

## GWERD QUALITY ASSURANCE PROJECT PLAN

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

## **The EPA Quality System and the HF Research Study**

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

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

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## **1.0 Project Management**

### **1.1 Project/Task Organization**

The organizational structure for the Hydraulic Fracturing Retrospective Case Study located in Wise and Denton Counties, Texas is shown in Figure 1. The roles and responsibilities of the 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. 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 Branch Chief for the Subsurface Remediation Branch. His HAZWOPER certification is current.

**Mr. Mike Overbay**, U.S. Environmental Protection Agency – Region VI (USEPA R6), Dallas, TX. Mr. Overbay will serve as the liaison between GWERD and USEPA R6 and is responsible for coordinating technical discussion and activities between NRMRL-Ada and EPA Region VI, as well as coordinating data collection activities with the state and local officials in Texas and with property owners and local stakeholders. 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 and validation of the final report. His HAZWOPER certification is current.

**Ms. Susan Mravik**, U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Robert S. Kerr Environmental Research Center (RSKERC), Ada, OK. Ms. Mravik will serve as Co-principal investigator and will be involved with all aspects of this case study. Ms. Mravik is also responsible for assisting with data management by transferring data from the PI to CB&I and NRMRL management. CB&I then uploads the data to a secure server. Ms. Mravik also assists the PIs by tracking the status of laboratory analysis of samples, data reports, ADQs, and final QA approvals of data. Her 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.

**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 within 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 coordination 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. Ferguson 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.

**Dr Randall Ross**, U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Robert S. Kerr Environmental Research Center

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(RSKERC), Ada, OK. Dr. Ross will assist in the analysis of hydrologic conditions at the Wise Co. 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 Wise Co. site and will assist in the development of the site hydrologic conditions. His HAZWOPER certification is current.

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

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

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

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

**Ms. Lisa Costantino**, 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. Costantino is responsible for assisting with ground water sampling. Her 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.

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

**Ms. Ashley McElmurry**, Student Contractor, Ada, OK. Ms. McElmurry is responsible for assisting with ground water sampling. Her HAZWOPER certification is current.

**Mr. Peter Pope**, Texas Railroad Commission (TRC). Mr. Pope will be the point of contact with the TRC.

**Mr. Keith Sheedy**, Texas Commission on Environmental Quality (TCEQ). Mr. Sheedy will be the point of contact with the TCEQ.

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

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

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

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

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

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

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

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

**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 Wise County, Texas will investigate the potential impacts to drinking water that may have resulted from hydraulic fracturing activities. Currently three different locations within Wise County, TX have been chosen initially for study based on homeowner complaints and information collected by USEPA Region VI (EPA R6) staff. The areas will be designated as Locations A, B, and C because of their geographical separation, potential differences in geology (Figures 2-5) and reported problems. The chosen sites were visited in June 2011 by the PI and USEPA R6 liaison to investigate selected potential sampling points at each location. In July 2011, the PI, EPA R6 liaison and EPA R6 Management met with representatives of the Texas Railroad Commission (TRC) and Texas Commission on Environmental Quality (TCEQ) to provide background on the overall HF Study Plan and specifics about the case study in Wise County. This study will be conducted in conjunction with the TRC, TCEQ, EPA R6, and U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Ground Water and Ecosystems Restoration Division (GWERD). GWERD will be the lead organization for this case study.

The selected locations have in common complaints about appearance, odors and taste associated with water in domestic wells. However, other issues not held in common will be discussed below. Potential sources of ground-water contamination include activities associated with oil and gas production such as leaking or abandoned pits, gas well completion and enhancement techniques, as well as activities associated with residential and agricultural practices; industrial sources of contamination; other anthropogenic sources of contamination; and naturally occurring sources of contamination. This study will use a tiered approach and each tier will be designed to narrow and target the source of contamination. Several tiers of investigation for this case study are anticipated. This iterative approach is being adopted so that early in the investigation screening investigations will take place (i.e., sampling domestic wells, surface water bodies), particularly at locations where concerns have been raised by local residents. Depending on the outcomes of the initial screening (Tier II), several different possibilities could arise. It is possible that no contamination or anomalous chemical signatures will be detected. If this were the outcome, a follow-up sampling event would be conducted using identical methods to confirm the result. On the other hand, if contamination is suspected, a confirmation sampling would be planned, but also additional studies and methods might be adopted to track the source of contamination, whatever that might be. This iterative approach is being adopted to meet the primary objective and the related secondary objective.

**Primary Objective:** (See Section 1.3)

Determine if ground-water resources in Wise Co., TX have been impacted by hydraulic fracturing processes.

**Secondary Objective 1:** (See Section 1.3)

Determine the likely source(s) of contamination

**Secondary Objective 2:** (See Section 1.3)

Determine the pathway by which the contaminants migrate to the drinking water.

1.2.1 Tier II Investigations

In Tier II, domestic wells and surface water bodies, identified during the site visits, will be sampled with subsequent analyses to determine if contamination exists in the wells and surface water. The wells selected for sampling are based on a site scoping trip conducted in June 2011 that included interviews with local residents and homeowners. If evidence of ground water or surface water contamination is indicated in Tier II sampling, additional Tier II sampling activities will be targeted to confirm the initial result. If these results are confirmed then Tier III sampling will be conducted to identify the source or sources of contamination. If no contamination is detected in the Tier II sampling events, it is anticipated that locations with no contamination will be dropped from the study. Water sampling for Tier II sampling is expected to take place in September 2011, and March 2012. In addition, geophysical measurements and

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analysis of Sr isotopes and stable isotopes of H and O in water will be included in Tier II sampling in March 2012 to further assess the potential for contamination and background values for Sr, O, H isotopes. Version 3 of this QAPP focuses on the special produced water sampling event in September 2012 (described below) for Tier II. Subsequent revision of the QAPP may include other activities and Tier III sampling, if appropriate, will occur following evaluation of Tier II results or whenever revisions are necessary.

Version 3 of the QAPP (dated 9/10/2012) was prepared for the September 2012 sampling (Location B) event. It was an opportunistic sampling event with a limited sampling and a reduced analyte list.

Addendum No. 2 (dated 1/10/2013) to version 3 of the QAPP was prepared to document the QC acceptance criteria for the analysis of samples for metals and VOCs by the Region VII contract laboratory (Southwest Research Institute, a subcontractor to ARDL, Inc.) for the December 2012 sampling event. The December 2012 sampling event was anticipated to be a Tier III activity in version 3 of the QAPP, but instead was conducted to confirm the results of the previous two Tier II sampling events and to help ascertain the natural variability in wells that are believed to represent the background aquifer conditions. During this sampling event a small pond was sampled that is down gradient of a production well pad. The erosional features in the land between the production well pad and the pond suggest that runoff from the pad flows into this pond. Samples from this sampling event will be analyzed using a full suite of analysis described in this document. All domestic wells in Location B were sampled in this event.

Version 4 of this QAPP (dated 2/12/2013) was prepared for the May 2013 sampling event. This sampling event sampled all the same wells and surface water bodies as in the December 2012 sampling event. The purpose of this sampling event was to delineate the natural variability of the analytes in this study location.

Version 5 of this QAPP provides 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.

The sampling results for Locations A and C from the initial screening and the subsequent follow up sampling did not indicate any contamination related to anthropogenic sources. Therefore, no additional sampling of Locations A and C are planned at this time.

### 1.2.2 Tier III Investigations

Tier III activities will likely involve additional surface water and ground-water sampling, monitoring well sampling, and may involve installation of temporary or permanent wells for hydrogeologic and geochemical characterization, core collection and analysis, and geophysical surveys. These will be used to develop and further refine the site conceptual model and the types of sampling and methodology will be outlined in future revisions to the QAPP for Tier III. Tier

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III sampling activities will likely begin in Location B in Spring/Summer of 2013. The Tier III activities planned could include sampling additional domestic wells, installation of monitoring wells, and a focused geophysical investigation at this location along with a detailed investigation of the hydrologic properties at this location.

#### 1.2.3 Integration of Tier II and III investigations and determination of impacts to drinking water resources

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.

#### 1.2.4 Site background- Location A

Location A is located in northeastern Wise Co. and has four properties (Figures 2 and 3). EPA has visited and had conversations with four property owners. All four of these property owners have stated concerns about the impacts of oil and gas operations nearby and the willingness to participate in this study. There are approximately 8 production wells located on or near the properties in this location and the drinking water supply is the Trinity Aquifer.

The complaints center primarily on concerns to drinking water and surface water. Complaints include odors, and leaks and spills. Three of the property owners have had private testing done on their drinking water some of which may indicate a problem with their water. However, this data cannot be definitively linked to oil and gas production in the area.

Based on interviews with respective homeowners, other potential impacts from the oil and gas operations in the area include the following. Drilling fluids have been observed being pumped into a fresh water pond where there was a subsequent fish kill. In addition, drill cuttings and drilling muds have been land applied to properties and in one case following precipitation events the wetting of the soil creates “gas bubbles” which reportedly will combust when an ignition source is present. There was also a produced water spill on one of the properties which overflowed the containment berm and spread over the land surface and flowed into Black Creek. An impoundment overflowed into a pasture area. The impoundment has since been removed and it was observed during its removal that the liner was torn. There is conflicting information as to whether the liner was buried on site or removed to another location. It has also been reported that the drilling muds breached containment and subsequently flowed down hill to a creek on an

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adjoining property. The planned soil sampling will not occur at this location, since EPA no longer has access to the property.

