GWERD QUALITY ASSURANCE PROJECT PLAN

Title: Hydraulic Fracturing Retrospective Case Study, Bakken Shale, Killdeer and Dunn County, ND

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

The EPA Quality System and the HF Research Study

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

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

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1.0 Project Management

1.1 Project/Task Organization

The organizational structure for the Hydraulic Fracturing Retrospective Case Study located in the Bakken Shale, near the city of Killdeer, ND is shown in Figure 1. The responsibilities of the principal personnel associated with this case study are listed below.

Dr. Douglas Beak, U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Robert S. Kerr Environmental Research Center, Ada, OK. Dr. Beak is 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 the collection, analysis, and interpretation of groundwater and surface water samples. He is the Health and Safety Officer for groundwater 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 is also assisting in the coordination of the Hydraulic Fracturing Case Studies with EPA NRMRL management and other parts of EPA ORD and EPA Offices. His HAZWOPER certification is current.

Mr. Gregory Oberley, U.S. Environmental Protection Agency – Region VIII, Denver, CO. Mr. Oberley is responsible for coordinating technical discussion and activities between NRMRL-Ada and EPA Region VIII and Region VIII Analytical Lab, as well as coordinating data collection activities with the state officials in North Dakota. He will also assist in ground water sampling. His HAZWOPER certification is current.

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

Ms. Cynthia Sonich-Mullin, U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Cincinnati, OH. Ms. Sonich-Mullin is the Director of NRMRL. Ms. Sonich-Mullin will approve all data releases to the

stakeholders and public. In addition, when disputes occur she is the ultimate decision maker with in NRMRL.

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

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

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

Ms. Michelle Latham, U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Water Supply and Water Resources Division, Cincinnati, OH. Ms. Latham will be responsible for communications between the case studies and ORD.

Ms. Kelly Smith, U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Robert S. Kerr Environmental Research Center (RSKERC), Ada, OK. Ms. Smith is the GWERD Research lead for case studies, replacing Dr. David Jewett. She assists in the coordination of communications and contract laboratories between RSKERC and NRMRL Management.

Mr. Russell Neill, Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Robert S. Kerr Environmental Research Center, Ada, OK. Mr. Neill is field team coordinator. He is responsible for assigning field personnel for sampling trips and assisting in water sampling. His HAZWOPER certification is current.

Dr Randall Ross, U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Robert S. Kerr Environmental Research Center (RSKERC), Ada, OK. Dr. Ross will assist in the analysis of hydrologic conditions at the

Killdeer site and will assist in the development of the site hydrologic conditions. His HAZWOPER certification is current.

Mr. Steve Acree, 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. Acree will assist in the analysis of hydrologic conditions at the Killdeer site and will assist in the development of the site hydrologic conditions. 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. Beak with health and safety issues related to the study. Her HAZWOPER certification is current.

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

Dr. 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. Sujith Kumar, Shaw Environmental, Ada, OK. Dr. Kumar is responsible for overseeing the analytical work performed under GWERD's on site analytical contract (VOC's, 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.

Mr Kris Roberts, North Dakota Department of Health, Division of Water Quality. Mr. Roberts is the primary point of contact in North Dakota for site access and pre-existing data and data collected by Denbury's contractor Terracon.

Mr. Lynn Helms, North Dakota Industrial Commission, Department of Mineral Resources. Mr. Helms is a point of contact for oil and gas information.

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

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

Mr Ryan Jacob, Denbury Onshore, LLC. Mr. Jacob is the primary point of contact with Denbury and will assist in coordination of field sampling activities. Mr. Jacob will also act as the liason between Denbury and EPA as well as Terracon Consultants the onsite contractor.

Mr. Michael Bullock, Terracon Consultants. Mr Bullock is the point of contact inside of Terracon.

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

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

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

Dr. Robert Ford, U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Land Remediation and Pollution Control Division, Cincinnati, OH. Dr. Ford is responsible for providing technical input on sections of the report prepared for this project.

Dr. Barbara Butler, U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Land Remediation and Pollution Control Division, Cincinnati, OH. Dr. Butler is responsible for providing technical input on sections of the report prepared for this project.

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

The PI is responsible for initiating contact with appropriate project participants as he deems 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 periodic meetings. The PI is responsible for tracking laboratory activities, ensuring that samples are received, working with the laboratories to address issues with sample analysis, and ensuring that data reports and raw data are received.

1.2 Problem Definition/Background

The retrospective case study in the Bakkan Shale will investigate the potential impacts, if any, caused by the loss of control (blow out) during the hydraulic fracturing on drinking water resources in Dunn County, near Killdeer, ND. The investigation will initially involve sampling ground water, which began on July 2011, from monitoring wells located on the pad and other wells in the area surrounding the well pad, Franchuk 44-20SWH, near Killdeer ND. This study will be conducted in conjunction with the North Dakota Industrial Commission, Oil and Gas Division (NDIC); North Dakota Department of Health, Division of Water Quality (NDDWQ); U.S. Environmental Protection Agency, Region VIII (EPA R8); Denbury Onshore, LCC (Denbury); Terracon Consultants (Terracon); and U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Ground Water and Ecological Restoration Division (GWERD). GWERD will be the lead organization for this case study.

Killdeer, North Dakota (ND) is located in Dunn County in West Central ND and has an estimated population of 1000 individuals. The area surrounding Killdeer is currently experiencing renewed oil and natural gas exploration using horizontal drilling technology and hydraulic fracturing is being employed to stimulate production in these wells. In September, 2010 an oil well (Franchuk 44-20SWH, operated by Denbury) (Figures 2 and 3) near Killdeer experienced an uncontrolled blow out during the fifth stage of a 23 stage fracturing operation when the seven inch intermediate casing burst. This resulted in the spilling of approximately 2000 barrels (84,000 gallons) of hydraulic fracturing fluids (See Table 1 for known constituents) and oil on to the surface. At this time it is suspected that hydraulic fracturing fluids and oil may have been released into the subsurface because the surface casing was compromised at 38.5 ft below land surface and there is still a question about whether the conductor casing was compromised at 60 ft below land surface. However, the fluids did spill onto the land surface. During the clean up process approximately 1007 (42,294 gallons) barrels of water and 125 barrels (5250 gallons) of oil were recovered. To date it is unknown if groundwater contamination occurred and what the extent of the groundwater contamination might have been. The Franchuk well is just outside the City of Killdeers Municipal Water Supply Wells, well head protection zone (~2.5 miles). In addition, there are several agricultural, domestic, municipal and supply wells in the vicinity of the Franchuk well (Figure 2).

The Killdeer Aquifer is underlying the site and is the source of drinking water for the City of Killdeer, several domestic wells and also serves to supply water for drilling operations in the area. In addition, an intermittent creek meanders along the sides of the well pad and is believed to be a potential source of recharge to the Killdeer Aquifer (Figure 3). The aquifer is overlain by till and clay.

Four groundwater monitoring wells (NDGW01- NDGW04) were installed by Terracon in September, 2010 to monitor for potential groundwater contamination in the Killdeer Aquifer. An additional five monitoring wells (NDGW05- NDGW09) were installed at the site in April, 2011. These wells were constructed using 2 in. diameter PVC and screening intervals are listed in Table 2 and shown in Figure 4.

The objectives of this case study are listed below.

Primary Objective: Evaluate if the Killdeer Aquifer was impacted by the blow out that occurred during hydraulic fracturing. (See Section 1.3)

> **Secondary Objective 1:** Determine the mechanism(s) of how the Killdeer Aquifer was impacted if there was an impact. (See Section 1.3)

Select domestic, municipal and monitoring wells as well as a North Dakota Water Commission well will be sampled with subsequent analyses to determine the nature of water contamination, if it exists. The wells selected for sampling are based on site investigation approved by the NDDWQ. GWERD water sampling began in July 2011.

Revision 1 of this QAPP provided updated information for the October 2011 sampling event. The Addendum to Revision 1 provided QA/QC information for the metals analysis by the Region 7 contract laboratory. Revision 2 of this QAPP incorporates the information from the Addendum as well as providing additional information about the uses and sources of secondary data. Additional information is also provided regarding the software and methods to be used in conducting data analysis. .

Multiple lines of evidence will be needed to arrive at conclusions concerning the sources of impacts to drinking water. Hydraulic fracturing chemicals and contaminants which can be mobilized from native geologic materials can have other sources (e.g., other industries and naturally present contaminants in shallow drinking water aquifers [e.g., As, U, Ba]). It will therefore be necessary to exclude other sources before assigning hydraulic fracturing operations responsibility for impacts to drinking water supplies. Some hydraulic fracturing chemicals are used in a host of different products and processes which could also find their way into drinking water supplies. Reactive transport models can be useful in supporting data from site assessments to support or refute conceptual models regarding exposure pathways and impacts. These same

models can also help in assessing uncertainties associated with conclusions regarding the source of impacts.

1.3 Project/Task Description

In order to accomplish the primary objective listed in section 1.2, the existing monitoring well network, domestic wells, municipal supply wells, and the supply wells will be sampled (Figures 1, 2, 3) and analyzed for the components of crude oil: Gasoline Range Organics (GRO), Diesel Range Organics (DRO), volatile organic compounds (VOC), semivolatile organic compounds (SVOC) and dissolved gases (methane, ethane, propane, butane). In addition, well samples will be analyzed for glycols, barium (Ba), and select hydraulic fracturing fluids components (potassium (K), alcohols, naphthalene, and boron (B)), potentially mobilized naturally occurring substances (arsenic (As), selenium (Se), strontium (Sr), and other trace metals), and changes in background water quality (DOC, DIC major anions and cations). Of these target analytes, those that are critical analytes supporting this primary objective are delineated in Table 3. A tiered approach will be applied to the use of the 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.

In order to address secondary objective 1, groundwater sampling will be needed. The target parameters listed in the primary objective will be needed to address this objective. Denbury and the State of North Dakota, prior to EPA involvement, had completed soil remediation efforts and installed a liner over the potentially impacted area. Because of this soil sampling will not be part of the investigation.

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

A proposed schedule for field activities is provided in Table 4.

1.4 Project Quality Objectives and Criteria

As part of this case study detailed site history (blow out event, hydrologic conditions and settings, Killdeer aquifer water quality data, monitoring well locations and construction (if available), background geology data, and data collected on the extent of contamination as well as agricultural and industrial activities in the area) will be collected. This data has been collected from the USGS and Terracon (on site contractor for Denbury Resources), NDIC and NDDWQ. The site history will be used to determine the background conditions at the site as well as the potential for other activities in the area to be a potential source of the impact to the Killdeer Aquifer. Natural sources of contaminants or other human activities could potentially create sample bias and effect the conclusions of the study.

The installed monitoring well network surrounding the Franchuk well should yield a representative data set that will address whether local contamination of the Killdeer aquifer occurred or if there is the potential for contamination in the future. To date EPA has received limited information on the hydrologic conditions near the well pad. We are currently relying on a monitoring well network installed by Denbury on site contractor, Terracon, and the NDIC and NDDWQ to adequately detect impacts near the well pad. During the initial and subsequent sampling events water level measurements will be taken and groundwater flow directions will be determined using standard techniques (Domenico and Schwartz, 1990).

Other project quality objectives, such as precision, accuracy, sensitivity, and etc. will be discussed primarily in sections 2, 3, and 4. SOPs are internal working documents that are not typically made publically available. The majority of these, however, have been made publically available on the Region 8 web site for a separate research effort:

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

1.5 Special Training/Certification

A current HAZWOPER certification is required for on-site work. HAZWOPER training and yearly refresher training is provided to GWERD personnel at an appropriate training facility chosen by GWERD SHEMP (Safety, Health, and Environmental Management Program) manager. The HAZWOPER 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 in the fields of analyses to be conducted, prior to performing such analyses. Competency may be demonstrated through documentation of certification/accreditation (where this is available for the type of analysis) or some other means as determined to be acceptable by project participants. This could include quality documentation, such as laboratory manuals, Quality Management Plans, and detailed SOPs. Information about the Agency's policy on assuring laboratory competency can be found at: http://www.epa.gov/fem/lab_comp.htm. The EPA GP laboratory and the Shaw laboratories, the 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 laboratory assessments and performance evaluation (PE) samples.

The USEPA 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) accreditation process through the state of Texas.

The Region III Laboratory will be used to analyze glycols, which is not identified as critical at this time. However, it is accredited under the NELAP through the state of New Jersey as the Accrediting Body. The particular method being used by Region III for these analyses 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. Therefore, initial data reported from the glycol analysis will be flagged as "screening" data from a method that is currently being developed. Once the data is validated, it will no longer be flagged as "screening" data. USGS laboratory will not provide data for critical analytes. The Region VII contract laboratory (subcontractor to ARDL, Inc.) will be used to analyze for metals. The laboratory must be accredited by NELAP for these parameters.

The ORD/NERL lab will be used to analyze acrylamide, alkylphenols, ethoxylated alcohols, ethoxylated alkylphenols, and gylcols (if the Region III Laboratory cannot receive samples). These are not identified as critical at this time. However, initial data reported for these compound analyses will be flagged as "screening" data from a method that is currently being developed. Once the data is validated, it will no longer be flagged as "screening" data.

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 the PI. Raw data for sub-contracted 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 as needed. All information needed to confirm final reported data will be included.

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

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

2.0 Data Generation and Acquisition

2.1 Sampling Process Design (Experimental Design)

First sampling event was in July 2011. The QAPP will be revised as needed to reflect changes in project. Once the revised QAPP is approved it will be posted to the EPA Hydraulic Fracturing Web Page.

2.1.1 Background Hydrological Information

The Killdeer aquifer (Figure 5) occupies an area of about 74 mi^2 (190 km^2) in Dunn County (Figure 5A). It extends southward to the Stark County line in the southeast corner. From this point the aquifer extends east along the northern edge of Stark County. The tributary channels extending northward from the Stark County are hydraulically connected to the aquifer in Stark County and are therefore considered to be part of the Killdeer aquifer (Klausing, 1979).

This aquifer composition is predominantly fine to medium sand. However several test holes indicate fine to coarse gravel near the base (Klausing, 1979). The maximum thickness is 233 ft (71 m) and the mean thickness of the aquifer is 80 ft (24 m) (Klausing, 1979). A geologic cross section of the aquifer near the Franchuk well is shown in Figure 5B. The aquifer is generally overlain by clay and silt soils (Klausing, 1979).

Klausing (1979) provides hydrologic data for the Killdeer aquifer. The transmissivity was determined to be approximately 10,000 $ft^2\ d^{-1}$ (929 $m^2\ d^{-1}$) and a storage coefficient of 0.02. Depending on the aquifer thickness and hydraulic conductivity the aquifer yield was estimated to range from 50 to 1000 gal min^{-1} (11 to 3785 L min^{-1}). The aquifer is recharged by infiltration of precipitation and discharged naturally by base flow into Spring Creek, Knife River and by evapotranspiration. Water levels in the aquifer range from about 0 .3 feet (0 .09 m) above lsd to about 37 ft (11 m) below lsd. Seasonal fluctuations range from about 1 ft (0.3 m) to a maximum of about 7 ft (2 m). The minimum seasonal fluctuations occur in a confined part of the aquifer, whereas the maximum fluctuations occur in an unconfined part. Klausing (1979) estimated that the water potentially available in storage of the Killdeer aquifer is 568,000 acre-ft.

