86}Sr)i$ assuming closed system evolution (i.e. no loss or gain of parent or daughter isotopes other than by radioactive decay). For tracer studies, the above decay equation may or may not be relevant. Initial Sr isotope values $(^{87}Sr/^{86}Sr)i$ values for igneous rock are valuable for characterizing the sources of magmas from which the rocks formed including possible assimilation of crustal rocks during ascent of the magmas. For this usage, the age of the system and the $(^{87}Rb/^{86}Sr)p$ must be known so that $(^{87}Sr/^{86}Sr)p$ can be corrected for the ingrowth of radiogenic ^{87}Sr. Other materials for which Sr isotopes can be effectively used as tracers or for characterization include calcite deposits such as in veins or 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 ±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.