#### 1.2.5 Site background- Location B

Location B is central Wise County (Figures 2 and 4). The main complaint in this location is changes in the taste of drinking water. In particular, there is a noticeable increase “salty taste” to the water the closer you get to a production well across the street. The drinking water wells are all of similar depth in the Trinity aquifer. There are nine domestic wells in the vicinity of the production well that will be sampled. There are other production wells in the area as well as a salt water injection well. Other impacts reported are corroding of appliances and the water that sometimes has a rotten egg smell. There is no existing water quality data on any of the wells at this location.

#### 1.2.6 Site background- Location C

Location C is in north central Wise County (Figures 2 and 5). The complaint relates to changes in the taste, quality, color and odor of the water. There are two domestic well at this location and there is preexisting data for one well. This data on one occasion indicated a possible problem with the water, but subsequent testing did not reveal any issues with the water. There are three production wells nearby.

### 1.3 Project/Task Description

The initial Tier II data collection consisted of sampling domestic wells (9), surface water (3) and a supply well for oil and gas operations. However the locations and identity of homeowners and actual locations of the wells are not provided in the QAPP for privacy reasons, but the approximate locations of the sampling points are indicated in Figures 2-5. Additional sampling points were included in the March 2012 sampling (4 domestic wells) and one domestic well owner refused access for this event and in the future. This brings the total domestic wells to 15 and surface water to 3 locations. The December 2012 sampling event included an additional surface water location in Location B. Also, during this event access to the supply well was not granted. Additional changes will be included in any subsequent QAPP revisions. Water analysis will include a range of organic and inorganic constituents, including Gasoline Range Organics (GRO), Diesel Range Organics (DRO), volatile organic compounds (VOCs), semi-volatile organic compounds (SVOCs), glycols, alcohols, low molecular weight acids, dissolved gases, and major and trace cations and anions, strontium isotopes, stable water isotopes, dissolved organic and inorganic carbon. Included in this set of measurements are a selection of components of hydraulic fracturing fluids (e.g., potassium, barium, glycols, alcohols, naphthalene, and boron), potentially mobilized naturally occurring substances such as arsenic, manganese, and other trace metals, and general water quality parameters (e.g., pH, TDS, major anions and cations). Of these target analytes, those that are critical analytes supporting this primary objective are delineated in Table 1. The results from Tier II sampling have indicated that DRO, GRO, and sVOC analytes have not been detected and thus have been removed from

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the critical analyte list. However, at this time no decision has been made about the collection and analysis of these analytes. If the decision not to collect and analyze these analytes is made this will be reflected in future revision of this QAPP. 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 1.

As previously indicated a special sampling event occurred in September 2012 for produced water. This sampling event had a reduced analyte list as described in Section 1.2.1. This was likely a onetime event.

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 2.

#### **1.4 Project Quality Objectives and Criteria**

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

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

SOPs are internal working documents that are not typically made publically available. The majority of these, however, have been made publically available on the EPA Region 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)

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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](http://www.epa.gov/fem/lab_comp.htm). The EPA GP laboratory and the CB&I (formerly Shaw Environmental) laboratories, the on-site contractor laboratory at RSKERC, will be used to analyze select critical analytes listed in Table 1. 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 specific critical analytes listed in Table 1. This laboratory is accredited by National Environmental Laboratory Accreditation Program (NELAP) through the state of Texas.

The Region III Laboratory will be used to analyze glycols, which is not identified as critical at this time. The Region III Laboratory is accredited under the NELAP through the state of New Jersey as the Accrediting Body. The particular method being used by Region III for the glycol 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 method 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 and VOCs. The laboratory must be accredited by NELAP for these parameters.

## **1.6 Documents and Records**

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

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.

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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. Sometime 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)

Tier II sampling began in September 2011 and the QAPP was revised prior to each Tier II sampling event. The QAPP will be revised again prior to initiating Tier III sampling events.

#### 2.1.1 Background Hydrological Information

The Trinity aquifer underlies 68 counties in Texas and Oklahoma (Nordstrom, 1982; Renken, 1998; Reutter and Dunn, 2000). It extends from Kinney County, TX in the southwest to McCurtain County in southeastern Oklahoma and underlies most of Wise County, TX. The major drinking water aquifer in Wise County, TX is the Trinity Aquifer and based on the information obtained from the site visit all the domestic wells included in this case study are screened in the Trinity aquifer.

The Trinity aquifer is divided into several formations of Cretaceous age (Nordstrom, 1982; Renken, 1998): the Pauluxy, the Glen Rose, the Twin Mountains and the Antlers formations. The aquifer is underlain and confined by low-permeability rocks that range in age from Precambrian to Jurassic and where the aquifer does not outcrop is confined by the Walnut Formation (Renken, 1998). The aquifer dips to the south and southeast and has a large amount of vertical anisotropy (Renken, 1998).

In the southern part of Wise Co. the Trinity aquifer is composed of the Pauluxy, Glen Rose and Twin Mountains formations (Nordstrom, 1982, Renken, 1998). However, as you proceed north the Glen Rose formation is pinched out and the Pauluxy and Twin Mountains formations coalesce to form one unit the Antlers formation (Nordstrom, 1982; Renken, 1998).

The Antlers Formation typically consists of a basal conglomerate of gravel overlain by a fine white to gray, poorly consolidated sand in massive-crossbedded layers interbedded with layers of red, purple, or gray clay in discontinuous lenses scattered throughout the formation (Nordstrom, 1982). The middle section contains considerably more clay beds than the upper or lower sections. The upper section of the Antlers formation contains limestone beds and white to yellow pack sand with thin beds of multicolored clay and gravel (Nordstrom, 1982). The thickness for the Antlers formation varies from about 122 m (400 ft) near the outcrops to 274 m (900 ft) near the pinch out of the Glen Rose formation (Nordstrom, 1982). The transmissibility ranges from 13656 to 71492 L d<sup>-1</sup> m<sup>-1</sup> (1100 to 5800 gal d<sup>-1</sup> ft<sup>-1</sup>); permeability ranges from 62 to 435 L d<sup>-1</sup> m<sup>-2</sup> (5 to 35 gal d<sup>-1</sup> ft<sup>-2</sup>); specific capacity ranges from 7.4 to 52 L min<sup>-1</sup> m<sup>-1</sup> (0.6 to 4.2 gal min<sup>-1</sup> ft<sup>-1</sup>); and yield 416 to 2301 L min<sup>-1</sup> (110 to 608 gal min<sup>-1</sup>) (Nordstrom, 1982).

The Twin Mountains formation in Wise Co. consists of medium- to coarse-grained sands, red and gray silty clays, and siliceous conglomerates of chert, quartzite, and quartz pebbles (Nordstrom, 1982). The thickness varies from 61 m (200 ft) near the outcrop to a maximum thickness of 305 m (1000 ft) down dip (Nordstrom, 1982), which a considerable distance away

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from Wise Co. The primary source of recharge to the Twin Mountains formation is precipitation falling on the outcrop area and discharges via springs, evapotranspiration, and pumpage (Nordstrom, 1982). Groundwater in this formation usually occurs under water table conditions in or near the outcrop but can be artesian conditions down dip and the rate of flow is approximately  $1 \text{ m yr}^{-1}$  ( $2 \text{ ft yr}^{-1}$ ) easterly down dip (Nordstrom, 1982). The transmissibility ranges from 51500 to 369000  $\text{L d}^{-1} \text{ m}^{-1}$  (4150 to 29724  $\text{gal d}^{-1} \text{ ft}^{-1}$ ); permeability ranges from 774 to 4073  $\text{L d}^{-1} \text{ m}^{-2}$  (19 to 100  $\text{gal d}^{-1} \text{ ft}^{-2}$ ); specific capacity ranges from 21 to 140  $\text{L min}^{-1} \text{ m}^{-1}$  (1.7 to 11.3  $\text{gal min}^{-1} \text{ ft}^{-1}$ ); and yield 606 to 7343  $\text{L min}^{-1}$  (160 to 1940  $\text{gal min}^{-1}$ ) (Nordstrom, 1982).

The Paluxy Formation is composed predominately of fine- to coarse-grained friable, homogeneous white quartz sand with interbedded sandy, silty, calcareous, or waxy clay and shale (Nordstrom, 1982). In general, the coarse-grained material is in the lower part of the formation. Pyrite and iron nodules are often associated with the sands and contribute to the high iron concentrations in the groundwater (Nordstrom, 1982). The maximum thickness, 122 m (400 ft) is in the northern part of the formation and thins to less than 12 m (40 ft) as you move south. The Paluxy formation yields small to moderate amounts of fresh to slightly saline water. The recharge to this formation is precipitation on the outcrop and seepage from surface water bodies and discharge naturally through springs and evapotranspiration as well artificially through pumping of wells (Nordstrom, 1982). The transmissibility ranges from 15680 to 171400  $\text{L d}^{-1} \text{ m}^{-1}$  (1263 to 13,806  $\text{gal d}^{-1} \text{ ft}^{-1}$ ); permeability ranges from 244 to 6110  $\text{L d}^{-1} \text{ m}^{-2}$  (6 to 150  $\text{gal d}^{-1} \text{ ft}^{-2}$ ); specific capacity ranges from 8.7 to 37  $\text{L min}^{-1} \text{ m}^{-1}$  (0.7 to 3.0  $\text{gal min}^{-1} \text{ ft}^{-1}$ ); and yield 300 to 3230  $\text{L min}^{-1}$  (79 to 853  $\text{gal min}^{-1}$ ) (Nordstrom, 1982).

The Glen Rose Formation consists of hard limestone strata alternating with marl or marly limestone (Nordstrom, 1982). Other information pertaining to this formation has not been found.

Historical water quality data has been reported and is shown in Table 3 (Nordstrom, 1982; Reutter and Dunn, 2000). In general the ranges from both sources are consistent. The data will serve as a historical reference for water quality data in Wise Co. and will provide a reference point for water quality changes that may have taken place since 2000 or as the result of hydraulic fracturing.