Klausing (1979) also reported on the water quality of the Killdeer aquifer (Table 5). In general the water is very hard and either a $NaHCO_3$ or $NaSO_4$ type water. In general the northern portion of the aquifer is of better quality than that of the south. The TDS in the northern portion rarely exceeds 1100 mg L^{-1}, but in the southern portion of the aquifer TDS commonly exceeds 2000 mg L^{-1}.

2.1.2 Installation of Monitoring Wells

Terracon (contractor for the well operator, Denbury Resources) was contracted for the installation of monitoring wells (Figure 4). The physical characteristics of the monitoring wells are provided in Table 2. According to the information provided by Terracon to the NDDWQ the

groundwater flow direction is to the southwest and has relatively uniform gradient of 0.0009 ft ft^{-1} to 0.0008 ft ft^{-1}. Although the ground water flow direction and gradient could vary seasonally due to precipitation and water usage. The North Dakota State water commission stated that the ground water flow within the Killdeer aquifer is <1 ft day^{-1}.

The monitoring wells were constructed using 2 inch PVC casing and slotted PVC screens. The screen intervals in the monitoring wells were based on information generated as part of Terracon's investigatory activities of the groundwater and the damaged well casing. The annular space between the borehole wall and the well screen was backfilled with 10-20 silica sand, usually to two feet above and below the screened interval. The remaining annular space above the sand pack was sealed with bentonite. The wells are then completed at the surface by concreting a stick up protective monitoring well cover at NDGW07, NDGW08 and NDGW09 and using flush mounted covers at the surface between the bentonite backfill and concrete cap. The designated measuring point and elevation datum at each monitoring well is defined as the ground surface immediately adjacent to the surficial concrete seal to the north and the top of the PVC well casing on the north side. These points will be surveyed by Terracon in the horizontal and vertical positions of the monitoring wells at some point (Information provided by Terracon to the NDDWQ).

The installed wells were developed by Terracon and the procedure used is not known. Once the wells were developed the monitoring wells were fitted with dedicated bladder pumps.

2.1.3 Ground-Water Monitoring

The ground-water sampling component of this project is intended to provide a survey of water quality in the area of investigation. GWERD, EPA R8, and NDIC, NDDWQ will survey the existing data and potentially speak to landowners near the Franchuk well to determine if ground water wells in the area could be sampled for the study if additional groundwater sampling locations are needed. These monitoring wells will be made available to GWERD for sampling and sampling by the NDIC and NDDWQ. Monitoring wells were installed in locations where contamination is suspected based on data collected by NDIC and Terracon immediately after the spill and considering the hydrogeologic conditions at the site. In addition to the nine monitoring wells, three domestic wells, and four water supply wells used for drilling activities in the area will be sampled along with the City of Killdeers Municipal Supply wells. The locations of the domestic wells and water supply wells are shown in Figure 2. The domestic well(s), near the Franchuk location will be sampled via homeowner taps. It is believed that most domestic wells are screened in the Killdeer Aquifer between 30 and 200 ft below ground surface. Similarly, the water supply wells will be sampled similar to the domestic wells and are shown in Figure 2. The City of Killdeers Municipal wells are located within the City of Killdeer and are screened in the Killdeer aquifer (Figure 2). It is anticipated that the monitoring wells will be sampled over a period of about two years (Table 4). The spacing of the ground-water sampling events will in part depend on weather conditions and also on when site access can be obtained but is will start in July 2011 and continue through October 2012. The minimum number of sampling events to

determine if an impact to the Killdeer aquifer happened is estimated to be three sampling events. The study area and locations of monitoring wells are illustrated in Figures 2, 3 and 4.

2.2 Sampling Methods

2.2.1 Ground-Water Sampling

Dedicated bladder pumps have been installed in the monitoring wells and will be used to sample water from these wells. The pump intake location within the screened interval is unknown at this time. Domestic wells, supply wells and municipal wells have dedicated pumps believed to be within the screened interval of the well and again this information is unknown at this time. This information will be collected in future as part of the ongoing site history investigation.

2.2.1.1 Monitoring wells

The following methodology will be used for sampling the monitoring wells (See Figure 6).

A comprehensive list of SOPs is provided in Table 8. SOPs are internal working documents that are not typically made publically available. The majority of these, however, have been made publically available on the Region 8 web site for a separate research effort: ftp://ftp.epa.gov/r8/pavilliondocs/LabSOPsAndLabProducedReports/AnalyticalMethodologyUsed-RobertSKerrLaboratory/

1) Water level measurements will be taken prior to pumping wells. The water level measurements will follow the RSKSOP-326 standard operating procedure. Water levels will be recorded in the field notebook or purge log (Figure 7) prior to sampling.

2) The dedicated piece of tubing will be connected to the sampling port of the well and the dedicated pump will be powered on. It is expected that the pump will yield a minimum initial flow rate of approximately 1 L min^{-1}). This flow will pass through a flow cell equipped with an YSI 5600 multiparameter probe (or equivalent probes). The rate of pumping will be determined by measuring the water volume collected after approximately 60 seconds into a 4 L graduated cylinder; the desirable pumping rate through the flow cell should be less than 2 L min^{-1}. The pumping rate will ideally maintain minimal drawdown. Water levels will be taken following sampling to confirm the drawdown caused by pumping.

3) The YSI probe (or equivalent probes and electrodes) will be used to track the stabilization of pH, oxidation-reduction potential (ORP), specific conductance (SC), dissolved oxygen (DO), and temperature. In general, the guidelines in Table 6 will be used to determine when parameters have stabilized. These criteria are initial guidelines; professional

judgment in the field will be used to determine on a well-by-well basis when stabilization occurs.

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

5) 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 as follows:

   a. Duplicate 40 mL VOA vials (amber glass) will be collected, without headspace, for VOC analysis using RSKSOP-299v1. Tribasic Sodium Phosphate (TSP) will be added to the VOA vial prior to shipping to the field for sampling 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., ethane, methane, butane, propane). The bottles will contain trisodium phosphate as a preservative and will be filled with no head space and sealed with a crimp cap. The samples will be stored and shipped on ice to Shaw, NRMRL-Ada's on-site contractor for analysis.

   c. Duplicate 1 L amber glass bottles will be collected for semi-volatile organic compounds. These samples will be stored and shipped on ice to EPA Region VIII Laboratory for analysis.

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

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

   f. 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 or ORD/NERL lab located in Las Vegas, Nevada.

   g. Duplicate 40 mL glass VOA vials will be collected for low molecular weight acids using RSKSOP-112v6. 1 M NaOH will be added to the VOA vial prior to shipping to the field for sampling as a preservative. The samples will be stored and shipped on ice to Shaw, NRMRL-Ada's on-site contractor for GC-MS analysis.

h. Two 1 L (amber glass) bottles will be collected for the analysis of ethoxylated alcohols, alkylphenol ethoxylates, and alkylphenols. These samples will be sent to the ORD/NERL lab located in Las Vegas, Nevada. The samples will be stored and shipped on ice.

i. Two 1 L (amber glass) bottles will be collected for the analysis of acrylamide. These samples will be sent to the ORD/NERL lab located in Las Vegas, Nevada. The samples will be stored and shipped on ice.

j. A1 L plastic bottle for metals analysis will be filled for unfiltered for the analysis of total metals concentrations. Analysis of these samples will be by ICP-OES (EPA Method 200.7) for Ag, B, Ba, Be, Ca, Co, Fe, K, Li, Mg, Mn, Na, P, Si, Sr, Ti, and Zn; by ICP-MS (EPA Method 6020A) for Al, As, Cd, Cr, Cu, Mo, Ni, Pb, Sb, Se, Sr, Th, Tl, U, and V; and Hg using cold vapor method (EPA Method 7470A). These samples will be preserved using concentrated HNO_3 to a pH < 2 (pH test strips will be used as spot checks on samples to confirm that the sample pH is <2). The samples will be stored and shipped on ice to a lab designated under the EPA Region 7 contract with ARDL, Inc.. The total metal samples will be Digested in accordance to the method outlined in EPA Method 200.7.

k. A 1-liter plastic beaker or glass jar will be filled for selected analyses to be conducted in the field. Field measurements will consist of turbidity, alkalinity, ferrous iron, and dissolved sulfide (Table 7). Turbidity (Standard Method 180.1) will be measured using a HACH 2100Q portable turbidimeter (or equivalent instrument). Alkalinity will be measured by titrating ground water with 1.6N H_2SO_4 to the bromcresol green-methyl red endpoint using a HACH titrator (HACH method 8203, equivalent to Standard Method 2320B for alkalinity). Ferrous iron will be measured using the 1,10-phenanthroline colorimetric method (HACH 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).

6) After the unfiltered samples have been collected a high-capacity ground-water filter (0.45µm, Pall Corporation, or equivalent manufacturer) will be placed on the end of the pump tubing and filtered samples will be collected into pre-labeled sample bottles. First, approximately 100 mL of ground water will be filtered and sent to waste and next the following series of samples will be collected:

a. A1 L plastic bottle for metals analysis will be filled for filtered for dissolved metals concentrations. Analysis of these samples will be by ICP-OES (EPA Method 200.7) for Ag, B, Ba, Be, Ca, Co, Fe, K, Li, Mg, Mn, Na, P, Si, Sr, Ti, and Zn; by

ICP-MS (EPA Method 6020A) for Al, As, Cd, Cr, Cu, Mo, Ni, Pb, Sb, Se, Sr, Th, Tl, U, and V; and Hg using cold vapor method (EPA Method 7470A). These samples will be preserved using concentrated HNO_3 to a pH < 2 (pH test strips will be used as spot checks on samples to confirm that the sample pH is <2). The samples will be stored and shipped on ice to a lab designated under the EPA Region 7 contract with ARDL, Inc.

b. One 60 mL clear plastic bottle for CE (capillary electrophoresis) sulfate, chloride, bromide and fluoride also filtered using RSKSOP-276v3 and RSKSOP-288v3 for Br in high Cl matrix. No preservative will be added. The samples will be stored and shipped on ice to the RSKERC general parameters lab.

c. One 60 mL clear plastic bottle for iodide analysis also filtered will be collected and analyzed using RSKSOP-223v2. No preservative will be added. The samples will be stored and shipped on ice to the RSKERC general parameters lab.

d. One 60 mL clear plastic bottle for nitrate + nitrite and ammonium also filtered and analyzed using EPA Methods 350.1 and 353.1. This sample will be preserved with sulfuric acid (H_2SO_4), pH < 2 (pH test strips will be used as spot checks on samples to confirm that the sample pH is <2). The samples will be stored and shipped on ice to the RSKERC general parameters lab.

e. Duplicate 40 mL glass VOA vials will be collected for analysis of dissolved inorganic carbon (DIC) also filtered and analyzed using EPA Method 9060A. No preservative added will be added to these samples. The samples will be stored and shipped on ice to the RSKERC general parameters lab..

f. Duplicate 40 mL glass VOA vials will be collected for analysis of dissolved organic carbon (DOC) also filtered and analyzed using EPA Method 9060A. These samples will be preserved with phosphoric acid to pH<2. The samples will be stored and shipped on ice to the RSKERC general parameters lab.

g. A 20 mL glass VOA will be collected for analysis of $\delta^{18}O$ and $\delta^{2}H$ of water using cavity ring-down spectrometry using RSKSOP334v0. The sample will be stored and shipped on ice to Shaw, NRMRL-Ada's on-site contractor for analysis.

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

See Tables 8 and 9 for numbers of sample bottles needed for each sample type and field QC samples for ground and surface water sampling.

2.2.1.2 Domestic and municipal wells

The domestic wells and municipal supply wells have a dedicated pump and taps for sampling water from these wells is available (Figures 8 and 9). It should be noted that in all cases the samples will be obtained at a point upstream of any water treatment (e.g. water softners, etc.) which could alter water chemistry. At this time it is unknown to EPA well diameters, well depths, screen intervals, or pump flow rates. However, the QAPP will be updated when this information becomes available.

1. The tap will be turned on. The pump flow rate will be measured to determine if the flow will need to be adjusted. The flow will be regulated to < 2 L min^{-1} and a sample will be taken for the monitoring of field parameters. 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^{-1} and rest of the total flow will be pass through to waste. It is likely that the total flow will not be adjustable and will be measured as described previously. The pumping rate will ideally maintain minimal drawdown, but this may not be possible for these wells since they are designed for purposes other than sampling.

2. The well will be purged for 20 minutes prior to sample collection. After 20 minutes water will be collected for field parameter measurements and a series of unfiltered samples and filtered samples will be collected as in section 2.2.1.1 number 5.

See Tables 8 and 9 for numbers of sample bottles needed for each sample type and field QC samples for ground and surface water sampling.

2.2.1.3 Water supply wells

Water supply wells are designed for high flows to fill water trucks and the flow rates cannot be adjusted and there is no tap in which samples can be collected. Terracon has designed an insert with a tap that is placed between the well and the truck tank to collect samples from (Figure 10).

1. The sampling insert will be connected to the well and to the tanker.

2. The dedicated pump will be powered on. The total flow will not be adjustable and cannot be measured. The pumping rate is likely to cause drawdown, since they are designed for purposes other than sampling.

3. The water will be allowed to flow for one to two minutes to purge the lines of water that is present and the sample collection will be initiated.

4. A series of unfiltered samples and filtered samples will be collected as in section 2.2.1.1 number 5.

See Tables 8 and 9 for numbers of sample bottles needed for each sample type and field QC samples for ground and surface water sampling.

2.2.1.4 North Dakota Water Commission Wells

A portable bladder pumps (QED Sample Pro or equivalent) will be used to sample the one water commission well (Figure 11). The following methodology will be used for the water commission wells.

1) Water level measurements will be taken prior to pumping wells. The water level measurements will follow the RSKSOP-326 standard operating procedure. Water levels will be recorded in the field notebook prior to sampling.

2) The portable bladder pump will be lowered into the well and the pump intake location will be placed within the screened interval of the well. The tubing connected to the sampling port will be connected to the YSI flow cell. The pump will be powered on. It is expected that the pump will yield a maximum initial flow rate of approximately 50 mL min^{-1}. This flow will pass through a flow cell equipped with an YSI 5600 multiparameter probe (or equivalent probes). The rate of pumping will be determined by measuring the water volume collected after 500 mL of water has been pumped into a 4 L graduated cylinder and the time it takes will be recorded. The pumping rate will ideally maintain minimal drawdown. Water levels will be taken following sampling to confirm the drawdown caused by pumping.

3) The YSI probe (or equivalent probes and electrodes) will be used to track the stabilization of pH, oxidation-reduction potential (ORP), specific conductance (SC), dissolved oxygen (DO), and temperature. In general, the guidelines in Table 6 will be used to determine when parameters have stabilized. These criteria are initial guidelines; professional judgment in the field will be used to determine on a well-by-well basis when stabilization occurs.