### 2.1.2 Ground-Water Monitoring

The ground-water and surface water sampling component of this project is intended to provide a survey of water quality in the area of investigation. GWERD will survey any existing data and speak to landowners to determine suitable ground water wells in the area for the study. Sampling locations were selected by interviewing individuals about their water quality and timing of water quality changes in relation to gas production activities. The locations of the domestic wells are shown in Figures 3-5. The domestic wells will be sampled using downhole pumps or via homeowner taps. It is anticipated that the wells will be sampled by GWERD over a period of about 2 years. The timing of the ground-water sampling events started in the fall of 2011 and is anticipated to continue throughout 2013 (if Tier 3 is initiated). The minimum number of sampling events to determine if an impact is present is estimated to be two (initial

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sampling and confirmation sampling) sampling events. Updates to sampling plans and events will be communicated in subsequent revisions to the QAPP. All information regarding domestic well construction (if available) collected in future parts of the ongoing site history investigation will be reported in revisions to the QAPP.

### 2.1.3 Geophysical Measurements

Geophysical measurements will utilize a combination of electrical and electromagnetic techniques to characterize the subsurface in the vicinity of several domestic wells included in the study. Specific techniques will include frequency domain electromagnetics, time domain electromagnetics, and electrical resistivity. These techniques are each useful for imaging of subsurface geoelectrical properties, especially electrical conductivity. Electrical conductivity is sensitive to moisture content and fluid saturation and useful for locating confining layers and lithological boundaries. Thus this data collection effort is expected to complement ongoing groundwater sampling in the area and provide valuable input to conceptual and/or numerical models for the site.

## 2.2 Sampling Methods

### 2.2.1 Ground-Water Sampling

Domestic wells will be sampled using dedicated pumps (home owner). The design of domestic wells in the case study locations water levels is not obtainable because the wells are sealed and there is no access port available. However, whenever possible, drawdown of the water table will be tracked by taking water level measurements every 10 to 15 minutes during well purging. The water level measurements will follow the RSKSOP-326 standard operating procedure. Water levels will be recorded in a field notebook during purging prior to sampling.

#### 2.2.1.1 Domestic wells

The following is the preferred methodology that will be used for the domestic wells. If it is not possible to use this approach, then these wells will be sampled from the homeowner's tap (ensuring that the tap is not downstream from a water treatment system such as a water softener).

- 1) At each sampling site, GPS coordinates will be collected with a handheld device during the initial round of sampling. Photos will be taken and stamped with the date. Pertinent information about each well will be recorded where possible (e.g., depth, well diameter, configuration, etc.). If possible, the ground-water level will be measured using a Solinst water level indicator (or equivalent) and recorded. In most cases, well construction details are not be available. The goal in domestic well sampling is to purge approximately 3 well screen volumes prior to sampling. In cases where the well volume can be calculated, 3 screen volumes will be targeted as the purge volume. In other cases professional judgment will be used in the field and consider variables such as water volume pumped, water level drawdown, and stabilization of geochemical parameters.

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Initially, the well will be purged for 30 to 60 minutes at a rate greater than 8 L/min to evacuate the standing water in the well. After the initial pumping of the well the flow rate will be reduced to less than 2 L/min and this flow will pass through a flow cell equipped with a YSI 5600 multiparameter probe (or equivalent probes). In all cases, the water volume pumped will be tracked by recording time and purge rate. The rate of pumping will be determined by measuring the water volume collected for a specific time interval into an appropriate calibrated vessel or a 4 L graduated cylinder; the desirable pumping rate through the flow cell should be less than 2 L/min. Draw down will be monitored by measuring the water level (where possible) approximately every 10 to 15 minutes.

- 2) The YSI probe (or equivalent probes) will be used to track the stabilization of pH, oxidation-reduction potential (ORP), specific conductance (SC), dissolved oxygen (DO), and temperature. In general, the criteria that will be used to determine when parameters have stabilized are listed in Table 5. These criteria are initial guidelines; professional judgment in the field will be used to determine on a well-by-well basis when stabilization occurs. The time-dependent changes in geochemical parameters recorded by the YSI probe will be logged by the handheld instrument and recorded on log sheets or in field notebooks.
- 3) Once stabilization occurs, the final values for pH, ORP, specific conductance, dissolved oxygen, and temperature will be recorded.
- 4) After the values for pH, ORP, SC, DO, and temperature have been recorded, the flow cell will be disconnected. A series of unfiltered samples will be collected as follows:
  - a. Four 40 mL VOA vials (amber glass) will be collected, without headspace, for VOC analysis using EPA Method 8260B. Hydrochloric Acid (HCl) will be added to the VOA vial after collection to obtain a pH < 2 as a preservative. The samples will be stored and shipped on ice to a lab designated under the EPA Region 7 contract with ARDL, Inc. for GC-MS analysis.
  - b. Duplicate 60 mL serum bottles will be collected, without headspace, for dissolved gas analysis (e.g., ethane, methane, n-butane, propane). The bottles will contain trisodium phosphate (TSP) 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 CB&I, NRMRL-Ada's on-site contractor for analysis.
  - c. Duplicate 40 mL VOA vials (amber glass) will be collected, without headspace, for low molecular weight acid analysis using RSKSOP-112v6. Sodium Hydroxide (NaOH) will be added to the VOA vial prior to shipping to the field as a preservative. The samples will be stored and shipped on ice to CB&I, NRMRL-Ada's on-site contractor for HPLC analysis.

- d. 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.
- e. Duplicate 1L amber glass bottles will be collected for diesel range organic (DRO) analysis. These samples will be preserved with HCl, pH <2, and shipped on ice to EPA Region VIII Laboratory for analysis.
- f. Duplicate 40 mL amber VOA vials will be collected without headspace for gasoline range organic analysis (GRO). These samples will be preserved with HCl, pH <2, and shipped on ice to EPA Region VIII Laboratory for analysis.
- g. Duplicate 40 mL amber VOA vials will be collected for glycol analysis. These samples will be stored and shipped on ice to EPA Region III Laboratory for analysis.
- h. A 1 L plastic bottle for metals analysis will be filled unfiltered for the analysis of total metals concentrations. Analysis of these samples will be by ICP-OES (EPA Method 200.7) for Ag, B, Ba, Be, Ca, Co, Fe, K, Li, Mg, Mn, Na, P, Si, Sr, Ti, and Zn; by ICP-MS (EPA Method 6020A) for Al, As, Cd, Cr, Cu, Mo, Ni, Pb, Sb, Se, Sr, Th, Tl, U, and V; and Hg using cold vapor method (EPA Method 7470A). These samples will be preserved using concentrated HNO<sub>3</sub> 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 (although ice is not required for metals, see Table 4) 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.
- i. Next a high-capacity ground-water filter (0.45-micron) will be attached to the end of the tubing and a series of filtered samples will be collected. Prior to filling sample bottles, at least 100 mL of ground-water will be passed through the filter to waste.
- j. A 1 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<sub>3</sub> 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 (although ice is not required for metals, see Table 4) to a lab designated under the EPA Region 7 contract with ARDL, Inc.
- k. One 60 mL clear plastic bottle for CE (capillary electrophoresis) sulfate, chloride, bromide and fluoride also filtered. No preservative will be added. The samples will be stored and shipped on ice to the RSKERC general parameters lab.

- l. One 60 mL clear plastic bottle for nitrate + nitrite and ammonium also filtered. This sample will be preserved with sulfuric acid ( $\text{H}_2\text{SO}_4$ ),  $\text{pH} < 2$  (pH test strips will be used as spot checks on samples to confirm that the sample pH is  $< 2$ ). The samples will be stored and shipped on ice to the RSKERC general parameters lab.
- m. One 60 mL clear plastic bottle for iodide analysis also filtered will be collected. No preservative will be added. The samples will be stored and shipped on ice to the RSKERC general parameters lab.
- n. Duplicate 40 mL glass VOA vials will be collected for analysis of dissolved inorganic carbon (DIC) also filtered. No preservative added will be added to these samples. The samples will be stored and shipped on ice to the RSKERC general parameters lab.
- o. Duplicate 40 mL glass VOA vials will be collected for analysis of dissolved organic carbon (DOC) also filtered. These samples will be preserved with phosphoric acid to  $\text{pH} < 2$ . The samples will be stored and shipped on ice to the RSKERC general parameters lab.
- p. A 20 mL glass VOA will be collected for analysis of  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  of water using cavity ring-down spectrometry. The sample will be stored and shipped on ice to CB&I, NRMRL-Ada's on-site contractor for analysis.
- q. 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.
- r. A 1-liter plastic beaker (not filtered) 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 6). Turbidity (EPA Method 180.1) will be measured using a HACH 2100Q portable turbidimeter (or equivalent instrument). Alkalinity will be measured by titrating ground water with 1.6N  $\text{H}_2\text{SO}_4$  to the bromocresol green-methyl red endpoint using a HACH titrator (HACH method 8203, equivalent to EPA Method 310.1 for alkalinity). Ferrous iron will be measured using the 1,10-phenanthroline colorimetric method (HACH DR/2010 spectrometer, HACH method 8146, equivalent to Standard Method 3500-Fe B for wastewater). Dissolved sulfide will be measured using the methylene blue colorimetric method (HACH DR/2010 spectrometer; HACH method 8131, equivalent to Standard Method 4500- $\text{S}^{2-}$  D for wastewater).

See Table 4 for numbers of sample bottles needed for each sample type and field QC (Table 7) samples for ground and surface water sampling.



### 2.2.1.2 Surface Water Sampling

The same set of samples will be collected for surface water sampling as described in section 2.2.1.1. In all cases these surface water samples will be collected from ponds that were identified during the June 2011 reconnaissance trip to the site and a pond identified in the initial sampling events. The sampling locations are based on where sediment collected in the pond as the result of runoff from the site. Sample bottles will be collected using a peristaltic pump with the end of the tubing above the bottom sediment. The locations of additional the sampling sites will be recorded with a handheld GPS device. The site will be photographed. General observations will be recorded in a field notebook. The sampling will be performed as to minimize any capture of sediment into the sampling bottles. Clean tubing will be used prior to any sampling and filtration. The readings from the YSI will be recorded by inserting the probe set with protective cover directly into the surface water body and allowing readings to stabilize. This is an initial screening of the surface water. If needed, a more detailed sampling to ensure representativeness will be performed in future sampling trips along with a revision to the QAPP outlining the details of how the sampling will be accomplished.

See Table 4 for numbers of sample bottles needed for each sample type and field QC (Table 7) samples for ground and surface water sampling.

### 2.2.1.3 Production well sampling

As described in version 3 of the QAPP for the September 2012 sampling event, produced water from the production well was sampled from the gas-liquid separator at a sampling port near the base of the gas-liquid separator tank. A piece of clean tubing was attached to the valve port and the other end of the tubing was attached to a 20 L carboy. The carboy was vented with a stack constructed using an approximately 6 foot PVC pipe. The valve on the port was opened far enough to allow a steady, but slow flow rate. Once the carboy was filled the valve on the port was closed and the tubing was disconnected from the port and carboy. A new clean piece of tubing was placed in the carboy just above the bottom of the carboy. This tubing was then connected to a peristaltic pump. The peristaltic pump was then turned on and sample bottles were filled. Once this was completed sample bottles were collected and preserved as described in Section 2.2.1.1. These samples were analyzed for stable isotopes of water, Sr isotopes, metals and anions.

## 2.2.2 Geophysical Methods

### 2.2.2.1 Data Acquisition

Shallow (0-3 m depth) characterization data will be acquired using the Geophysical Survey Systems, Inc. Profiler EMP400 frequency domain electromagnetic induction instrument.

Surveys will be performed on two separate rectangular grids. Grid locations will be determined by field personnel on site based on consultation with the case study PI and Carl Miller. The grid will be set up with parallel profiles and at least two crossing profiles will be included. Data acquisition will be performed in accordance with RSKSOP 333 (2011). Data will be acquired at 1 kHz, 8 kHz, and 15 kHz with the instrument carried in the vertical dipole inline mode with the low carry handle. Acquisition rate will be set to continuous at a rate of 1 reading per second. GPS data will be acquired concurrently with the electromagnetic data. The GPS will be powered on at least 10 minutes prior to beginning the survey to allow the GPS adequate time to acquire a signal and establish a stable positioning fix. GPS validity criteria will be set to “number of visible satellites  $\geq 4$ ”. Spacing between individual profiles will not exceed 3 meters.

Intermediate (up to 20 m depth) characterization data will be acquired using an Advanced Geosciences, Inc. Supersting R8 Earth Resistivity Meter. Electrical resistivity data acquisition will be performed in accordance with RSKSOP 336 (2012). Calibration of the SuperSting R8 resistivity instrument is performed by the manufacturer, typically on an annual basis. During this procedure, correction values are stored in the system memory. When utilizing the instrument, calibration of the measurements is performed automatically by the microprocessor based on these stored correction values. A copy of the most recent calibration certificate has been requested from the equipment supplier. This documentation will be maintained with the raw data for this field study.

Depending upon the number of areas of interest determined by the frequency domain electromagnetic survey, up to 1.5 days of electrical resistivity surveying will be performed which equates to roughly 5 to 6 survey lines. Electrode spacing for each survey line will be determined in the field based on the number and location of anomalous regions defined by the Profiler survey. Electrode spacing will be at least 0.5 m and will not exceed 3 m. Survey line layout will be performed using a tape measure. The electrodes will be hammered into place and then the cabling will be attached. Contact resistance will be measured each time the electrodes are moved. In cases where contact resistance exceeds 2000 ohms, the electrode will be hammered deeper into the ground and if necessary a dilute salt water solution (approximately 0.33 L) will be used to wet the ground in the vicinity of the electrode. .

Deep (>20 m) characterization data will be acquired using time-domain electromagnetics (TDEM). TDEM data acquisition will be performed in accordance with RSKSOP 335 (2012). The TEM 47 calibration is performed within the TEST submenu by selecting AUTO CALI. When this operation is performed, a set of calibration components will be stored in the memory and kept until AUTO CALI is executed again. Procedures in case the system fails to automatically calibrate are described later in this section. The automatic system calibration will

be performed before starting any new survey and repeated at least weekly for longer term surveys. A calibration check is performed within the TEST submenu by selecting CALI CHECK. If any of the system components fails the check, a message “FAIL” will be displayed. Procedures in case the system fails a calibration check are described later in this section. The system calibration check will be performed at the start of each day of data acquisition at a minimum. If the system fails to automatically calibrate or fails a calibration check, reset the receiver and run AUTO CALI again. If failed again, use CALI CHECK with “time constant = DC” to determine which gates are abnormal and whether compensation or correction can be made manually after data acquisition. Date and time of all calibration procedures (i.e. AUTO CALI and CALI CHECK) will be recorded in a field notebook. In case of a calibration failure or calibration check failure, all steps taken to correct the failure will be recorded in a field notebook.

Domestic water wells in this area are typically completed in the Trinity Aquifer at depths between 90 and 120 meters. Based on this, survey parameters will be selected to allow electrical conductivity imaging to a depth of approximately 150 meters. Equipment used for this survey will be rented. The description of data acquisition activities provided here is based on the Geonics Protem 47/57 Time Domain Electromagnetics system. If this particular system is not available for rental, a system with equivalent specifications will be used instead and this will be documented in the field notes and survey report. Survey configuration will be a central loop sounding. In this configuration, a large square transmitter loop will be laid out at each TDEM sounding location. Different loop sizes will be tested to ensure that the depth of investigation is adequate for characterizing the site (approximately 150 m depth is desired). A calibrated multi-turn receiver coil will be placed in the center of this loop to measure the time decaying magnetic field associated with transmitter turn-off. The receiver voltage varies rapidly immediately after shut off and more slowly as time progresses, thus time gates for sampling the voltage will be chosen accordingly in order to adequately characterize the decay curve.

#### 2.2.2.2 Data Processing

The raw data measured by the Profiler EMP400 instrument is the magnitude of the in-phase and quadrature component of the secondary field at each frequency, output in parts per million (ppm) relative to the primary field. Data processing will include linear interpolation of survey line data to smooth the GPS positioning data in case signal coverage is lost during the survey. The data for each grid will be plotted in contour maps to allow for interpretation of the shallow geoelectrical structure and identification of areas of interest for further investigation using the electrical resistivity method. Survey outputs will be the raw data files, contour plots of in phase and quadrature data at each frequency, and contour plots of apparent conductivity for the 15 kHz data. A linear repeat section at least 20 meters in length will be walked at the beginning and end

of each survey for QA/QC purposes. Results from this repeat section, along with the orthogonal crossing profiles, will be used to evaluate data repeatability for each survey. Minor differences are expected for repeat measurements of the EM data at a specific location. These differences typically arise due to inherent system noise and changes in height or orientation of the coils. If the relative percent difference exceeds 10 percent for any repeat measurement at a specific location, an attempt will be made to determine the cause of the difference (e.g. large differences would be anticipated following a precipitation event). If time and resources allow, a new set of measurements will be acquired in the area of concern. If reacquisition is not possible, the data will be flagged and used at the discretion of the project geophysicist.

Data output for the electrical resistivity surveys is apparent resistivity, measured in ohm-meters. The data will be pre-processed to remove data with low signal to noise and/or large standard deviation for repeat measurements. The data will then be modeled using commercially available 2D electrical resistivity inversion software. Images showing electrical resistivity versus depth along the profiles will be the ultimate output of the electrical resistivity surveying. These images will be presented as contour plots. Modeling uncertainty will be evaluated based on the RMS misfit and by constructing region of data influence images as described in Oldenburg and Li (1999).

The raw data for the TDEM survey is the voltage induced in the receiver coil measured at several discrete times following transmitter shut-off. Data processing will consist of discarding data values with excessively high standard deviation. In the event the standard deviation of a measurement exceeds 50% of the magnitude of the measurement, the measurement will be discarded without further analysis. All data with standard deviation of less than 10% of the measurement magnitude will be retained. For standard deviation greater than 10% but less than 50%, the data will be flagged and retained at the discretion of the project geophysicist. These values are typically found in either the very early time or late time data and thus only affect the shallowest and deepest portions of the modeling. Inverse modeling will be used to construct 1D models of electrical resistivity versus depth. Where station spacing is relatively close, the 1D inversion models will be stitched together to produce 2D images of electrical conductivity. At least two soundings will be performed in an area where an electrical resistivity model is available so that comparison of the TDEM results with the electrical resistivity results is possible.

### 2.2.2.3 Interferences

The geophysical methods planned for this site characterization are susceptible to similar sources of external interference. These sources include buried metallic objects, surface metallic objects, overhead power lines, radio and radar waves, electrical storms and geological interferences. To the extent possible, these sources of noise will be avoided, and if not avoidable, will be

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documented in the field notes and the survey report. For example, surveys transects running perpendicular to a metallic fence will be less affected than surveys performed parallel to the same fence. All of the equipment to be used for this study includes data filters designed to minimize power line noise. Additionally, all data will be stacked, meaning that multiple measurements will be recorded at each location in order to allow for reduction in random noise.