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

5) After the values for pH, ORP, SC, DO, and temperature have been recorded, the flow cell will be disconnected. A series of unfiltered samples and filtered samples will be collected as in section 2.2.1.1 number 5.

See Tables 8 and 9 for numbers of sample bottles needed for each sample type and field QC samples for ground and surface water sampling.

2.2.2 Slug Testing

Slug tests will be used to estimate the transmissivity and saturated hydraulic conductivity of the Killdeer aquifer in monitoring wells located on the well pad. The methology for performing slug test will follow RSKSOP-260v1.

2.2.2.1 Slug Test Procedure

1. When tests will be performed in multiple wells using the same slugs and transducers, test wells from least contaminated to most contaminated, if possible.

2. Develop the well or monitoring point, if it has not been adequately developed. Appropriate well development techniques are dependent on factors such as well construction, installation method, and geologic properties of the screened materials. Techniques are discussed in Aller *et al.* (1991), ASTM (1999a), Driscoll (1986), and Geoprobe Systems (2002). If the well or monitoring point is re-developed, record the development techniques that are used in the field notebook and wait at least 24 hours after development before performing slug tests.

3. Measure the depth to water in the well with respect to an established measurement point (*e.g.*, top of casing) and record the value in the field notebook (see RSKSOP-326).

4. Measure the total depth of the well using a weighted steel tape or equivalent tool, if value is not available from construction log or other installation information.

5. Measure and record the height of the top of the well casing above land surface.

6. Measure and record inside diameter of well.

7. Connect the transducer to the data logger.

8. Measure the length of the slug to 0.1 ft and the diameter to 0.01 ft. Calculate the volume of the slug using the equation in Section 2.2.2.2, Step 1. Record the slug length, diameter, and volume in the field notebook.

9. Referring to the instruction manual as needed, program the data logger for data acquisition using an acquisition rate that will obtain sufficient data to determine the important features of the recovery curve(s), such as oscillations and breaks in slope. Geologic formations with high hydraulic conductivity will require faster acquisition rates than formations with lower conductivity. In general, an acquisition rate of approximately two readings per second should provide sufficient data for analyses in formations with hydraulic conductivity less than approximately 0.02 cm/s. Lower acquisition rates, such as one reading per second or less, may be appropriate in formations with hydraulic conductivity less than approximately 0.001 cm/s and result in smaller data files without loss of interpretive power.

10. Insert the pressure transducer into the well or monitoring point and lower it to a depth such that the top of the transducer is approximately 1 ft deeper than the depth to ground water plus the length of the slug measured in Step 8 but the bottom of the transducer is not touching the bottom of the well, is above any accumulated sediments, and is within the pressure range of the transducer. Secure the transducer cable to the well head or other fixed structure to prevent movement of the transducer during the test.

11. Using the water level indicator, measure and record the depth to water in the well or monitoring point and the time the measurement was obtained. If the difference between this measurement and the depth to water measured in Step 3 is greater than 0.1 ft, periodically (*e.g.*, every 5 min) measure and record the depth to water until it returns to static conditions along with the time each measurement was obtained.

12. Start the data logger.

13. Initiate the falling head slug test as rapidly as possible by smoothly lowering the slug to a depth such that the top of the slug is below the depth to water in the well or monitoring point.

14. Continue data collection using the data logger until recovery of the water level to static conditions is at least 90% complete.

15. Initiate the rising head slug test as rapidly as possible by smoothly removing the slug from the well or monitoring point.

16. Continue data collection using the data logger until recovery of the water level to static conditions is at least 90% complete.

17. Stop the data logger. Download the data from the data logger using the computer and the software supplied by the manufacturer of the data logger. Save the data file on the computer and record the file name in the field notebook.

18. Select another slug of approximately twice the volume of the slug selected in Step 8.

19. Measure the length of the slug to 0.1 ft and the diameter to 0.01 ft. Calculate the volume of the slug using the equation in Section 2.2.2.2, Step 1. Record the slug length, diameter, and volume in the field notebook.

20. Referring to the instruction manual as needed, program the data logger for data acquisition using the same acquisition rate as used in Step 9.

21. Repeat Steps 12 through 17.

22. At contaminated sites, decontaminate all equipment that contacts contaminated materials (*e.g.*, pressure transducer, cable, and slugs) between use at different wells or monitoring points and at the conclusion of testing using a procedure consistent with site-specific documents such as the QAPP and health and safety plan.

23. Backup all electronic data files on suitable media (*e.g.*, flash drive, portable hard drive, compact disk).

2.2.2.2 Slug Test Calculations

Calculate the volume of the cylindrical slug using the following equation:

Slug volume (ft^3) = Slug length (ft) × (Slug diameter (ft) / 2)^2 × 3.14159

2.3 Sample Handling and Custody

2.3.1 Water Sample Labeling

Samples collected from each well will include the unique label, the date, the initials of the sampler, and designation of the sample type, e.g., "metals" and preservation technique (when applicable). This information will be recorded onto labeling tape, using water-insoluble ink, affixed to each sample bottle. Samples will be labeled as follows. Ground water samples will be labeled NDGWxx-mmyyyy. The xx will move in sequence (i.e., 01, 02, etc.). The mmyyyy will record the month and year (i.e., 072011 for July 2011). If the same points are sampled in subsequent trips, the number designation will remain the same (linked to the site), but the date and month will change accordingly. Duplicate samples will be marked by dup following the label above. Equipment blanks will be labeled Equipment Blank XX-mmyyyy, where xx will move in sequence and the mmyyyy will record the month and year. Similarly, Field and Trip Blanks will use the same system, but the Equipment Blank will be replaced with Field Blank or Trip Blank depending on the type of blank to be collected.

2.3.2 Water Sample Packing, Shipping, and Receipt at Laboratories

Samples collected from each location will placed together in a sealed Ziploc plastic bag. The bags will be placed on ice in coolers. Glass bottles will be packed with bubble wrap to prevent breakage. The coolers will be sent via Fedex or UPS, overnight, to the appropriate lab with chain of custody forms (see Figure 12**)** and custody seal.

R.S. Kerr Environmental Research Center
919 Kerr Research Drive
Ada, OK 74820
580-436-8568 or 580-436-8507
ATTN: Tiffany Thompson or Trina Perry
(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 the temperature blank is > 6^{o} C. These samples will be flagged accordingly.

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

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

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

US Environmental Protection Agency - Region 3, OASQA
701 Mapes Rd.
Fort Meade, MD 20755-5350
410-305-3032
ATTN: Kevin Martin

Samples for Sr isotope analysis will be sent to:

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

For samples shipped to ORD/NERL lab located in Las Vegas, Nevada

Patrick DeArmond
944 East Harmon Avenue
Las Vegas, NV 89119
1-702-798-2102

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

Samples to be shipped to the EPA Region 7 contract with ARDL, Inc. will be overnight via UPS or Fedex, to the contract laboratory awarded the work, with appropriate chain of custody forms (see Figure 12) and the cooler will be sealed with custody seals. Sample receipt and log-in will be conducted per the contract labs SOPs.

2.4 Analytical Methods

2.4.1 Ground Water

Ground-water samples will be collected and analyzed using RSKERC standard operating procedures (RSKSOPs, the majority of these SOPs can be found at ftp://ftp.epa.gov/r8/pavilliondocs/LabSOPsAndLabProducedReports/AnalyticalMethodologyUsed-RobertSKerrLaboratory/) at RSKERC and EPA Methods at the Region VIII laboratory (Table 10).

Region III's LC-MS-MS method for glycols is under development with the intent to eventually have a validated, documented method. The samples are analyzed according to Region III's OASQA (Office of Analytical Services and Quality Assurance) "On Demand" Procedures. See the Region III Laboratory QA Manual, Section 13.1.4.2, *Procedure for Demonstration of Capability for "On-Demand" Data* (Metzger et al., 2011). Aqueous samples are injected directly on the HPLC after tuning MS/MS with authentic standards (2-butoxyethanol, di-, tri-, and tetraethylene glycols) and development of the HPLC gradient. HPLC column is Waters (Milford MA) Atlantis dC18 3um, 2.1 x 150mm column (p/n 186001299). HPLC gradient is with H_2O and CH_3CN with 0.1% formic acid. The 3 glycols are run on a separate gradient than the 2-butoxyethanol. All details of instrument conditions will be included in 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 (IC). The working, linear range varies for each compound but is about 10-100 $\mu g\ L^{-1}$ and may change with further development. Initial

Calibration (IC) is performed before each day's sample set, calibration verification is done at the beginning, after every 10 sample injections, and at the end of a sample set. The correlation coefficient (r^2) of the calibration curve must be $\geq$0.99. An instrument blank is also run after every 10 sample injections. The performance criteria are provided in Table 10. The system is tuned with individual authentic standards (at 1mg L^{-1} concentration) of each compound according to the manufacturer's directions using the Waters Empower "Intellistart" tune/method development program in the MRM (multiple reaction monitoring) ESI+ (electrospray positive) mode. Tune data is included in the case file. Target masses, transition data and voltages determined in each tune for each compound are compiled into one instrument method. Only one MS tune file (which determines gas flow rates and source temperatures) may be used during a sample set. For these samples, the tetraethylene glycol tune is used as it provides adequate response for all targets. Due to differences in optimal chromatographic separation, the three glycols are analyzed in one run and 2-butoxyethanol is analyzed separately. Exact mass calibration of the instrument is done annually with the preventive maintenance procedure. Mass calibration was successfully performed according to manufacturer's specifications with NaCsI on 6/17/2010 by a certified Waters Corp Service technician. 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.

Analysis at RSKERC includes capillary electrophoresis (CE, for anions), flow injection analysis (FIA) for N-series), FIA for iodide, carbon analysis using combustion and infrared detection, gas chromatography (GC, for dissolved gas analysis), and cavity ring-down spectrometry (for $\delta^{18}O$ and $\delta^{2}H$ of water). Analysis by the EPA Region VIII laboratory includes GC for GRO, DRO, and GC-MS for semivolatiles with appropriate sample preparation and introduction techniques. These analytical methods are presented in Table 8

The RSKSOPs and their associated target analyte list are presented in Table 11. 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 semivolatiles the target analyte list is presented in Table 12. Surrogates used include phenol-d6, 2-fluorophenol, 2,4,6-tribromophenol, nitrobenzene-d5, 2-fluorobiphenyl, and p-terphenyl-d14. The concentrations used for the surrogates shall be spiked at 5 $\mu g\ mL^{-1}$. For samples containing components not associated with the calibration standards, non-target peaks will be reported as tentatively identified compounds (TICs) based on a library search. Only after visual comparison of sample spectra with the nearest library search results will tentative identifications be made. Guidelines for making tentative identification are:

- A peak must have an area at least 10% as large as the area of the nearest internal standard.
- Major ions in the reference spectrum (ions > 10% of the most abundant ion) should be present in the sample spectrum.

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

Commercial standards for DRO calibration is locally procured DF #2 (source: Texaco station).. Surrogates used in DRO include o-terphenyl at spiking concentrations of 10 $\mu g\ L^{-1}$.

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 $\mu g\ L^{-1}$.

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).

Samples analyzed for ethoxylated alcohols, alkylphenols, and acrylamides will be analyzed by the ORD/NERL-Las Vegas laboratory using a method in development as follows. Water samples are extracted using an automated Autotrace SPE workstation. The ethoxylated alcohols, alkylphenols, and alkylphenol ethoxylates are extracted using Waters Oasis HLB SPE cartridges (6cc, 200 mg), however, any polystyrene-divinylbenzene SPE cartridge that has been demonstrated to show sufficient recovery can be used. Additionally, acrylamide is extracted using activated carbon (500 mg) cartridges from Biotage. Because highly polar acrylamide is not retained by HLB cartridges, the flowthrough from the HLB cartridge sample loading is collected for the acrylamide extraction, which is subsequently extracted using activated carbon cartridges. The HLB extraction method begins by conditioning the SPE cartridges with 5 mL MeOH, followed by 5 mL H2O. Next, 500 mL sample is loaded onto the cartridges. The volumetric flasks that contained the samples are then rinsed with 50 mL water, which is also loaded onto the cartridges. The SPE cartridges are rinsed with 2 mL water, and then they are dried for 30 min with N2. The analytes are eluted off the cartridge by eluting 2 times with 3 mL of 2:2:1 MeOH/acetone/ethyl acetate, containing 0.1% formic acid. This eluate should contain the ethoxylated alcohols, alkylphenols, and alkylphenol ethoxylates, and it is concentrated to 0.5 mL using a TurboVap Concentrator. After concentration, samples may be filtered using 0.2 micron syringe filters. The flowthrough that was collected during sample loading of the HLB SPE is then extracted for acrylamide using activated carbon. The activated carbon SPE cartridge is first

conditioned with 8 mL MeOH and then 8 mL H2O. The samples are then loaded onto the cartridges. The volumetric flasks that contained the samples are then rinsed with 50 mL water, which is also loaded onto the cartridges. The SPE cartridges are rinsed with 2 mL water, and then they are dried for 30 min with N2. The analytes are eluted off the cartridge by eluting with 10 mL of MeOH. The eluates are concentrated with a TurboVap Concentrator. The extracted samples are then analyzed by LC-MS. Positive ionization mode is used for the ethoxylated alcohols, alkyphenol ethoxylates, and acrylamide. Negative ionization mode is used for the alkylphenols. Full scan mode is used for the ethoxylated alcohols, alkylphenols and alkylphenol ethoxylates. Multiple reaction monitoring MS/MS is used for the acrylamide. QC criteria for analysis conduct at the ORD/NERL lab are given in Table 13.

The samples analyzed the Region 7 contract with ARDL, Inc. include metals by Inductively Coupled Plasma – Mass Spectrometry (ICP-MS), Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES) mercury by cold vapor AAS and volatile organic compounds (VOCs) by purge and trap-GC/MS. The contract laboratory will analyze water samples for Al, As, Cd, Cr, Cu, Mo, Ni, Pb, Sb, Se, Sr, Th, Tl, U, and V by ICP-MS. In addition, the contract laboratory analyze water samples for Ag, B, Ba, Be, Ca, Co, Fe, K, Li, Mg, Mn, Mo, Na, P, Sb, Si, Sr, Ti, and Zn by ICP-OES. The contract laboratory performed the analysis in accordance with the EPA Methods 6020A for ICP-MS and 200.7 for ICP-OES. Both total and dissolved metals were analyzed. Sample digestion for total metals was done according to EPA Method 200.7. Samples for dissolved metals were not digested. Samples collected for mercury and volatile organic compounds in accordance with EPA Methods 7470A and EPA Method 8260B, respectively. For the metals and VOCs the target analyte lists are presented in Tables 14 and 15.

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 16. 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:

(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 semivolatiles are as provided in Table 12. The DL and RL for DRO and GRO are both at 20 µg/L.

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

(6) See Table 17 for QC types and performance criteria.

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

For analyses done by the Region III laboratory, QA/QC requirements are:

(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 ppb (Table 18).

(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) See Table 10 for QC types and performance criteria.