#### 2.2.2.4 Location Surveying

Measurement locations will be surveyed using a Wide Area Augmentation System (WAAS) enabled GPS receiver. This is expected to provide a measurement accuracy of approximately 1.0 m laterally and 1.5 m vertically. This level of accuracy assumes a clear view of the southern sky which is expected at this particular site. For the purposes of this preliminary site characterization, this level of accuracy is sufficient. However, key measurement locations (start, midpoint, and end of each survey line) will be marked with wooden brush-top stakes to allow for more accurate surveying at a later time, should the need arise. Additionally, these markings will provide for reoccupation of measurement locations if deemed necessary.

### 2.3 Sample Handling and Custody

#### 2.3.1 Before Sampling Packing

Before going to sample, sample containers for each sampling point will be placed into a cooler designated by that location.

#### 2.3.2 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 WISCTXGWxx-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. Labeling of surface water samples will follow the same approach, except instead of GW, SW will be used in the identification.

#### 2.3.3 Water Sample Packing, Shipping, and Receipt at Laboratories

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Samples collected from each location will be 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. With the exception of samples to be analyzed at GWERD, coolers will be sent via Fedex or UPS, overnight, to the appropriate lab with chain of custody forms (see Figure 6) and custody seal. Those destined for GWERD could be shipped back to GWERD or in some instances will be transported back in the field crew's vehicles.

R.S. Kerr Environmental Research Center  
919 Kerr Research Drive  
Ada, OK 74820  
580-436-8942 or 580-436-8507  
ATTN: Tiffany Thompson or Trina Perry  
(for samples analyzed by both CB&I and EPA General Parameters Laboratory)

Upon receipt at RSKERC, all samples shall be logged-in and distributed to appropriate analysts by CB&I using RSKSOP-216v2, *Sample Receipt and Log-in Procedures for the On-site Analytical Contractor*. Before opening the ice chests the custody seal is checked by the sample custodian to verify it is intact. Ice chests are opened and the temperature blank is located to take the temperature and it is noted whether or not ice is still present. Chain-of-custody (COC) form and samples are removed. Samples are checked against the COC. The observations concerning temperature, custody seal, if ice was not present, and any sample discrepancies are noted on the COC and the sample custodian signs the form. A copy of the COC is distributed to the PI and CB&I retains a copy. The PI should be notified immediately if samples arrive with no ice and/or if temperature is  $>6^{\circ}\text{C}$ .

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

EPA Region 8 Lab  
16194 West 45<sup>th</sup> 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  
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ATTN: Kevin Martin

Samples for Sr isotope analysis will be sent to:

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

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

Samples to be shipped to the EPA Region 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 6) and the cooler will be sealed with custody seals. Sample receipt and log-in will be conducted as described in the contract lab's SOPs.

## **2.4 Analytical Methods**

### **2.4.1 Ground, Surface, and Produced Waters**

Ground-water samples will be collected and analyzed using the methods listed in Table 4. SOPs are internal working documents that are not typically publically available. The majority of these, however, have been made available on the EPA Region 8 web site for a separate research effort: <ftp://ftp.epa.gov/r8/pavilliondocs/LabSOPsAndLabProducedReports/AnalyticalMethodologyUsed-RobertSKerrLaboratory/>.

Region III's LC-MS-MS method for glycols is under development with the intent to eventually have a validated, documented method. Aqueous samples are injected directly on the HPLC after tuning MS/MS with authentic standards (2-butoxyethanol, di-, tri-, and tetraethylene glycols) and development of the HPLC gradient. HPLC column is Waters (Milford MA) Atlantis dC18 3um, 2.1 x 150mm column (p/n 186001299). HPLC gradient is with H<sub>2</sub>O and CH<sub>3</sub>CN 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

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for the instrument calibration. The working, linear range varies for each compound but is about 10-1000  $\mu\text{g L}^{-1}$  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  $>0.99$ . An instrument blank is also run after every 10 sample injections. The performance criteria are provided in Table 8. The system is tuned with individual authentic standards (at  $1\text{mg L}^{-1}$  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  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  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 4.

The RSKSOPs and their associated target analyte list are presented in Table 9.

For the semivolatiles the target analyte list is presented in Table 10. Surrogates used include phenol-d6, 2-fluorophenol, 2,4,6-tribromophenol, nitrobenzene-d5, 2-fluorobiphenyl, and p-terphenyl-d14. The concentrations used for the surrogates shall be spiked at  $5\ \mu\text{g mL}^{-1}$ . 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  $\pm 20\%$ . (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  $10 \mu\text{g L}^{-1}$ .

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  $50 \mu\text{g L}^{-1}$ .

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).

The samples analyzed by 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 will perform the analysis in accordance with the EPA Methods 6020A for ICP-MS and 200.7 for ICP-OES. Both total and dissolved metals will be analyzed. Sample digestion for total metals will be done accordance with EPA Method 200.7. Samples for dissolved metals will not digested. Samples collected for mercury and volatile organic compounds will be analyzed in accordance with EPA Methods 7470A and EPA Method 8260B, respectively. For the metals and VOCs the target analyte lists are presented in Tables 11 and 12.

## 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 13. Matrix spikes sample spiking levels are determined at the discretion of the individual analysts (based on sample concentrations) and are included with the sample results. Corrective actions are outlined in the appropriate SOPs and when corrective actions occur in laboratory analysis it will be documented and the PI will be notified as to the nature of the corrective action and the steps taken to correct the problem. The PI will review this information and judge if the corrective action was appropriate.

Corrective Actions: If any samples are affected by failure of a QC sample to meet its performance criteria, the problem shall be corrected and samples will be re-analyzed. If re-analysis is not possible (such as lack of sample volume), 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 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, quantization (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 10. The DL and RL for DRO and GRO are both at 20 µg/L.

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

(6) See Table 14 for QC types and performance criteria.

Corrective Actions: If any samples are affected by failure of a QC sample to meet its performance criteria, the problem shall be corrected and samples will 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 15).
- (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 8 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 16):

- (1) Data verification shall be performed by USGS to ensure data meets their SOP requirements.
- (2) Complete data packages shall be provided electronically including tabulation of final results, copies of chain-of-custody forms, list of SOPs used (title and SOP #), calibration data, QA/QC data, data qualifiers, deviations from method, and interpretation of impact on data from deviations from QC or method requirements.
- (3) See Table 16 for QC types and performance criteria

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

For analyses 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. VOCs: 14 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 (unless otherwise noted in the SOW) and all applicable QC criteria shall be met based on the method utilized (initial calibration, continuing calibration, tune, internal standard, surrogate, etc).
  - b. The project plan submitted by the contractor for this project must include the accuracy, precision, & relative percent difference applicable to each target compound/analytes required in the SOW. The submitted limits shall be at least as stringent as those specified in the method being utilized. If the contractor does not have established internal limits for a given parameter, then the limits in the method shall apply.
- (3) Complete data package shall be provided electronically by 2:00pm CST on the 35th day after receipt of the last sample for a given sampling event. (NOTE: If the due date falls on a Holiday, Saturday or Sunday, then the deliverables are due to EPA by 12:00pm on the first subsequent business day). Electronic deliverables shall include all analytical results (field and laboratory QC samples) and the associated narrative. In addition to the

normal narrative and Excel spreadsheet required, the laboratory shall provide an electronic “CLP type” data package that includes the written narrative, Forms 1’s, QC data, & all supporting raw data. The package shall be organized and paginated. The entire data package shall be provided in a .pdf file format. The complete data package in .pdf format shall be provided within 48 hours of the electronic results and narrative. The associated narrative shall address each of the applicable areas listed below for every parameter group in the task order. This includes a statement that the QA/QC criteria for every applicable area were in control or, conversely, that one or more QC outliers were present. For areas with outliers, the narrative shall specify each parameter which was out of control and the associated samples that were affected. In addition, the narrative shall indicate any and all corrective actions taken and the results of those actions as well as impact on the associated samples. (Holding Times, Initial Calibration, Continuing Calibration, Surrogates, Internal Standards, Laboratory Duplicate, Matrix Spike/Matrix Spike Duplicate, Laboratory Control Sample, and Method Blanks)

- (4) Contract required quantitation limits (CRQL) for the metals and VOCs are as provided in Tables 11 and 12.
- (5) The laboratory shall be subject to an on-site QA audit. A QA audit was conducted on Southwest Research Institute, the subcontractor to ARDL, Inc. If a different laboratory is selected for future analyses, it will be audited. The laboratory must also analyze Performance Evaluation (Proficiency Testing ) samples. The laboratory must be NELAP-accredited, which are required to analyze these samples twice a year.
- (6) See Tables 17, 18, 19 and 20 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

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solution. This is done by summing and comparing the net positive and negative charge from the measured concentrations of anions and cations. The agreement should be within 10%. Poor agreement would suggest that some major solute(s) is not accounted for in the analytical measurements or could otherwise point to an analytical error. 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 9. 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. 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.

### 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  $a > b$ .

For duplicate samples collected in the field, the RPD will only be calculated where analyte concentrations for both samples (primary and duplicate) are >5 times the quantitation level.

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RPDs are expected to be less than or equal to 30%. If RPDs are greater than 30%, actions will be taken to better understand the reason and data will be flagged. The duplicate samples will be used for the purposes of determining reproducibility. In all cases, results reported in prepared reports or publications will be based on the primary sample. Results for duplicate samples will be reported in QA appendices or supporting material. Analytes detected in various blank samples will be evaluated and flagged, if appropriate, in presentations of data. Generally, blank contamination will be evaluated for significance when blank contaminants are above reporting limits. Samples will be flagged if their concentrations are less than 10 times that in the associated blank and greater than the QL.

### **Matrix Spike Recovery**

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

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

## **2.6 Instrument/Equipment Testing, Inspection, and Maintenance**

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

SOPs are internal working documents that are not typically publically available. The majority of these, however, have been made available on the EPA Region 8 web site for a separate research effort:

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

## **2.7 Instrument/Equipment Calibration and Frequency**

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

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

For the Region III and Region VIII laboratories, as well as the Region VII contract laboratory, these requirements are identified in their SOPs and in Tables 8 and 14, 17-20, Table 16 for the USGS laboratory and Table 13 for RSKERC.

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 5), 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  $\pm 10\%$  of known concentrations and in the case of pH must be within  $\pm 0.2$  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  $1 \text{ mg Fe}^{2+} \text{ L}^{-1}$  standard and the results should be between  $0.90 - 1.10 \text{ mg Fe}^{2+} \text{ L}^{-1}$ . Similarly, the precision will be tested using the standard performing the measurement three times on this solution. The single operator standard deviation should be  $\pm 0.05 \text{ mg Fe}^{2+} \text{ L}^{-1}$ . For sulfide method the accuracy and precision will be checked using a standard solution of sodium sulfide prepared in the laboratory that has been titrated with sodium thiosulfate to determine its concentration. Accuracy should be within  $\pm 10\%$  of the expected concentration and the coefficient of variation should be  $<20\%$ . Turbidity will be checked against turbidity standards supplied by Hach (or equivalent) in the field at the beginning of the day, midday, and at the end of the day and should be within  $\pm 10\%$  of expected readings. 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 be run. This process will continue until there is no detectable analyte in the blanks.

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For turbidity, blank measurements of  $\leq 1.0$  NTU are acceptable. Standards for redox sensitive species such as sulfide and ferrous iron are difficult to use in the field because once exposed to atmospheric oxygen their concentrations can change. Similarly calibration standards for alkalinity are sensitive to atmospheric carbon dioxide. Alkalinity measurements will use a 1.6N or 0.16N  $\text{H}_2\text{SO}_4$  solution to titrate samples and standards in the field. The titrator will be checked in the laboratory using a 250  $\text{mg L}^{-1}$  standard made from  $\text{Na}_2\text{CO}_3$ . The analyzed value should be in the range of 225- 275  $\text{mg L}^{-1}$ . Duplicates will be performed once a day or on every tenth sample. Duplicate acceptance criteria are  $\text{RPD} \leq 15$ . The values obtained for each duplicate sample will be recorded in the field notebook and RPD will be calculated (section 2.5.4) and recorded in the field notebook. If the duplicate samples fail an additional duplicate sample will be taken and reanalyzed. If the additional duplicate samples fail to meet the QC criteria, then the instruments will be checked and corrective action taken. The corrective actions will be recorded in the field notebook. Samples collected between the last valid duplicate sample and the failed duplicate sample will be flagged.

## **2.8 Inspection/Acceptance of Supplies and Consumables**

RSKSOPs, Region VIII, Region III, and Region VII contract laboratory SOPs, and the USGS strontium isotope procedure 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 21. It should be noted that the vendors listed in Table 21 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. Water used for field blanks, equipment blanks, and trip blanks will be taken from the RSKERC (NANOPure). Water will be filled into several high-capacity carboys and taken to the field.

## **2.9 Non-direct Measurements**

Non-direct measurements (also known as existing data or secondary data) are data from sources other than those 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 Texas Water Development Board have published reports and databases for ground water data for the Trinity Aquifer and surface water data in Wise Co., TX. 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 were made available in some cases from the individual homeowners. Homeowner data were used as background information for the PI to assist with project planning. Homeowner data could be used as part of the reporting process in delineating background water quality conditions. Other data sources such as data from published peer reviewed literature could also be used. The data quality issues will most likely be unknown for these types of data. However, since the data 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 specific retrospective hydraulic fracturing case study. This will be done in accordance with the ORD PPM 13.2, *Paper Laboratory Records* as well as EPA Records Schedule 501, *Applied and Directed Scientific Research*. Finally, the Hydraulic Fracturing Quality Management Plan Rev. No. 1, Section 5, contains additional information on data management for Hydraulic Fracturing Research.

Data will be submitted to the PI as either hard copies (field notes), or electronically (laboratory data) in Excel spreadsheets on CD or DVD or via email. Data in hard copy form will be 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 spot-checks, the entries will be corrected. Detection of an error will prompt a more extensive inspection of the data, which could lead to a 100% check of the data set being entered at that time if multiple errors are found.

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

### 2.10.1 Data Recording

Data collected will be recorded into field notebooks and entered into 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 to compile all data and records.

### 2.10.3 Analysis of Data

All data collected associated with groundwater and surface water sampling will be summarized by the PI 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 by the QA staff (see Section 4.2). If errors are found they will be corrected by the PI and resubmitted to the QA staff to verify that the data corrections were made and the final data 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

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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<sub>4</sub>, HCO<sub>3</sub>, pH) and temperature are entered into a user interface. The software uses the Debye-Hückel equation to estimate ion activity coefficients and a selectable thermodynamic database in order to calculate mineral saturation indices for minerals that may be undersaturated, at equilibrium, or oversaturated in the prescribed system (Bethke, 1996). The Lawrence Livermore National Laboratory database (thermo.com.v8.r6) will be used for calculating aqueous speciation and mineral saturation. This software may also be used to construct activity-activity diagrams, such as Eh-pH diagrams. Such diagrams can be helpful in describing processes that impact the concentration of redox-sensitive elements, like iron and manganese.

## **3.0 Assessment and Oversight**

### **3.1 Assessments and Response Actions**

Technical Systems Audits (TSAs), Audits of Data Quality (ADQs), and Performance Evaluations (if not currently done) will be conducted early in the project to allow for identification and correction of any issues that may affect data quality. TSAs will be conducted on both field and laboratory activities. Laboratory TSAs will focus on the critical target analytes. Detailed checklists, based on the procedures and requirements specified in this QAPP, related SOPs, and EPA Methods will be prepared and used during these TSAs. These audits will be conducted with QA contract support, with oversight by 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 EPA QAMs or by a QA support contractor, 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 September 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 CB&I-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. CB&I and the EPA GP Lab analyze PE samples routinely on a quarterly basis. The Region VIII laboratory is currently analyzing Performance Evaluation (aka Proficiency Testing) samples twice a year and data from the past two studies have been provided to the QAM. Glycols analyzed by Region III are not critical, but even if they become critical, PE samples are not available commercially, so PEs will not be done by their laboratory for glycols. Strontium isotopes analyzed by the USGS laboratory are not critical and 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. Those prepared by the QA support contractor will be reviewed and approved by the QAM prior to release. Specific actions will be identified in the reports.

## **4.0 Data Validation and Usability**

### **4.1 Data Review, Verification, and Validation**

Criteria that will be used to accept, reject, or qualify data will include specifications presented in this QAPP, including the methods used and the measurement performance criteria presented in Tables 5, 8, 13, 14, 16, 17, 18, 19 and 20. In addition, sample preservation and holding times will be evaluated against requirements provided in Table 4.

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

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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 22 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 by 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-276v4. Determination of Major Anions in Aqueous Samples Using Capillary Ion Electrophoresis with Indirect UV Detection and Empower 2 Software. 11 p.

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

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## 6.0 Tables

**Table 1. Critical analytes.**

| Analyte <sup>†</sup>  | Laboratory Performing the Analysis |
|---|------------------------------------|
|   |                                    |
| Volatile Organic Compounds (VOC)*                                   | Region VII contract laboratory     |
| Dissolved Gases**   | CB&I                               |
| Metals (As, B, Ba, Fe, Mn, Se, Sr, V, U)                            | Region VII contract laboratory     |
| Major Cations (Ca, Mg, Na, K)                                       | Region VII contract laboratory     |
| Major Anions (Cl, Br <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup> ) | RSKERC general parameters lab      |

\*alcohols (isopropyl alcohol and t-butyl alcohol), naphthalene

\*\*methane, ethane, propane, n-butane

<sup>†</sup>DRO, GRO and sVOCs are no longer considered critical because these have not been detected in previous samplings. However, no decision has been made to discontinue collection and analyses to date.

Many target analytes were initially considered as critical. A tiered approach will be used to further refine the identification of specific compounds as critical. Data from the Tier II 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.

**Table 2. Tentative schedule of field activities for the Hydraulic Fracturing Case Study Wise County, TX.**

| Media          | Tier II    |            |                  |           |          |
|----------------|------------|------------|------------------|-----------|----------|
|                | Sept. 2011 | March 2012 | Sept. 2012       | Dec. 2012 | May 2013 |
| Location A     |            |            |                  |           |          |
| Groundwater    | XXX        | XXX        |                  |           |          |
| Surface Water  | XXX        | XXX        |                  |           |          |
| Location B     |            |            |                  |           |          |
| Groundwater    | XXX        | XXX        | XXX <sup>S</sup> | XXX       | XXX      |
| Geophysics     |            | XXX        |                  |           |          |
| Produced Water |            |            | XXX              |           |          |
| Surface Water  |            |            |                  | XXX       | XXX      |
| Location C     |            |            |                  |           |          |
| Groundwater    | XXX        | XXX        |                  |           |          |

<sup>S</sup>Special sampling for produced water.