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

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

For analyses done by USGS, QA/QC requirements are (Table 19):

(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 19 for QC types and performance criteria

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

For analyses done by Region 7 contract with ARDL, Inc., QA/QC requirements are:

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

2. Data verification shall be performed by the contract laboratory to ensure data meets their SOW requirements.

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

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

3. Complete data package shall be provided electronically by 2:00pm CST on the 21st day after receipt of the last sample for a given sampling event. (NOTE: If the due date falls on a Holiday, Saturday or Sunday, then the deliverables are due to EPA by 12:00pm on the first subsequent business day). Electronic deliverables shall include all analytical results (field and laboratory QC samples) and the associated narrative. In addition to the normal narrative and Excel spreadsheet required, the laboratory shall provide an electronic "CLP type" data package that includes the written narrative, Forms 1's, QC data, & all supporting raw data. The package shall be organized and paginated. The entire data package shall be provided in a .pdf file format. The complete data package in .pdf format shall be provided within 48 hours of the electronic results and narrative. The associated narrative shall address each of the applicable areas listed below for every parameter group in the task order. This includes a statement that the QA/QC criteria for every applicable area were in control or, conversely, that one or more QC outliers were present. For areas with outliers, the narrative shall specify each parameter which was out of control and the associated samples that were affected. In addition, the narrative shall indicate any and all corrective actions taken and the results of those actions as well as impact on the associated samples. (Holding Times, Initial Calibration, Continuing Calibration, Surrogates, Internal Standards, Laboratory Duplicate, Matrix Spike/Matrix Spike Duplicate, Laboratory Control Sample, and Method Blanks).

Contract required quantitation limits (CRQL) for the metals are as provided in Table 14. See Tables 20, 21, and 22 for QC types and performance criteria.

Corrective Actions: If any samples are affected by failure of a QC sample to meet its performance criteria, the problem shall be corrected and the data will be qualified with a determination as to impact on the sample data. Failures and resulting corrective actions shall be reported.

For analyses done by ORD/NERL, QA/QC requirements are (Table 13):

(1) Data verification shall be performed by ORD/NERL 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 13 for QC types and performance criteria

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

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. At the discretion of the PI, discrepancies in 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 11. Any updates to these detection limits will be provided in their data reports. Detection limits for the analyses done by Region VIII and III and Region 7 contract with ARDL, Inc are discussed in Section 2.5.1. They are adequate for project objectives. 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.

2.5.4 QA/QC Calculations

% Recovery or Accuracy

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

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

Precision

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

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

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

Matrix Spike Recovery

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

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

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 (the majority of the RSKSOPs can be found online at ftp://ftp.epa.gov/r8/pavilliondocs/LabSOPsAndLabProducedReports/AnalyticalMethodologyUsed-RobertSKerrLaboratory/) 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 Region VIII laboratory, these requirements are identified in their SOPs and in Tables 10 and 17. Since the information about SOPs is quite voluminous, it was elected to not present it in the QAPP. The majority of these are publically available on the Region 8 web site for a separate research effort: ftp://ftp.epa.gov/r8/pavilliondocs/LabSOPsAndLabProducedReports/AnalyticalMethodologyUsed-RobertSKerrLaboratory/

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 shall be traceable to NIST (Table 6), 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 each test meter will be checked that it is in good working order. Calibration data will be recorded in a bound waterproof notebook and personnel making entries will adhere to the GWERD Notebook policy. Calibration of instruments will be performed daily prior to initiation of sample collection and will be performed according to manufacturer's instructions and will be recorded in the field notebook. In addition calibration checks will be performed using known standards or buffers before use, 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 cell (RSKSOP-211v3, *Field Analytical QA/QC*).

Hach spectrophotometers (ferrous iron and sulfide) and turbidimeters (turbidity) will be inspected prior to going to the field and their function verified. These instruments are factory-calibrated and will be checked in the lab prior to going to the field per the manufacturer's instructions. For the Hach spectrophotometers this will consist of checking the accuracy and precision for that method. The ferrous iron accuracy will be checked by measuring a 1 mg Fe^{2+} L^{-1} standard and the results should be between 0.90 -1.10 mg Fe^{2+} L^{-1}. Similarly, the precision will be tested using the standard performing the measurement three times on this solution. The single operator standard deviation should be ± 0.017 mg Fe^{2+} L^{-1}. For sulfide method the precision will be checked using a 0.75 mg S^{-} L^{-1} standard solution and the standard deviation to be obtained is ± 0.02 mg S^{-} L^{-1}. Turbidity will be checked against turbidity standards supplied by Hach. In addition, blanks (deionized water) will be run at the beginning of the day, midday, and at the end of the day. The values for the blanks will be recorded in the field notebook and any problems associated will be recorded. If blanks have detectable concentrations of any

analyte the sample cells will be decontaminated and a new blank will the run. This process will continue until there is no detectable analytes in the blanks. Standards for redox sensitive species such as sulfide and ferrous iron are difficult to use in the field because once exposed to atmospheric oxygen there concentrations can change. Similarly calibration standards for alkalinity are sensitive to atmospheric carbon dioxide. 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 250 mg L^{-1} standard made from Na_2CO_3. The analyzed value should be in the range of 225- 275 mg L^{-1}. Duplicates will be performed once a day or on every tenth sample. Duplicates 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.

2.8 Inspection/Acceptance of Supplies and Consumables

RSKSOPs and Region VIII SOPs provide requirements for the supplies and consumables needed for each method. The analysts are responsible for verifying that they meet the SOP requirements. Other supplies that are critical to this project are listed in Table 17. It should be noted that the vendors listed in Table 24 are suggested vendor and equivalent parts may be available from other vendors or substitute for based on purchasing rules. The PI is responsible for ensuring these are available and to ensure they are those as listed previously.

2.9 Non-direct Measurements

The locations for the monitoring wells were determined by Terracon Consultants, Inc. the site contractor for Denbury Resources, Inc. Data was made available from the NDIC and NDDWQ.

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

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

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

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

The USGS and the North Dakota State Water Commission have published reports and databases for ground water data for the Killdeer Aquifer and surface water data in Dunn Co., ND. There is variability in the constituents contained in these databases. The USGS databases are the National Uranium Evaluation (NURE) database (USGS 2012), the National Water Information System (NWIS) data base (USGS, 2013) and the USGS Produced Water Database. Data from these databases may be used for assisting in the delineation of background water quality conditions at the study locations or in assisting with the understanding of the source of formation water and the produced water from the oil and gas activities in the area. The data will be assessed for duplication between the databases so that the duplicate data does not bias its intended use and the results of the study.

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

industrial complexes. Data that is removed from the analysis because of potential contamination will be acknowledged in any use of the data.

Data was made available in some cases from the individual homeowners. Homeowner data was used as background information for the PI to assist with project planning. Homeowner data could be used as part of the reporting process in delineating background water quality conditions. Other data sources such as data from published peer reviewed literature could also be used. The data quality issues will most likely be unknown for these types of data. However, since the data has gone through a peer review process, it could still be used. Data from homeowner's and peer reviewed sources will be evaluated in the same manner as described above.

2.10 Data Management

The PI is responsible for maintaining data files, including their security and integrity. All files (both electronic and hard copy) will be labeled such that it is evident that they are for the hydraulic fracturing project at Killdeer, ND. This will be done in accordance with the ORD PPM 13.2, *Paper Laboratory Records* as well as EPA Records Schedule 501, *Applied and Drected Scientific Research*. Finally, the Hydraulic Fracturing Quality Management Plan Rev. No. 1, Section 5, contains additional information on data management for Hydraulic Fracturing Research.

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

Data in electronic form shall be electronically transferred to the spreadsheets. Data will be spot-checked by the PI to ensure accuracy of the transfer. If errors are detected during 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.

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

2.10.1 Data Recording

Data collected during the ground-water investigation will be recorded into field notebooks and entered into 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 the compiling of all data and records.

2.10.3 Analysis of Data

All data collected associated with groundwater and surface water sampling will be summarized in EXCEL spreadsheets. Data will be spot-checked (10 % of samples) by the PI to ensure accuracy. If errors are detected during the spot-check, the entries will be corrected. Detection of an error will prompt a more extensive inspection of the data, which could lead to a 100% check of the data set being entered at that time if multiple errors are found. During the data verification/validation process an independent 100 % check of the data will be initiated. If errors are found they will be corrected and resubmitted to verify that the data corrections were made and the final data is error free.

When possible, data sets will be graphically displayed using Excel and/or Origin to reveal important trends. The AqQA program will be used for preparing water quality diagrams, such as Piper or Durov diagrams, to visualize multi-parameter data collected in this study, and for aiding in comparisons with secondary historical data. Statistical calculations, such as determinations of the mean, median, and standard deviation, and data population tests, such as analysis of variance and other non-parametric tests will be carried out using MS Excel or the SYSTAT software package. For this study, some of these calculations will be conducted by Ecology and Environment, Inc. through a contractual mechanism. For concentration data below the MDL, a value of ½ the MDL will be used. However, this approach should only be followed in cases where detections above the MDL are available for 50% or more of the concentration values in a data series to be used for calculating statistical parameters (USEPA, 2010). This guideline will be followed and any exceptions will be noted. Analysis of primary and secondary data will also be carried out using the Geochemist's Workbench software package. Geochemical calculations will be performed to estimate the saturation state of ground water and surface water with respect to naturally occurring minerals (e.g., calcite, gypsum). The software is analogous to other packages (e.g., MinteqA2 and Phreeq-C). Major ion data (e.g., Ca, Mg, Na, K, Cl, SO_4, HCO_3,

pH) and temperature are entered into a user interface. The software uses the Debye-Hückel equation to estimate ion activity coefficients and a selectable thermodynamic database in order to calculate mineral saturation indices for minerals that may be undersaturated, at equilibrium, or oversaturated in the prescribed system (Bethke, 1996). The Lawrence Livermore National Laboratory database (thermo.com.v8.r6) will be used for calculating aqueous speciation and mineral saturation. This software may also be used to construct activity-activity diagrams, such as Eh-pH diagrams. Such diagrams can be helpful in describing processes that impact the concentration of redox-sensitive elements, like iron and manganese.

3.0 Assessment and Oversight

3.1 Assessments and Response Actions

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

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

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

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

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

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

3.1.1 Assessments

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

Laboratory TSAs focussed on the critical target analytes (Table 1) and were conducted on-site at RSKERC (involved both EPA and Shaw-operated labs) on July 28, 2011 and at the Region VIII laboratory on July 26, 2011 which analyzes for semi-volatile organic, DRO and GRO analyses. The Laboratory TSA took place prior to the first sampling event in September 2011. Laboratory TSAs will not be repeated if they have been done previously for another case study and significant findings were not identified. A laboratory TSA was conducted November 27, 2012 on the Region VII contract laboratory (Southwest Research Institute, subcontractor to ARDL, Onc.).

ADQs will be conducted on a representative sample of data for the critical target analytes. These will be conducted on at least 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 analyze PE samples routinely on a quarterly basis. The Region VIII laboratory is currently analyzing Performance Evaluation (aka Proficiency Testing) samples twice a year and data from the past two studies have been provided to the QAM. Glycols analyzed by Region III are not critical, but even if they become critical, PE samples are not available commercially, so PEs will not be done by their laboratory for glycols. Strontium isotopes analyzed by the USGS laboratory are not critical and PE samples are not available commercially, therefore, PEs will not be done. The Region VII contract laboratory will analyze PE samples as this is required for NELAP-accredited laboratories.

3.1.2 Assessment Results

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

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

3.2 Reports to Management

All final audit reports shall be distributed as indicated in 3.1.2. Audit reports will be prepared by the QAM 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, 13, 16, 17, 20, 21, 22 and 23. In addition, sample preservation and holding times will be evaluated against requirements provided in Table 8.

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

4.2 Verification and Validation Methods

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

For the Region VIII laboratory, QA/QC requirements include data verification prior to reporting and detailed description can be found in the QSP-001-10 QA Manual (Burkhardt and Batschelet, 2010). Results are reported to the client electronically, unless requested otherwise. Electronic test results reported to the client include the following: Data release memo from the analysts, LQAO, 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. Verify that the calibration and instrument performance was checked by analyzing a

second source standard (SCV). (The concentration of the second source standard must be in the range of the calibration.) Results must be within the method, procedure, client or in-house limits. 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 the samples analyzed under the Region 7 contract with ARDL, Inc. metals and VOCs, initial data validation shall be conducted by the laboratory according to the SOW and documented in the laboratory report narrative. ARDL, Inc. shall perform a data assessment on the laboratory's hardcopy and electronic deliverable based on the requirements of the SOW and methods used.

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

For field measurements, the PI will verify the field data collected to ensure they meet requirements as defined in the QAPP. The USGS laboratory will verify their isotope data; these data are not considered critical.

Laboratory data reports are reviewed by the PI for completeness, correctness, and conformance with QAPP requirements. All sample results are verified by the PI to ensure they meet project requirements as defined in the QAPP and any data not meeting these requirements are appropriately qualified in the data summary prepared by the PI. See Table 23 for the Data Qualifiers. The Contract Laboratory Program guidelines on organic (USEPA, 2008) and inorganic (USEPA, 2010) methods data review 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 or Audit of Data Quality will be performed by a party independent of the data collection activity. Data validation activities may be performed by EPA QAMs or by a QA support contractor with oversight be the EPA QAM. Data summaries that have been prepared by the PI as well as laboratory reports and raw data shall be provided to the QAM, who will coordinate the data validation for the critical analytes. The data validation team shall evaluate data against the QAPP specifications. NRMRL SOP #LSAS-QA-02-0, "Performing Audits of Data Quality" will be used as a guide for conducting the data validation. The data validation team will review the information presented in the case narrative, review data, and ensure that appropriate project-specific data qualifiers were added to the data summary tables. The outputs from this process will include the validated data and the data validation report (ADQ report). The report will include a summary of any identified

deficiencies, and a discussion on each individual deficiency and any effect on data quality and recommended corrective action.

The PI will use the information from these data verification/validation activities to assist in determining what corrective actions are needed and make appropriate revisions to the data summary. Corrective actions may include the option to re-sample or re-analyze the affected samples. If corrective actions are not possible, the PI will document the impact in the final report such that it is transparent to the data users how the conclusions from the project are affected. After the data validation (ADQ) process is completed, QA staff or designees will perform transcription checks on 100% of the data in the data summary. Transcription check review comments will be provided to the PI and QA staff will verify that the PI's responses are acceptable. The data summary may then be QA approved by the QAM. Additional editorial reviews may be done, but will have no effect on the data.

4.3 Reconciliation with User Requirements

The PI shall analyze the data, as presented below. The PI shall use the results from the data verification and validation process to assess whether or not the data quality has met project requirements and thereby the user requirements. The PI, shall analyze the data, as presented below. The PI 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 may impact their use, the impact will be evaluated by the PI, with assistance from QA staff. If there are disagreements between the PI and GWERD QA staff relating to data usability, the issue will follow the dispute resolution process as described in the Hydraulic Fracturing Quality Management Plan

The types of statistical analyses that will be performed include summary statistics (mean, median, standard deviation, minimum, maximum, etc.) if applicable.