**Table 3. Water quality of the Trinity Aquifer in Wise County, TX. Data from Reutter and Dunn, 2000; Nordstrom, 1982.**

| Parameter   | Reutter and Dunn, 2000 |      |      | Nordstrom, 1982 |      |
|---|------------------------|------|------|-----------------|------|
|   | Min                    | Max  | Mean | Min             | Max  |
| Specific Conductance ( $\mu\text{S cm}^{-1}$ )        | 510                    | 2380 | 1096 | 706             | 2880 |
| pH  | 6.6                    | 9.0  | 7.4  | 6.8             | 8.8  |
| Dissolved Oxygen ( $\text{mg L}^{-1}$ )               | 0.1                    | 2.9  | 1.4  |                 |      |
| Ammonia ( $\text{mg N L}^{-1}$ )                      | <0.01                  | 1.1  | 0.2  |                 |      |
| Nitrate ( $\text{mg n L}^{-1}$ )                      | <0.05                  | 6.30 | 1.72 | 0.4             | 44   |
| Total P ( $\text{mg P L}^{-1}$ )                      | <0.01                  | 0.04 | 0.01 |                 |      |
| Dissolved P ( $\text{mg P L}^{-1}$ )                  | <0.01                  | 0.04 | 0.01 |                 |      |
| Bicarbonate ( $\text{mg L}^{-1}$ )                    | 160                    | 517  | 400  | 303             | 550  |
| Alkalinity ( $\text{mg CaCO}_3 \text{ L}^{-1}$ )      | 130                    | 420  | 328  |                 |      |
| Bromide ( $\text{mg Br L}^{-1}$ )                     | 0.12                   | 3.00 | 0.68 |                 |      |
| Calcium ( $\text{mg Ca L}^{-1}$ )                     | 4                      | 200  | 79   | 1               | 182  |
| Chloride ( $\text{mg Cl L}^{-1}$ )                    | 16                     | 500  | 112  | 8               | 680  |
| Fluoride ( $\text{mg F L}^{-1}$ )                     | <0.01                  | 1.20 | 0.30 | 0.1             | 1.5  |
| Hardness ( $\text{mg CaCO}_3 \text{ L}^{-1}$ )        | 19                     | 850  | 305  | 5               | 770  |
| Dissolved Iron ( $\mu\text{g Fe L}^{-1}$ )            | <3                     | 320  | 46   | 0.1             | 1.3  |
| Magnesium ( $\text{mg Mg L}^{-1}$ )                   | 2                      | 86   | 26   | 1               | 82   |
| Potassium ( $\text{mg K L}^{-1}$ )                    | 1.0                    | 4.3  | 2.6  |                 |      |
| Dissolved Silica ( $\text{mg SiO}_2 \text{ L}^{-1}$ ) | 9                      | 26   | 19   | 8               | 27   |
| Sodium ( $\text{mg Na L}^{-1}$ )                      | 30                     | 310  | 114  | 34              | 600  |
| Sulfate ( $\text{mg SO}_4 \text{ L}^{-1}$ )           | 20                     | 200  | 74   | 24              | 263  |
| Dissolved Aluminum ( $\mu\text{g Al L}^{-1}$ )        | 1                      | 5    | 3    |                 |      |
| Dissolved Arsenic ( $\mu\text{g As L}^{-1}$ )         | <1                     | 4    | 1    |                 |      |
| Dissolved Barium ( $\mu\text{g Ba L}^{-1}$ )          | 32                     | 240  | 106  |                 |      |
| Dissolved Chromium ( $\mu\text{g Cr L}^{-1}$ )        | <1                     | 8    | 1    |                 |      |
| Dissolved Copper ( $\mu\text{g Cu L}^{-1}$ )          | <1                     | 18   | 6    |                 |      |
| Dissolved Lead ( $\mu\text{g Pb L}^{-1}$ )            | <1                     | 4    | 1    |                 |      |
| Dissolved Manganese ( $\mu\text{g Mn L}^{-1}$ )       | <1                     | 120  | 15   |                 |      |
| Dissolved Molybdenum ( $\mu\text{g Mo L}^{-1}$ )      | <1                     | 2    | 1    |                 |      |
| Dissolved Nickel ( $\mu\text{g Ni L}^{-1}$ )          | <1                     | 4    | 1    |                 |      |
| Dissolved Selenium ( $\mu\text{g Se L}^{-1}$ )        | <1                     | 14   | 2    |                 |      |
| Dissolved Uranium ( $\mu\text{g U L}^{-1}$ )          | <1                     | 93   | 22   |                 |      |
| Dissolved Zinc ( $\mu\text{g Zn L}^{-1}$ )            | 4                      | 96   | 22   |                 |      |
| Dissolved Organic Carbon ( $\text{mg L}^{-1}$ )       | 0.2                    | 1.3  | 0.5  |                 |      |



**Table 4. Ground and Surface Water Sample Collection.**

| Sample Type   | Analysis Method (EPA Method)   | Sample Bottles/# of bottles* | Preservation/ Storage   | Holding Time(s)       |
|---|--|------------------------------|---|-----------------------|
| Dissolved gases                                     | No EPA Method (RSKSOP-194v4 &-175v5)                                       | 60 mL serum bottles/2        | No Headspace<br>TSP <sup>†</sup> , pH>10;<br>refrigerate ≤6°C <sup>††</sup> | 14 days               |
| Dissolved Metals (filtered)                         | EPA Methods 200.7,6020A, and 7470A   | 1 L plastic bottle/1         | HNO <sub>3</sub> , 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 <sub>3</sub> , pH<2; room temperature                                   | 6 months (Hg 28 days) |
| SO <sub>4</sub> , Cl, F, Br                         | EPA Method 6500 (RSKSOP-276v4 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 <sub>3</sub> + NO <sub>2</sub> , NH <sub>4</sub> | EPA Method 350.1 and 353.1 (RSKSOP-214v5)                                  | 60 mL plastic/1              | H <sub>2</sub> SO <sub>4</sub> , 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/4 | H <sub>3</sub> PO <sub>4</sub> , pH<2; refrigerate ≤6°C                     | 28 days               |
| Volatile organic compounds (VOC)                    | EPA Method 8260B   | 40 mL amber glass VOA vial/4 | No Headspace<br>HCl, pH<2; refrigerate ≤6°C                                 | 14 days               |
| Low Molecular Weight Acids                          | No EPA Method (RSKSOP-112v6)   | 40 mL glass VOA vial/2       | 1M NaOH, 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                |
| Semi-volatile                                       | EPA Method   | 1L Amber glass bottle/2      | Refrigerate ≤6°C  | 7 days until          |

| Sample Type                              | Analysis Method (EPA Method)                          | Sample Bottles/# of bottles*   | Preservation/ Storage   | Holding Time(s)                                   |
|--|---|--|---|---|
| organic compounds                        | 8270D, (ORGM-515 r1.1)                                | 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                              |   | 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 $\leq 6^{\circ}\text{C}$                 | 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<br>HCl, pH<2; refrigerate $\leq 6^{\circ}\text{C}$ | 14 days   |
| Gylcols                                  | No EPA Method (Region III method**)                   | 40 mL amber glass VOA vial/2   | Refrigerate $\leq 6^{\circ}\text{C}$                            | 14 days   |
| $^{87}\text{Sr}/^{86}\text{Sr}$ analysis | No EPA Method (Thermal ionization mass spectrometry ) | 500 mL plastic bottle/2  | Refrigerate $\leq 6^{\circ}\text{C}$                            | 6 months  |

† trisodium phosphate

†† above freezing point of water

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

\*\*under development

**Table 5. Field parameter stabilization criteria and calibration standards.**

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

**Table 6. Ground Water Field Analytical Methods.**

| Parameter            | Method   | Equipment  |
|----------------------|--|--|
| Alkalinity           | EPA Method 310.1; 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 <sup>2-</sup> 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 7. 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 preservative.   | In the field, reagent water is collected into sample containers with preservatives.   | One per day of sampling   | < QL: Sample will be flagged if >QL and analyte concentration < 10x concentration in blank..                     |

\*\*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° C. These samples will be flagged accordingly.

**Table 8. 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 9. RSKERC Detection and Quantitation limits for various analytes.**

| Analyte  | Method                                      | MDL                  | QL or LOQ            |
|--|---|----------------------|----------------------|
| Dissolved Gases*   |   | $\mu\text{g L}^{-1}$ | $\mu\text{g L}^{-1}$ |
| 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  |   | $\text{mg L}^{-1}$   | $\text{mg L}^{-1}$   |
| DOC  | EPA Method 9060A <sup>A</sup>               | 0.067                | 0.50                 |
| DIC  | EPA Method 9060A <sup>A</sup>               | 0.017                | 0.50                 |
| Anions   |   | $\text{mg L}^{-1}$   | $\text{mg L}^{-1}$   |
| Br <sup>-</sup>  | EPA Method 6500 <sup>B,C</sup>              | 0.248 ( 0.110)       | 1.00 (1.00)          |
| Cl <sup>-</sup>  | EPA Method 6500 <sup>B</sup>                | 0.118                | 1.00                 |
| SO <sub>4</sub> <sup>2-</sup>                              | EPA Method 6500 <sup>B</sup>                | 0.226                | 1.00                 |
| F <sup>-</sup>   | EPA Method 6500 <sup>B</sup>                | 0.052                | 0.20                 |
| I <sup>-</sup>   | RSKSOP-223v2 (No EPA Method)                | 1.61 $\mu\text{g/L}$ | 10 $\mu\text{g/L}$   |
| NO <sub>3</sub> <sup>-</sup> +NO <sub>2</sub> <sup>-</sup> | EPA Method 350.1 <sup>D</sup>               | 0.014                | 0.10                 |
| NH <sub>4</sub> <sup>+</sup>                               | EPA Method 353.1 <sup>D</sup>               | 0.012                | 0.05                 |
| Low Molecular Weight Acids                                 |   | $\text{mg L}^{-1}$   | $\text{mg L}^{-1}$   |
| 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                |

\*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.

<sup>A</sup>RSKSOP-330v0 is the GWERD SOP for the implementation of this method.

<sup>B</sup>RSKSOP-276v4 is the GWERD SOP for the implementation of this method.

<sup>C</sup>RSKSOP-288v3 is the GWERD SOP for the implementation of this method in a high Cl<sup>-</sup> matrix.