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 potentially 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 Wise County site showing well locations and concentrations of analytes.

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RSKSOP-152v3. Ground-Water Sampling. 5 p.

RSKSOP-175v5. Sample Preparation and Calculations for Dissolved Gas Analysis in Water Samples Using a GC Headspace Equilibration Technique. 33 p.

RSKSOP-179v2. Standard Operating Procedure for Total Nitric Acid Extractable Metals from Aqueous Samples by Microwave Digestion. 9 p.

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

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

RSKSOP-212v6. Standard Operating Procedure for Quantitative Analysis of Low Molecular Weight Acids in Aqueous Samples by HPLC. 22 p.

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

RSKSOP-214v5, Quality Control Procedures for General Parameters Analyses using the Lachat Flow Injection Analyses (FIA), 10 p.

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

RSKSOP-260v1. Standard Operating Procedure for Performance of Slug Tests in Saturated Porous Media Using Solid Slugs. 8p.

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

RSKSOP-275v1. Collection of Water Samples from Monitoring Wells. 10 p.

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

RSKSOP-288v3. Determination of Major Anions in the Presence of High Levels of Chloride and/or Sulfate in Aqueous Samples using Capillary Ion Electrophoresis. 13 p.

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

RSKSOP-299v1. Determination of Volatile Organic Compounds (Fuel Oxygenates, Aromatic and Chlorinated Hydrocarbons) in Water Using Automated Headspace Gas Chromatography/Mass Spectrometry (Agilent 6890/5973 Quadrupole GC/MS System). 25 p.

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.

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6.0 Tables

Table 1. Known constituents of the Hydraulic Fracturing Fluid Component use for the Franchuk well.

Active Ingredients	CAS Number	Chemical Formula
Glutaraldehyde	111-30-8	$C_5H_8O_2$
Alkyl dimethyl ethylbenzyl chloride (68% C12, 32% C14)	85409-23-0	
Alkyl dimethyl benzyl ammonium chloride (C12 -18)	68391-01-5	
Tert-Butyl Hydroperoxide	75-91-2	$C_4H_{10}O_2$
Acetic Acid	64-19-7	$C_2H_4O_2$
Potassium Hydroxide	1310-58-3	KOH
Potassium Carbonate	584-08-7	KC_2O_3
Ethoxylated nonyl phenol	9016-45-9	$C_{17}H_{28}O_2$
Sodium Tetraborate	1330-43-4	$Na_2B_4O_7$
Amine Phosphonate 1	Proprietary	
Methanol	67-56-1	CH_4O
Hydrochloric Acid	7647-01-0	HCl
Isopropyl Alcohol	67-63-0	C_3H_8O
2-Ethylhexanol	104-76-7	$C_8H_{18}O$
Diethylenetriamine	111-40-0	$C_4H_{13}N_3$
Heavy Aromatic Solvent Naphtha	64742-94-5	
Naphthalene	91-20-3	$C_{10}H_8$

Active Ingredients	CAS Number	Chemical Formula
Benzene, 1-1'-oxybis-, tetrapropylene derivatives, sulfonated	119345-03-8	
Diethylenetriamine Alkylbenzene Sulfate	40139-72-8	
Tetramethylammonium Chloride	75-57-0	$C_4H_{12}ClN$
2-Ethylhexanol	104-76-7	$C_8H_{18}O$
Acetic acid	64-19-7	$C_2H_4O_2$
Acrylamide	76-06-1	C_3H_5NO
Acrylamide sodium	38193-60-1	
Alcohols, C10-16, ethoxylated	68002-97-1	
Benzene, 1-1'-oxybis-,tetrapropylene derivitives, sulfonated	119345-03-8	$C_{36}H_{58}O_7S_2$
Boric Acid	1303-86-2	$B(OH)_3$
Canola Oil		
Colemanite	1318-33-8	$CaB_3O_4(OH)_3 \cdot H_2O$
dihexamethylenetriaminepentakis(methylene phosphonic acid) [aka - amine phosphonate]	119345-03-8	$(C_{17}H_{44}N_3O_{15}P_5)$
Disodium ethylenediaminetetraacetate	38011-25-5	$Na_2C_{10}H_{14}N_2O_8$
Dowicil 75	4080-31-3	$C_9H_{16}Cl_2N_4$
Emulsion Breaker	29316-47-0	
Emulsion Breaker	153795-76-7	
Emulsion Breaker	68036-95-3	
Emulsion Breaker	30704-64-4	
Ethoxylated sorbitan monostearate	9005-67-8	$C_{54}H_{106}O_{21}$
formaldehyde	50-00-0	CH_2O

Active Ingredients	CAS Number	Chemical Formula
Hydroxypropyl Guar	39421-75-5	
Mineral Oil	64742-46-7	
Organophilic Clay	68953-58-2	
Petroleum Distillate Blend	64741-84-1	
Phosphoric Acid	7664-38-2	H_3PO_4
Propylene Carbonate	108-32-7	$C_4H_6O_3$
Sodium Chloride	7647-14-5	NaCl
Sodium Glycolate	2836-32-0	$NaC_2H_3O_3$
Sodium hydroxide	1310-73-2	NaOH
Sorbitan monooleate	1338-43-8	$C_{24}H_{44}O_6$
Tetrasodium ethylenediaminetetraacetate	64-02-8	$Na_4C_{10}H_{12}N_2O_8$
triethanolamine hydrochloride	637-39-8	$C_6H_{15}O_3N$ HCl
Trisodium ethylenediaminetetraacetate	19019-43-3	$Na_3C_{10}H_{13}N_2O_8$
Trisodium nitrilotriacetate	5064-31-3	$Na_3C_6H_6NO_6$
Xanthan gum	various CAS #s listed	

Table 2 . The physical characteristics of the monitoring wells near the Franchuk 44-20SWH well (Data provided by NDIC and Terracon Consultants, Inc.)[*].

Well	Screen Interval (ft)	Screen Length (ft)	Total Depth (ft)
NDGW01	37- 47	10	47
NDGW02	37-47	10	47
NDGW03	27-42	15	42
NDGW04	32-72	40	72
NDGW05	30-45[†]	15[†]	45[†]
NDGW06	30-45[†]	15[†]	45
NDGW07	55-70[†]	15[†]	70[†]
NDGW08[‡]	80-120[†]	60[†]	120[†]
NDGW09[‡]	180-245[†]	65[†]	245[†]
NDGW10[**]	*	*	*
NDGW11[**]	90-110	20	110
NDGW12[**]	*	*	*
NDGW13[***]	90-175	85	180
NDGW14	*	*	*
NDGW15[§]	140-165	25	165
NDGW16[§]	85-125	40	125

[*] Only limited information for these well has been supplied to EPA at this time.
[†] Information provided by Terracon to the State of ND in a proposal. The exact depths, screen intervals and lengths need to be verified once the wells are surveyed in the Summer 2011.
[‡] Well cluster.
[**] Domestic well
[***] Water Supply well
[§] City of Killdeer municipal well

Table 3. Critical analytes.

Analyte[†]	Laboratory Performing the Analysis
Volatile Organic Compounds (VOC)*	Shaw Environmental
Semivolatile Organic Compounds (SVOC)	EPA Region VIII Laboratory
Dissolved Gases**	Shaw Environmental
Metals (As, Se, Sr, Ba, B)	EPA Region VII Contract Laboratory
Major Cations (Ca, Mg, Na, K)	EPA Region VII Contract Laboratory
Major Anions (Cl, NO_3^-+NO_2^-, SO_4^{2-})	RSKERC General Parameters Laboratory

*alcohols (isopropyl alcohol and t-butyl alcohol), naphthalene (using RSKSOP-299v1)
**methane, ethane, propane, butane
[†]DRO and GRO are no longer considered critical because these have not been detected in previous samplings. However, DRO and GRO will continue to be collected and analyzed.

Only those SVOC compounds in Table 12 that have DL, RL, and Control Limits listed may be used as critical analytes. Others only as screening data.

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

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

Table 4. Schedule of field activities for the Hydraulic Fracturing Case Study Bakken Shale, Killdeer and Dunn County, ND.

Media	July 2011	October 2011	October 2012
Groundwater	XXX	XXX	XXX

Table 5. Water quality of the Killdeer Aquifer. Data from Klausing, 1979.

Parameter	Units	Minimum	Maximum	Mean
TDS	mg/L	234	5030	1531
Na	mg/L	50	1350	413
HCO_3^-	mg/L	374	1250	713
SO_4^{2-}	mg/L	33	3000	626
Cl^-	mg/L	0	25	4.5
F^-	mg/L	0.1	1.6	0.66
Fe	µg/L	0	5500	1029
NO_3^-	mg/L	0.3	6.7	1.2
B	µg/L	0	3700	534

Table 6. Field parameter stabilization criteria and calibration standards.

Parameter	Stabilization Criteria	Calibration Standards
pH	≤0.02 pH units min^{-1}	pH 4, 7, and 10 buffers
Oxidation Reduction Potential (ORP)	≤ 2mV min^{-1}	231 mV Zobells Solution
Specific Conductance (SC)	≤ 1% min^{-1}	1413 µS Conductivity Standard

Table 7. Ground Water Field Analytical Methods.

Parameter	Method	Equipment
Alkalinity	Standard Method 2320B; HACH method 8203	HACH Model AL-DT Digital Titrator (or equivalent device)
Ferrous Fe	Standard Method 3500-Fe B; HACH Method 8146	HACH DR890 Portable Colorimeter (or equivalent device)
Dissolved Sulfide	Standard Method 4500-S^{2-} D; HACH Method 8131	HACH DR890 Portable Colorimeter (or equivalent device)
Turbidity	EPA Method 180.1	HACH 2100Q Portable Turbidimeter
pH	EPA Method 150.2	YSI 556MP or equivalent combination of meters and probes
DO	EPA Method 360.1	YSI 556MP or equivalent combination of meters and probes
Temperature	EPA Method 170.1	YSI 556MP or equivalent combination of meters and probes
Specific Conductance	EPA Method 120.1	YSI 556MP or equivalent combination of meters and probes
ORP	No EPA Method	YSI 556MP or equivalent combination of meters and probes
TDS*	No EPA Method	YSI 556MP or equivalent combination of meters and probes

***A calculated value from the YSI 556MP based on the specific conductance measurement.**

Table 8. Ground and Surface Water Sample Collection.

Sample Type	Analysis Method[§] (EPA Method)	Sample Bottles/# of bottles*	Preservation/ Storage	Holding Time(s)
Dissolved gases	No EPA Method (RSKSOP-194v4 &-175v5)	60 mL serum bottles/2	No Headspace TSP[†], pH>10; refrigerate ≤6°C[††]	14 days
Dissolved Metals (filtered)	EPA Methods 200.7,6020A, and 7470A	1 L plastic bottle/1	HNO_3, pH<2; room temperature	6 months (Hg 28 days)
Total MetalsMetals (unfiltered)	EPA Methods 200.7,6020A, and 7470A: Digestion EPA method 200.7	1 L plastic bottle/1	HNO_3, pH<2; room temperature	6 months (Hg 28 days)
SO_4, Cl, F, Br	EPA Method 6500 (RSKSOP-276v3 and RSKSOP-288v3 for Br (in high Cl matrix))	60 mL plastic/1	Refrigerate≤6°C	28 days
Iodide	(No EPA Method) RSKSOP-223v2	60 mL plastic/1	Refrigerate≤6°C	28 days
NO_3 + NO_2, NH_4	EPA Method 350.1 and 353.1 (RSKSOP-214v5)	60 mL plastic/1	H_2SO_4, pH<2; refrigerate ≤6°C	28 days
DIC	EPA Method 9060A (RSKSOP-330v0)	40 mL clear glass VOA vial/2	refrigerate ≤6°C	14 days
DOC	EPA Method 9060A (RSKSOP-330v0)	40 mL clear glass VOA vial/2	2- H_3PO_4, pH<2; refrigerate ≤6ºC	28 days
Volatile organic compounds (VOC)	RSKSOP-299v1 (EPA Method 5021A+8260C)	40 mL amber glass VOA vial/2	No Headspace TSP[†], pH>10; refrigerate ≤6°C	14 days
Low Molecular Weight Acids	No EPA Method (RSKSOP-112v6)	40 mL glass VOA vial/2	TSP[†], pH>10; refrigerate≤6°C	30 days
O, H stable isotopes of water	No EPA Method (RSKSOP-334v0)	20 mL glass VOA vial/1	Refrigerate at ≤6°C	stable

Sample Type	Analysis Method[§] (EPA Method)	Sample Bottles/# of bottles*	Preservation/ Storage	Holding Time(s)
Semi-volatile organic compounds	EPA Method 8270D, (ORGM-515 r1.1)	1L Amber glass bottle/2 and for every 10 samples of ground water need 2 more bottles for one selected sample, or if <10 samples collected, collect 2 more bottles for one select sample	Refrigerate ≤6°C	7 days until extraction, 30 days after extraction
DRO	EPA Method 8015D, (ORGM-508 r1.0)	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	EPA Method 8015D, (ORGM-506 r1.0)	40 mL amber glass VOA vial/2 and for every 10 samples of ground water need 2 more bottles for one selected sample, or if <10 samples collected, collect 2 more bottles for one select sample	No Headspace HCl, pH<2; refrigerate ≤6°C	14 days
Gylcols	No EPA Method (Region III method**)	40 mL amber glass VOA vial/2	Refrigerate ≤6ºC	14 days
$^{87}Sr/^{86}Sr$ analysis	No EPA Method (Thermal ionization mass spectrometry)	500 mL plastic bottle/2	Refrigerate ≤6°C	No inform-ation
Acrylamide	SPE and LC-MS (Method under development)	1L amber glass bottle/2 and for every 10 samples of ground water need 2 more bottles for one selected sample, or if <10 samples collected, collect 2 more bottles for one select sample	Refrigerate <6°C	30 days

Sample Type	Analysis Method[§] (EPA Method)	Sample Bottles/# of bottles*	Preservation/ Storage	Holding Time(s)
Alkylphenols	SPE and LC-MS (Method under development)	1L amber glass bottle/2 and for every 10 samples of ground water need 2 more bottles for one selected sample, or if <10 samples collected, collect 2 more bottles for one select sample	Refrigerate <6°C	30 days
Ethoxylated alcohols/ ethoxylated alkylphenols	SPE and LC-MS (Method under development)	1L amber glass bottle/2 and for every 10 samples of ground water need 2 more bottles for one selected sample, or if <10 samples collected, collect 2 more bottles for one select sample	Refrigerate <6°C	30 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
[§]SOPs are available at ftp://ftp.epa.gov/r8/pavilliondocs/LabSOPsAndLabProducedReports/AnalyticalMethodologyUsed-RobertSKerrLaboratory/

Table 9. 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.	< QL: Sample will be flagged if >QL and analyte concentration < 10x concentration in blank.
Equipment Blanks	Assess contamination from field equipment, sampling procedures, decon procedures, sample container, preservative, and shipping.	Apply only to samples collected via equipment, such as filtered samples: Reagent water is filtered and collected into bottles and preserved same as filtered samples.	One per day of sampling	< QL: Sample will be flagged if >QL and analyte concentration < 10x concentration in blank.
Field Duplicates	Represent precision of field sampling, analysis, and site heterogeneity.	One or more samples collected immediately after original sample.	One in every 10 samples, or if <10 samples collected for a water type (ground or surface), collect a duplicate for one sample**	Report duplicate data; RPD $\leq$ 30 for results greater than 5xQL. The affected data will be flagged as needed.
Temperature Blanks	Measure temperature of samples in the cooler.	Water sample that is transported in cooler to lab.	One per cooler.	Record temperature; condition noted on COC form***
Field Blanks	Assess contamination introduced from sample container with applicable	In the field, reagent water is collected into sample containers with preservatives.	One per day of sampling	< QL: Sample will be flagged if >QL and analyte concentration < 10x

	preservative.			concentration in blank..

**At least two per sampling event if >12 samples are collected.

*** The PI should be notified immediately if samples arrive with no ice and/or if the temperature recorded from the temperature blank is greater than 6^{o} C. These samples will be flagged accordingly.

Table 10. Region III Laboratory QA/QC Requirements for Glycols.

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

RL = Reporting Limit

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

Table 11. RSKERC Detection limits for various analytes.

Analyte	Method[§]	MDL	QL or LOQ
Dissolved Gases*		µg L^{-1}	µg L^{-1}
Methane	RSKSOP-194v4 & RSKSOP-175v5 (No EPA Method)	0.08	1.5
Ethane	RSKSOP-194v4& RSKSOP-175v5 (No EPA Method)	0.20	2.91
Propane	RSKSOP-194v4& RSKSOP-175v5 (No EPA Method)	0.24	4.1
n-Butane	RSKSOP-194v4& RSKSOP-175v5 (No EPA Method)	0.22	5.22
DIC/DOC		mg L^{-1}	mg L^{-1}
DOC	EPA Method 9060A[A]	0.067	0.50
DIC	EPA Method 9060A[A]	0.017	0.50
Anions		mg L^{-1}	mg L^{-1}
Br^-	EPA Method 6500[B,C]	0.248 (0.110)	1.00 (1.00)
Cl^-	EPA Method 6500[B]	0.118	1.00
SO_4^{2-}	EPA Method 6500[B]	0.226	1.00
F^-	EPA Method 6500[B]	0.052	0.20
I^-	RSKSOP-223v2 (No EPA Method)	1.61 µg/L	10 µg/L
NO_3^-+NO_2^-	EPA Method 350.1[D]	0.014	0.10
NH_4^+	EPA Method 353.1[D]	0.012	0.05
Low Molecular Weight Acids		mg L^{-1}	mg L^{-1}
Lactate	RSKSOP-112v6 (No EPA Method)	0.020	0.100
Acetate	RSKSOP-112v6 (No EPA Method)	0.011	0.100
Propionate	RSKSOP-112v6 (No EPA Method)	0.022	0.100
Butyrate	RSKSOP-112v6 (No EPA Method)	0.025	0.100

Analyte	Method	MDL (µg L^{-1})	QL or LOQ (µg L^{-1})
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	10.0
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
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

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

[A]RSKSOP-330v0 is the GWERD SOP for the implementation of this method.

[B]RSKSOP-276v3 is the GWERD SOP for the implementation of this method.

[C]RSKSOP-288v3 is the GWERD SOP for the implementation of this method in a high Cl^- matrix.

[D]RSKSOP-214v5 is the GWERD SOP for the implementation of this method.

[§]SOPs are available at ftp://ftp.epa.gov/r8/pavilliondocs/LabSOPsAndLabProducedReports/AnalyticalMethodologyUsed-RobertSKerrLaboratory/

Table 12. Region VIII Detection and Reporting limits and LCS and MS control limits for semivolatile organic compounds (SVOC) using Method 8270 (Region VII SOP ORGM-515 r1.1).

Analyte	MDL (µg/L)	QL (µg/L)	Lab Duplicates RPD Limits (%)	Matrix Spike Recovery Limits (%)	Matrix Spike Duplicate RPD Limits (%)
(R)-(+)-Limonene	0.257	1.00	20	60-130	30
1,2,4-Trichlorobenzene	0.399	1.00	20	35-105	30
1,2-Dichlorobenzene	0.399	1.00	20	35-100	30
1,2-Dinitrobenzene	0.460	1.00	20	45-110	30
1,3-Dichlorobenzene	0.375	1.00	20	30-100	30
1,3-Dimethyl adamantane	0.277	1.00	20	60-130	30
1,3-Dinitrobenzene	0.460	1.00	20	45-110	30
1,4-Dichlorobenzene	0.377	1.00	20	30-100	30
1,4-Dichlorobenzene-d4				-	
1,4-Dinitrobenzene	0.450	1.00	20	45-110	30
1-Methylnaphthalene	0.482	1.00	20	45-105	30
2,3,4,6-Tetrachlorophenol	1.08	2.00	20	50-110	30
2,3,5,6-Tetrachlorophenol	1.05	2.00	20	50-110	30
2,4,5-Trichlorophenol	1.15	2.00	20	50-110	30
2,4,6-Trichlorophenol	1.19	2.00	20	50-115	30
2,4-Dichlorophenol	1.05	2.00	20	50-105	30
2,4-Dimethylphenol	0.937	2.00	20	30-110	30
2,4-Dinitrophenol	1.75	3.00	20	15-140	30
2,4-Dinitrotoluene	0.413	1.00	20	50-120	30
2,6-Dinitrotoluene	0.497	1.00	20	50-115	30
2-Butoxyethanol	0.698	1.00	20	60-130	30
2-Butoxyethanol phosphate	0.698	1.00	20	60-130	30
2-Chloronaphthalene	0.498	1.00	20	50-105	30
2-Chlorophenol	0.911	2.00	20	35-105	30
2-Methylnaphthalene	0.468	1.00	20	45-105	30
2-Methylphenol	0.999	2.00	20	40-110	30
2-Nitroaniline	0.556	1.00	20	50-115	30
2-Nitrophenol	0.864	2.00	20	40-115	30
3 & 4-Methylphenol	2.08	5.00	20	30-110	30
3-Nitroaniline	1.30	3.00	20	20-125	30
4,6-Dinitro-2-methylphenol	0.958	2.00	20	40-130	30
4-Bromophenyl phenyl ether	0.566	1.00	20	50-115	30

Analyte	MDL (µg/L)	QL (µg/L)	Lab Duplicates RPD Limits (%)	Matrix Spike Recovery Limits (%)	Matrix Spike Duplicate RPD Limits (%)
4-Chloro-3-methylphenol	1.22	2.00	20	45-110	30
4-Chloroaniline	1.05	3.00	20	15-110	30
4-Chlorophenyl phenyl ether	0.612	1.00	20	50-110	30
4-Nitroaniline	1.13	3.00	20	35-120	30
4-Nitrophenol	1.08	3.00	20	0-125	30
Acenaphthene	0.588	1.00	20	45-110	30
Acenaphthylene	0.562	1.00	20	50-105	30
Adamantane	0.280	1.00	20	60-130	30
Aniline	0.202	1.00	20	0-150	30
Anthracene	0.410	1.00	20	55-110	30
Azobenzene	0.596	1.00	20	50-115	30
Benzo (a) anthracene	0.377	1.00	20	55-110	30
Benzo (a) pyrene	0.475	1.00	20	55-110	30
Benzo (b) fluoranthene	0.428	1.00	20	45-120	30
Benzo (g,h,i) perylene	0.423	1.00	20	40-125	30
Benzo (k) fluoranthene	0.416	1.00	20	45-125	30
Benzoic acid	1.59	3.00	20	20-115	30
Benzyl alcohol	0.549	1.00	20	50-150	30
Bis(2-chloroethoxy)methane	0.523	1.00	20	45-105	30
Bis(2-chloroethyl)ether	0.463	1.00	20	35-110	30
Bis(2-chloroisopropyl)ether	0.480	1.00	20	25-130	30
Bis-(2-Ethylhexyl) Adipate	0.494	1.00	20	40-125	30
Bis(2-ethylhexyl)phthalate	1.12	2.00	20	40-125	30
Butyl benzyl phthalate	0.610	1.00	20	45-115	30
Carbazole	0.913	3.00	20	50-115	30
Chrysene	0.340	1.00	20	55-110	30
Dibenz (a,h) anthracene	0.425	1.00	20	40-125	30
Dibenzofuran	0.589	1.00	20	55-105	30
Diethyl phthalate	0.480	1.00	20	40-120	30
Dimethyl phthalate	0.516	1.00	20	25-125	30
Di-n-butyl phthalate	0.626	1.00	20	55-115	30
Di-n-octyl phthalate	0.544	1.00	20	35-135	30
Diphenylamine	0.521	1.00	20	55-115	30
Fluoranthene	0.384	1.00	20	55-115	30
Fluorene	0.626	1.00	20	50-110	30
Hexachlorobenzene	0.487	1.00	20	50-110	30
Hexachlorobutadiene	0.304	1.00	20	25-105	30

Analyte	MDL (µg/L)	QL (µg/L)	Lab Duplicates RPD Limits (%)	Matrix Spike Recovery Limits (%)	Matrix Spike Duplicate RPD Limits (%)
Hexachlorocyclopentadiene	0.227	1.00	20	0-95	30
Hexachloroethane	0.320	1.00	20	30-95	30
Indeno (1,2,3-cd) pyrene	0.441	1.00	20	45-125	30
Isophorone	0.578	1.00	20	50-110	30
Naphthalene	0.426	1.00	20	40-100	30
Nitrobenzene	0.453	1.00	20	45-110	30
N-Nitrosodimethylamine	0.488	1.00	20	25-110	30
N-Nitrosodi-n-propylamine	0.598	1.00	20	35-130	30
Pentachlorophenol	0.928	2.00	20	40-115	30
Phenanthrene	0.411	1.00	20	50-115	30
Phenol	0.967	2.00	20	20-115	30
Pyrene	0.386	1.00	20	50-130	30
Pyridine	0.014	1.00	20	0-150	30
Squalene	1.33	2.00	20	60-130	30
Terpiniol	0.617	1.00	20	60-130	30

[1] Subject to change. The values reported are those reported December 2012.

Table 13. Data quality indicators for measurement at the ORD/NERL laboratory.

QC Check	Frequency	Completeness	Precision	Accuracy	Corrective Action
5- point calibration	Prior to sample analysis	100 %	< 30 %	r^2 > 0.99	No samples will be run until calibration passes criteria.
Laboratory blank	One per batch of samples[a]	100 %	< 50 %	< PQL[b]	Inspect the system and reanalyze the blank. Samples must be bracketed by acceptable QC or they will be invalidated.
Instrument blank	In between samples	100 %	< 50 %	< PQL[b]	Inspect the system and reanalyze the blank. Samples must be bracketed by acceptable QC or they will be invalidated.
Laboratory control sample	One per batch of samples[a]	100 %	< 30 %	> 70 %	Check the system and reanalyze the standard. Reprepare the standard if necessary. Recalibrate the instrument if the criteria cannot be met. Samples must be bracketed by acceptable QC or they will be invalidated.
Laboratory fortified matrix	One per batch of samples[a]	100 %	< 30 %	> 70 % recovery	Review data to determine whether matrix interference is present. If so, narrate interference and flag recovery. If no interference is evident, verify the instrument is functioning properly by running a lab blank. Reanalyze recollected sample to verify recovery. Samples must be bracketed by acceptable QC or they will be invalidated.
Laboratory Replicates	One per batch of samples[a]	100 %	< 30 %	> 70 % recovery	Inspect the system, narrate discrepancy. Samples must be bracketed by acceptable QC or they will be invalidated.
Continuing calibration verification	One at beginning of each 8-hr analytical	100 %	< 30 %	> 70 % recovery	Inspect system and perform maintenance as needed. If system still fails CCV, perform a new

QC Check	Frequency	Completeness	Precision	Accuracy	Corrective Action
	day, one at beginning of each batch of samples[a], and one at end of analytical day				5-point calibration curve. Samples must be bracketed by acceptable QC or they will be invalidated.
Laboratory fortified blank	One per batch of samples[a]	100 %	< 30 %	> 70 % recovery	Inspect the system and reanalyze the standard. Reprepare the standard if necessary. Re-calibrate the instrument if the criteria cannot be met. Samples must be bracketed by acceptable QC or they will be invalidated.
Minimum detection limit	Each Chemical	100 %	TBD for each HF chemical	TBD for each HF chemical	TBD for each HF chemical

[a]Batch of samples not to excced 20.

[b]PQL= practical quantitation limit, 5 times the MDL.

Table 14. Region 7 Contract Lab Metal Quantitation limits. ICP-AES uses EPA Method 200.7; ICP-MS uses EPA Method 6020A; Total digestions follow EPA Method 200.7; and Hg analysis follows EPA Method 7470A.

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

[1]AES: Atomic Emission Spectroscopy, equivalent to OES.

[2]For Hg the method is cold vapor atomic absorption spectroscopy.

Table 15. RSKERC Laboratory 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 blank, first and last in sample queue; water blank before samples)	85-115% of known value (After helium blank at first of analysis queue, before helium blank at end of sample set, and every 15 samples)	85-115% of known value (After first calibration check)	RPD≤20 (Every 15 samples)	NA
SO_4, Cl, F, Br	RSKSOP-276v3& -288v3	<MDL (Beginning and end of each sample queue)	90-110% Rec. (Beginning, end, and every 10 samples)	PE sample acceptance limits (One per sample set)	RPD<10 (every 15 samples)	80-120% Rec. (one per every 20 samples)
I^-	RSKSOP-223v2	<QL (Beginning and at the end of each set of samples.)	90 – 110% of known value (At beginning of each analytical run. Every tenth sample and at end of analytical run.)	90-110% of known value (Beginning of sample set and every 20 samples)	RPD < 10% (Every 20 samples)	MS: 80 – 120% Recovery (Every 20 samples)/ LCS: 80 – 120% (If matrix spike fails)
$NO_3 + NO_2$, NH_4	RSKSOP-214v5	<½ lowest calib. std. (Beginning and end of each sample	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)
		queue)				
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
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)
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)	RPD<20 (every 20 samples)	70-130% Rec. (every 20 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.
Corrective actions are outlined in the SOPs.
MDL = Method Detection Limit
QL = Quantitation Limit
PE = Performance Evaluation

Table 16. Region VIII Laboratory QA/QC Requirements for Semivolatiles, GRO, DRO.

QC Type	Semivolatiles	DRO	GRO	Frequency
Method Blanks	<RL Preparation or Method Blank, one with each set of extraction groups. Calibration Blanks are also analyzed	<RL Preparation or Method Blank	<RL Preparation or Method Blank and IBL	At least one per sample set
Surrogate Spikes	Limits based upon DoD statistical study (rounded to 0 or 5) for the target compound analyses.	60-140% of expected value	70-130% of expected value	Every field and QC sample
Internal Standards Verification.	Every sample, EICP area within -50% to +100% of last ICV or first CCV.	NA	NA	Every field and QC sample
Initial multilevel calibration	ICAL: minimum of 6 levels (.25 -12.5 ug/L) , one is at the MRL (0.50 ug/L), prior to sample analysis (not daily) RSD≤20%, r^2≥0.990	ICAL: 10-500 ug/L RSD<=20% or r^2>=0.990	ICAL: .25-12.5 ug/L for gasoline (different range for other compounds) RSD<=20% or r^{2}>=0.990	As required (not daily if pass ICV)
Initial and Continuing	80-120% of expected value	80-120% of expected value	80-120% of expected value	At beginning of sample set,

QC Type	Semivolatiles	DRO	GRO	Frequency
Calibration Checks				every tenth sample, and end of sample set
Second Source Standards	ICV1 70-130% of expected value	ICV1 80-120% of expected value	ICVs 80-120% of expected value	Each time calibration performed
Laboratory Control Samples (LCS)	Statistical Limits from DoD LCS Study (rounded to 0 or 5) or if SRM is used based on those certified limits	Use an SRM: Values of all analytes in the LCS should be within the limits determined by the supplier. Otherwise 70-130% of expected value	Use and SRM: Values of all analytes in the LCS should be within the limits determined by the supplier. Otherwise 70-130% of expected value	One per analytical batch or every 20 samples, whichever is greater
Matrix Spikes (MS)	Same as LCS	Same as LCS	70-130% of expected value	One per sample set or every 20 samples, whichever is more frequent
MS/MSD	% Recovery same as MS RPD $\leq$ 30	% Recovery same as MS RPD $\leq$ 25	% Recovery same as MS RPD $\leq$ 25	One per sample set or every 20 samples, whichever is more frequent
Reporting Limits*	0.1 µg/L (generally)[1] for target compounds HF special compounds are higher	20 µg/L[1]	20 µg/L[2]	NA

[1]Based on 1000 mL sample to 1 mL extract; [2]Based on a 5 mL purge; *see QAPP Table 12

Table 17. Region III Detection and Reporting limits for glycols.

Analyte‡	Detection Limit (µg L^{-1})†	Reporting Limit (µg L^{-1})†
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 Region 3 Laboratory QA manual for procedures. See Section 13.1.4.2 Procedure for Demonstration of Capability for "On-Demand" Data (Metzger et al., 2011)

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

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

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

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

Table 19. Region 7 Contract Laboratory QA/QC requirements for ICP-MS metals.

QC Type or Operation	Acceptance Criterion	Frequency
Instrument Calibration	The acceptance criterion for the initial calibration correlation coefficient is r≥0.998.	Daily. Each time instrument is turned on or set up, after ICV or CCV failure, and after major instrument adjustment. The lowest non-blank standard shall be set at the RL for all analytes.
Initial Calibration Verification	90-110% Recovery	Following instrument calibration for each mass used.
Initial Calibration Blank	≤RL	Following each instrument calibration, immediately after the ICV.
Continuing Calibration Verification	90-110% Recovery	For each mass used, at a frequency of at least after every 10 analytical runs, and at the end of each run.
Low Level Initial Calibration Verification (LLICV) and Low Level Continuing Calibration Verification (LLCCV) at the RL (identified by lab as CRDL)	70-130% Recovery	LLICV, following each instrument calibration., and LLCCV analyzed at the end of each run.
Continuing Calibration Blank	≤RL	At a frequency of at least after every 10 analytical runs, and at the end of each run. Performed immediately after the last CCV.
Interference Check Sample	For solution AB, ±20% of the analyte's true value; for solution A ±5 ppb or ±2 times the RL of the analyte's true value, whichever is greater.	At the beginning of the run after the ICB but before the CCV.
Serial Dilution	If the analyte concentration is sufficiently high (minimally a factor of 50 above the RL in the original sample), the serial dilution (a five-fold dilution) shall then agree within 10% of the original determination after correction for dilution.	Every 20 samples.

QC Type or Operation	Acceptance Criterion	Frequency
Preparation or Method Blank	≤RL	Every 20 samples.
Laboratory Control Sample	80-120% Recovery	Every 20 samples.
Matrix Spike	75-125% Recovery (Recovery calculations are not required if sample concentration >4x spike added.)	Every 20 samples.
Post-Digestion Spike	80-120% Recovery per 6020A (Note that the lab SOP uses 75-125% Recovery)	Each time Matrix Spike Recovery is outside QC limits.
Duplicate Sample	RPD≤20% for sample values ≥5x RL	Every 20 samples.
ICP-MS Tune	Mass calibration must be within 0.1 amu of the true value in the mass regions of interest. The resolution must also be verified to be less than 0.9 amu full width at 10% peak height.	Prior to calibration.
Internal Standards	The absolute response of any one internal standard in a sample must not be <70% from the response in the calibration standard.	Internal standards shall be present in all samples, standards, and blanks (except the tuning solution) at identical levels.
Determination of Method Detection Limits		Annually and after major instrument adjustment.

Table 20. Region 7 Contract Laboratory QA/QC requirements for ICP-AES metals.

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

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

Table 21. Region 7 Contract Laboratory QA/QC requirements for Mercury by Cold Vapor AAS.

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

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

Table 22. Supplies or consumables needed not listed in SOPs*.

Item	Vendor	Part Number
Buffer Solution, pH 4	Fisher Scientific	SB101-500
Buffer Solution, pH 7	Fisher Scientific	SB108-500
Buffer Solution, pH 10	Fisher Scientific	SB115-500
Conductivity Standard, 1413µmho	Fisher Scientific	15-077-951
Zobell Solution	Fisher Scientific	15-176-222
Oakton DO Probe Membranes	Fisher Scientific	15-500-039
Bromcresol Green-Methyl Red Indicator	HACH	94399
Sulfuric Acid Cartridges, 0.1600N	HACH	1438801
Sulfuric Acid Cartridges, 1.600N	HACH	1438901
Delivery Tubes for Digital Titrator	HACH	1720500

Item	Vendor	Part Number
Iron, Ferrous Reagent	HACH	103769
Sulfide 1 Reagent	HACH	181632
Sulfide 2 Reagent	HACH	181732
POL DO cap Membrane Kit/ Electrolyte Solution	YSI	605307
Silicone Tubing, size 24	Fondriest Environmental	77050009
Silicone Tubing, size 36	Fondriest Environmental	77050011
Polyethylene Tubing 0.25” ID x 0.375” OD	Fondriest Environmental	77050502
Polyethylene Tubing 0.375” ID x 0.50” OD	Fondriest Environmental	77050503
De-ionized Water	Varies	N/A
Distilled Water	Varies	N/A

*Equivalent products from other vendors can be used if needed.

Table 23. Data qualifiers

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

Data Descriptors

Descriptor	Definition
NA	Not Applicable (See QAPP)
NR	Not Reported by Laboratory or Field Sampling Team
ND	Not Detected
NS	Not Sampled

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

7.0 Figures

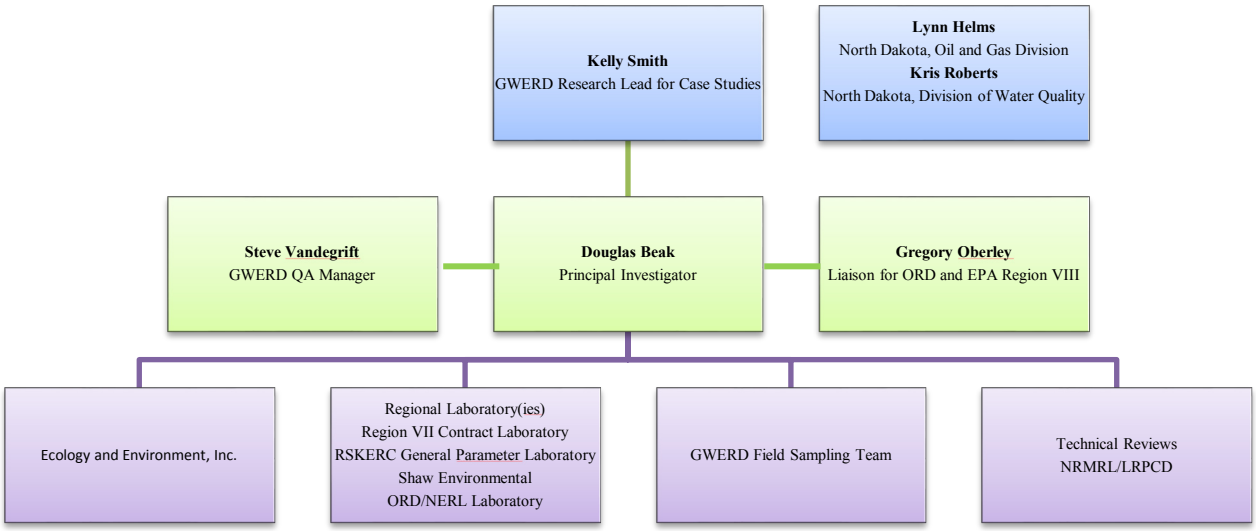

Figure 1. Organizational chart for the Hydraulic Fracturing Retrospective Case Study, Bakken Shale, Killdeer and Dunn County, ND

Figure 2. Topo map showing the location of the Franchuk 44-20SHW well to the city of Killdeer, North Dakota and the surrounding area.

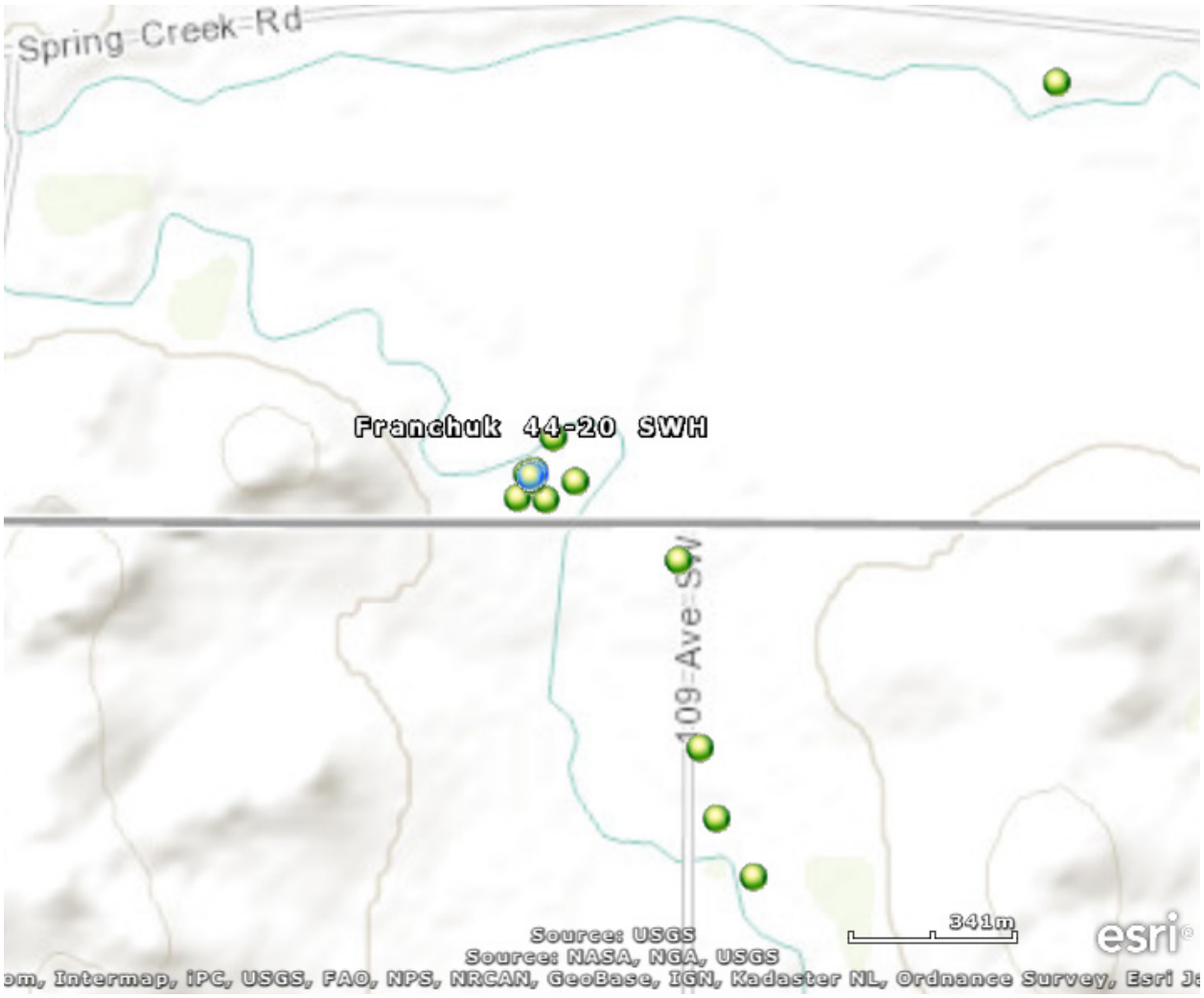

Figure 3. A higher resolution topo map of the Franchuk 44-20SWH well and surrounding wells.

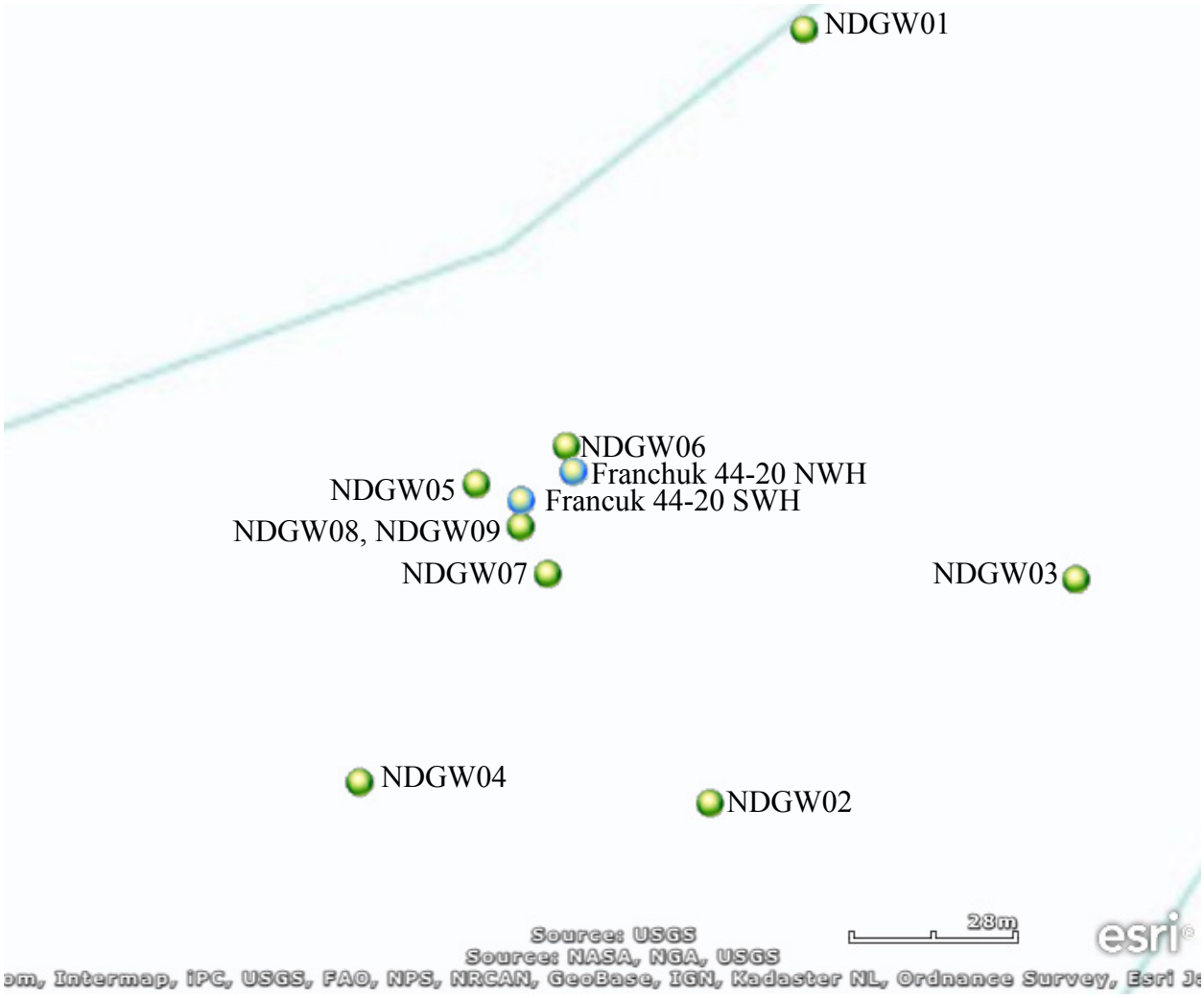

Figure 4. Locations of Monitoring well network for the Franchuk 44-20SWH well.

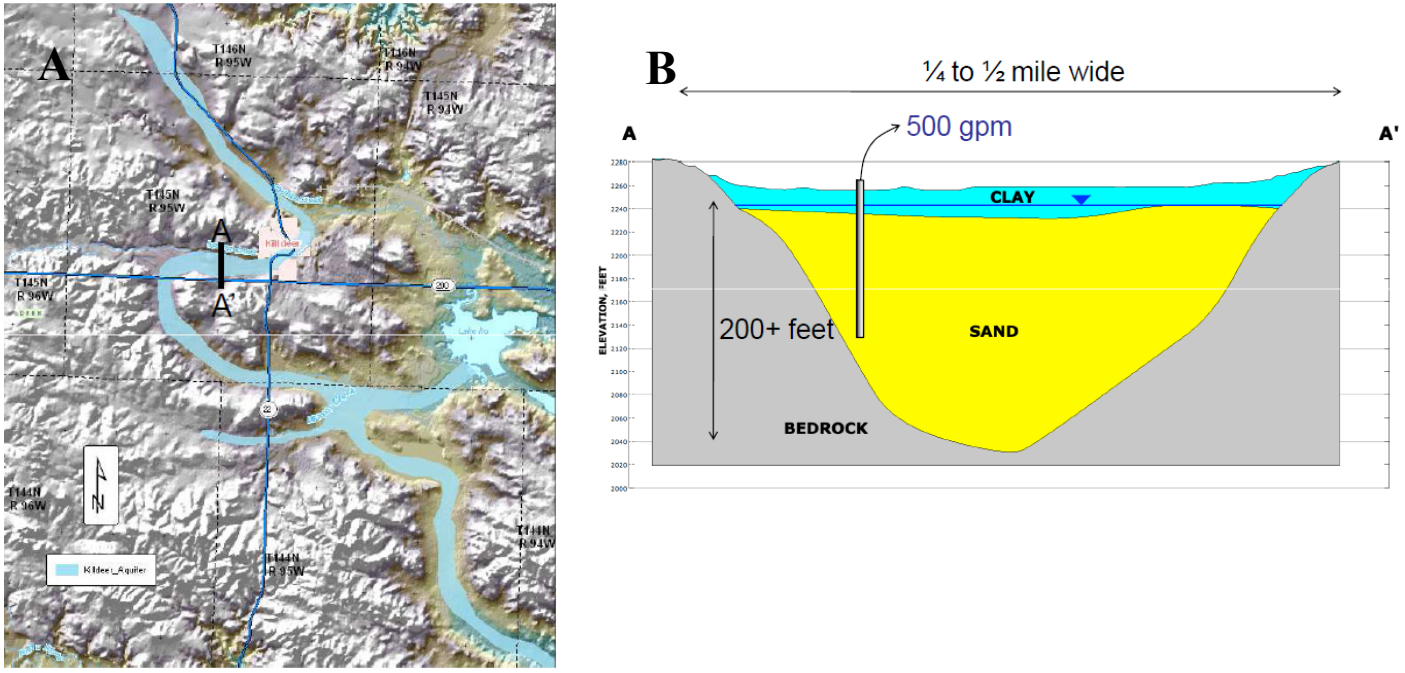

Figure 5. Map showing (A) the extent of the Killdeer Aquifer in Dunn County, North Dakota and (B) a geologic cross section of the Killdeer Aquifer (Shaver, 2009).

Figure 6. An example of sampling a monitoring well.

Killdeer, ND Groundwater purge log

Well Id:_____ Date:_____

Start Purge Time:_____ Purge Rate:_____

Water Levels (ft), Initial:_____ Final:_____.

Weather Conditions:_____

Time	Temp (ºC)	Sp. Cond. (mS/cm)	TDS (g/L)	DO (mg/L)	pH	ORP (mV)	Comments

Figure 7. Example of a blank purge log.

Figure 8. Example of sampling point for a domestic well.

Figure 9. Example of a municipal supply well sampling tap.

Figure 10. Water supply well and sampling insert.

Figure 11. North Dakota Water Commission well sampling and bladder pump controller.

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

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Figure 12. Chain of Custody form for submittal of water samples to laboratories.

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.

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YMPB USGS TECHNICAL PROCEDURE

Rb-Sr Isotope Geochemistry

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

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

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

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

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 x 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 H2SO4, HCl, HClO4,or HNO3 with concentrated HF. After refluxing on a hot plate to dryness the resultant precipitate is brought into solution with HCl or HNO3 and centrifuged. The supernatant solution is pipetted in small volumes onto an ion-exchange resin column pretreated with HCl or HNO3. After washing with a measured volume of HCl or HNO3 acid, the final solution containing the purified Sr is collected in a Teflon beaker and dried on low heat. The sample is transferred to the mass spectrometer laboratory for isotopic analysis.

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

6.1.2.2 Carbonate Samples: Carbonate samples are typically weighed and dissolved in weak HCl or HNO3 leaving admixed silicates intact. Other methods of leaching include, but are not limited to 10 percent CH3COOH (acetic acid), or

10 percent disodium EDTA (ethylenedinitrilotetraacetate). For isotope dilution determination, a weighed amount of Sr spike is added to the sample before dissolution. The leachate is separated from the insoluable material by centrifuging and the supernatant liquid is transferred to separate container. After drying the leachate with low heat, the residual is dissolved in a small amount of HNO3 acid. To estimate the proportion of carbonate in the original sample, the acid-leached residue is washed with ultra high purity (UHP) H2O, dried and weighed. Ion exchange procedures to isolate Sr from the solution are similar to those described above in Para. 6.1.2.1 for the silicate samples.

6.1.2.3 Water Samples: Water samples are weighed and spiked with Sr isotope (if necessary) then evaporated to dryness in Pyrex or Teflon beakers in an environmental hood. The dried sample is brought up in HNO3 and centrifuged. A portion of sample solution may be prepared for trace element concentration determination by ICP MS in accordance with YMPB-USGS-GCP-38, *Determination of Chemical Composition by Inductively Coupled Plasma Mass Spectrometry*. Sr is isolated by ion-exchange methods, following the procedures in Para. 6.1.2.1.

6.1.3 Mass Spectrometry: Isotopic analyses of Rb and Sr will be done by thermal ionization mass spectrometry (TIMS). A drop of 1.0N HCl is added to the Sr sample (0.1-5 micrograms of Sr), which was prepared as described above in section. 6.1.2. Prior to loading any solutions the rhenium or tantalum filaments used will be outgassed in a vacuum to remove impurities. The Sr sample is dried on the filaments by passing a low current (1.5-2.0 amps) through the filaments. The rhenium sample filaments are configured with an ionizing filament and placed sample turret of the mass spectrometer. Tantalum filaments are used for single filament runs. Following pump down to a source pressure of approximately 4×10^{-7} mm of Hg, an ion beam is generated by heating the sample filaments with the ionizing filament operating at approximately 1.8×10^{3} C. When a stable Sr beam of approximately 0.5-5 volts of ^{88}Sr is attained, data collection is started. Five or more blocks of data are to be taken until an average $^{87}Sr/^{86}Sr$ 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) H2O (18.2 x 10^6 ohms resistivity)
- Ultrex, Baker Analyzed, C Star Suprapur (EM Science) and/or reagents of equivalent or higher purity of the following: H2SO4 (concentrated) HF (concentrated) HClO4 (concentrated) HNO3 (concentrated) HCl (concentrated) CH3COOH (acetic acid) Disodium EDTA (ethylenedinitrilotetraacetate)
- Platinum dishes
- Teflon covers, jars, beakers, tubes and other equipment
- Electronic analytical balance
- NIST traceable weights
- ^{87}Rb spike solution
- NIST SRM-607 Rb standard
- ^{84}Sr spike solution
- NIST SRM-610 or 611 Sr standard
- Hot plate
- Centrifuge
- Ion-exchange resins and columns
- Parafilm
- Environmental hood or laminaire flow hoods
- Appropriate standard laboratory equipment including, but not limited to: quartz, Teflon, and Pyrex beakers; graduated cylinders; and glass and plastic centrifuge tubes (accuracies in all ranges to $\pm$5 percent)
- NIST glass and rock standards such as, but not limited to, SRM-610, SRM-611 and SRM-987 for strontium and SRM-607 for rubidium.

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

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

Collected data will be traceable to the M&TE used to collect that data by lab notebooks and computer printouts from the mass spectrometer.

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

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

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

Standard materials include, but are not limited to NIST glass and rock standards such as SRM-610, SRM-611, and SRM-987 for strontium or SRM-607 for rubidium. Operational checks on the mass spectrometers are performed at least every 30 samples or as necessary by analyzing a laboratory standard material For Sr the laboratory standard is calcium carbonate prepared from a modern *tridacna* (giant clam) shell collected from Enewetok Lagoon 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-USGSQMP-12.01, *Control of Measuring and Test Equipment*, including application of calibration status stickers and reporting of out of calibration conditions. Measuring and test equipment (M&TE) that requires calibration include:

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

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

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

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

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

14. ELECTRONIC MANAGEMENT OF INFORMATION. Data will not be released from the laboratory until all samples of a given set have been examined for internal coherence. Mass spectrometric measurements of isotopic ratios are obtained on hard copy as output from the instruments. The relevant ratios are transferred by data entry to electronic media and then retrieved from this media for double back-checking against the mass spectrometer records.

Sample weights and spike weights are also entered into electronic media and then double-back checked against entries in the laboratory notebooks. All of the checking is done before the technical data submittal. The maintenance of security and integrity of any electronic data files shall be ensured by using password protected drives which are routinely backed up.

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

15.1.1 Data Records: The basic completed analytical data sets obtained will consist of the Rb and Sr contents (if applicable) and the $^{87}Sr/^{86}Sr$ 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.

Revision History

Revision Number	Date Approved	Revision
0	6/20/11	New document
1	8/29/2011	• Added $^{87}Sr/^{86}Sr$ isotopes to analyte list • Added O, H stable isotopes of water • Added section for phased approach for case studies • Revised sampling protocols for domestic wells, supply wells, and water commission wells • Revised background information based on new information from Denbury • Added USGS Laboratory contact information • Revised Analysis of Data section • Revised Assessment Results section- Reports will now be submitted to Technical Research Lead for Case Studies • Revised Reports to Management section- Audit reports will be sent to Technical Research Lead for Case Studies • Updated Reference section to include new references for isotopes and field paramenters • Updated Table 3, 8, and 11 to include current methods used • Updated Table 9 to clarify Field QC samples needs • Revised Table 13 to reflect QC sample frequencies • Revised Table 14 to reflect new QC information provided by EPA R8 lab • Added Table 16 for USGS QA/QC requirements • Added Figure (Figure 6) to show sampling of municipal supply wells and sampling port • Added Figure (Figure 7) to show sampling of water supply well and and sampling adaptor • Added Figure (Figure 8) to show the sampling of ND Water Commission well using a portable bladder pump • Added Appendix A for Sr isotope methodology used by USGS
2	9/30/2013	• Revised cover page with new Technical Lead and updated distribution list • Sec. 1.1 was updated to reflect new personnel and their roles • Removed all personnally identifiable information (PII) and

		confidential information • Section 1.4, updated to address Battelle comments • Section 1.5, updated to address Battelle comments and address ORD/NERL, USGS, and Region VII contract laboratory analysis • Section 2.2.1.1, updated to address Battelle comments and updated sampling description for addition of ethoxylated alcohols, alkylphenols, and acrylamide, the use of the Region VII contract laboratory for metals analysis, and removed the collection of an archive sample • Section 2.2.2, added methodology for slug tests • Section 2.3.1, updated description of sample labeling • Section 2.3.2, added information for ORD/NERL and Region VII contract laboratories • Section 2.4.1, updated to address Battelle comments and added information for ORD/NERL and Region VII contract laboratories • Section 2.5.1, added information for ORD/NERL and Region VII contract laboratories • Section 2.6 and 2.7, updated to address Battelle comments • Section 2.9, updated for the use of available databases for historical data, QA requirements, and evaluation of data. • Section 2.10, updated to address Battelle comments and to discuss additional data analysis needs and software packages • Section 3.1.1, updated with current information on assessments • Section 4.1 and 4.2, updated to address Battelle comments • Section 4.2, added information for the Region VII contract laboratory and added text to clarify the data verifcation/validation process • Section 4.3, updated with dispute resolution process • References, updated • Table 3, revised to remove DRO/GRO as critical analytes • Table 4, updated to accurately refelct new sampling schedule • Table 7, updated to include all field parameters • Table, 8, revised to include information from Addendum 1 for the Region VII contract laboratory, replaced the method for H and O isotopes of water with current method, added iodide, acrylamide, ethoxylated alcohols and alkylphenols, and added

		SOP for bromide in high chloride matrix • Table 9, updated with current information • Table 12, updated with current MDLs and QLs • Table 16, updated by adding iodide and removing metals • Added tables of MDLs, QLs, and QA/QC requirements for Region VII contract laboratory methods • Added table for Data Qualifers • Figures 2,3,4,6,7,8,9,10,and 11, replaced or added new figures