<sup>D</sup>RSKSOP-214v5 is the GWERD SOP for the implementation of this method.

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**Table 10. 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                                    |
| 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                                    |



| Analyte                     | MDL<br>(µg/L) | QL<br>(µg/L) | Lab<br>Duplicates<br>RPD Limits<br>(%) | Matrix Spike<br>Recovery<br>Limits (%) | Matrix Spike<br>Duplicate<br>RPD Limits<br>(%) |
|-----------------------------|---------------|--------------|--|--|--|
| 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   |
| 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   |

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| Analyte                   | MDL<br>(µg/L) | QL<br>(µg/L) | Lab<br>Duplicates<br>RPD Limits<br>(%) | Matrix Spike<br>Recovery<br>Limits (%) | Matrix Spike<br>Duplicate<br>RPD Limits<br>(%) |
|---------------------------|---------------|--------------|--|--|--|
| 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   |
| Terpinol                  | 0.617         | 1.00         | 20                                     | 60-130                                 | 30   |

<sup>1</sup> Subject to change. The values reported are those reported December 2012.

**Table 11. 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 <sup>1</sup> |            | ICP-MS <sup>2</sup> |           |
|-----------------|----------------------|------------|---------------------|-----------|
|                 | 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     |                     |           |

<sup>1</sup>AES: Atomic Emission Spectroscopy, equivalent to OES.

<sup>2</sup>For Hg the method is cold vapor atomic absorption spectroscopy.

**Table 12. Region 7 Contract Lab VOC Quantitation limits.**

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

**Table 13. RSKERC Laboratory QA/QC Requirements Summary\* from SOPs.**

| Measurement   | Analysis Method          | Blanks<br>(Frequency)  | Calibration Checks<br>(Frequency)  | Second Source<br>(Frequency)   | Duplicates<br>(Frequency)       | Matrix Spikes<br>(MS)/<br>Laboratory<br>Control Sample<br>(LCS)<br>(Frequency)                   |
|---|--------------------------|--|--|--|---------------------------------|--|
| Dissolved gases                                     | RSKSOP-194v4<br>&-175v5  | ≤MDL<br>(He/Ar blank, first<br>and last in sample<br>queue; water blank<br>before samples) | 85-115% of known<br>value<br>(After helium/Ar<br>blank at first of<br>analysis queue,<br>before helium/Ar<br>blank at end of<br>sample set, and<br>every 15 samples) | 85-115% of known<br>value<br>(After first<br>calibration check)                | RPD≤20<br>(Every 15 samples)    | NA   |
| SO <sub>4</sub> , Cl, F, Br                         | RSKSOP-276v4 (-<br>288v3 | <MDL<br>(Beginning and<br>end of each sample<br>queue)                                     | 90-110% Rec.<br>(Beginning, end,<br>and every 10<br>samples)   | PE sample<br>acceptance limits<br>(One per sample<br>set)                      | RPD<10<br>(every 15 samples)    | 80-120% Rec.<br>(one per every<br>20 samples)  |
| I <sup>-</sup>                                      | RSKSOP-223v2             | <QL ( Beginning<br>and at the end of<br>each set of<br>samples.)                           | 90 – 110% of<br>known value (At<br>beginning of each<br>analytical run.<br>Every tenth sample<br>and at end of<br>analytical run.)                                   | 90-110% of known<br>value (Beginning<br>of sample set and<br>every 20 samples) | RPD < 10% (Every<br>20 samples) | MS: 80 – 120%<br>Recovery (Every<br>20 samples)/<br>LCS: 80 – 120%<br>(If matrix spike<br>fails) |
| NO <sub>3</sub> + NO <sub>2</sub> , NH <sub>4</sub> | RSKSOP-214v5             | <½ lowest calib.   | 90-110% Rec.   | PE sample  | RPD<10                          | 80-120% Rec.   |

| Measurement                         | Analysis Method | Blanks<br>(Frequency)   | Calibration Checks<br>(Frequency)  | Second Source<br>(Frequency)   | Duplicates<br>(Frequency)   | Matrix Spikes<br>(MS)/<br>Laboratory<br>Control Sample<br>(LCS)<br>(Frequency) |
|-------------------------------------|-----------------|---|--|--|---|--|
|                                     |                 | std.<br>(Beginning and<br>end of each sample<br>queue)                                | (Beginning, end,<br>and every 10<br>samples)   | acceptance limits<br>(One per sample<br>set)   | (every 10 samples)  | (one per every<br>20 samples)  |
| DIC/DOC                             | RSKSOP-330v0    | <MDL<br>(Beginning and<br>end of each sample<br>set)                                  | 90-110% of known<br>value<br>(Beginning, end,<br>and every 10<br>samples)                              | PE sample<br>acceptance limits;<br>90-110% of known<br>value for others<br>(One per sample<br>set) | RPD $\leq$ 10<br>(every 10 samples)   | 80-120% Rec.<br>(one per 20 or<br>every set)                                   |
| Low Molecular<br>Weight Acids       | RSKSOP-112v6    | <MDL<br>(Beginning of a<br>sample set; every<br>10 samples; and<br>end of sample set) | 85-115% of the<br>recovery<br>(Prior to sample<br>analysis; every 10<br>samples; end of<br>sample set) | 85-115% of<br>recovery<br>(Prior to sample<br>analysis)  | $\leq$ 15 RPD<br>(Every 20 samples )  | 80-120 %<br>recovery<br>(Every 20<br>samples )                                 |
| O and H Stable<br>Isotopes in Water | RSKSOP-334v0    | NA  | $\leq$ 1.5‰ for $\delta^2\text{H}$ ;<br>$\leq$ 0.3‰ for $\delta^{18}\text{O}$<br>(Beginning of         | NA   | $\leq$ 1.5‰ for $\delta^2\text{H}$ and<br>$\leq$ 0.3‰ for $\delta^{18}\text{O}$<br>(Beginning of each | NA   |

| Measurement | Analysis Method | Blanks<br>(Frequency) | Calibration Checks<br>(Frequency)                      | Second Source<br>(Frequency) | Duplicates<br>(Frequency)  | Matrix Spikes<br>(MS)/<br>Laboratory<br>Control Sample<br>(LCS)<br>(Frequency) |
|-------------|-----------------|-----------------------|--|------------------------------|--|--|
|             |                 |                       | sample set; every<br>20 samples; end of<br>sample set) |                              | sample queue, after<br>every 20 <sup>th</sup> sample,<br>and at the end of the<br>sample queue.) |  |

\*This table only provides a summary; SOPs should be consulted for greater detail.

Corrective actions are outlined in the SOPs.

MDL = Method Detection Limit; QL = Quantitation Limit; PE = Performance Evaluation

**Table 14. Region VIII Laboratory QA/QC Requirements for Semivolatiles, GRO, DRO.**

| QC Type                                   | Semivolatiles  | DRO  | GRO  | Frequency   |
|---|--|--|--|---|
| Method Blanks                             | <RL<br>Preparation or Method Blank, one with each set of extraction groups. Calibration Blanks are also analyzed                                   | <RL<br>Preparation or Method Blank   | <RL<br>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)<br>RSD≤20%, r <sup>2</sup> ≥0.990 | ICAL: 10-500 ug/L<br>RSD≤20% or r <sup>2</sup> ≥0.990                        | ICAL: .25-12.5 ug/L for gasoline (different range for other compounds)<br><br>RSD≤20% or r <sup>2</sup> ≥0.990                                       | As required (not daily if pass ICV)                                   |
| Initial and Continuing Calibration Checks | 80-120% of expected value  | 80-120% of expected value  | 80-120% of expected value  | At beginning of sample set, every tenth sample, and end of sample set |
| Second Source Standards                   | ICV1<br>70-130% of expected value  | ICV1<br>80-120% of expected value  | ICVs<br>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:<br>Values of all analytes in the LCS should be within the limits | Use and SRM:<br>Values of all analytes in the LCS should be within the limits determined by the supplier.<br><br>Otherwise 70-130% of expected value | One per analytical batch or every 20 samples, whichever is greater    |



| QC Type            | Semivolatiles   | DRO  | GRO                                    | Frequency  |
|--------------------|---|--|--|--|
|                    |   | determined by the supplier.<br><br>Otherwise 70-130% of expected value |  |  |
| Matrix Spikes (MS) | Same as LCS   | Same as LCS  | 70-130% of expected value              | One per sample set or every 20 samples, whichever is more frequent |
| MS/MSD             | % Recovery same as MS<br>RPD $\leq$ 30  | % Recovery same as MS<br>RPD $\leq$ 25                                 | % Recovery same as MS<br>RPD $\leq$ 25 | One per sample set or every 20 samples, whichever is more frequent |
| Reporting Limits*  | 0.1 $\mu\text{g/L}$ (generally) <sup>1</sup> for target compounds HF special compounds are higher | 20 $\mu\text{g/L}$ <sup>1</sup>  | 20 $\mu\text{g/L}$ <sup>2</sup>        | NA   |

<sup>1</sup>Based on 1000 mL sample to 1 mL extract

<sup>2</sup>Based on a 5 mL purge

\*see QAPP Table 10

**Table 15. Region III Detection and Reporting limits for glycols.**

| Analyte <sup>‡</sup> | Detection Limit ( $\mu\text{g L}^{-1}$ ) <sup>†</sup> | Reporting Limit ( $\mu\text{g L}^{-1}$ ) <sup>†</sup> |
|----------------------|---|---|
| 2-butoxyethanol      | NA  | NA  |
| diethylene glycol    | NA  | NA  |
| triethylene glycol   | NA  | NA  |
| tetraethylene glycol | NA  | NA  |

<sup>†</sup> Detection and reporting limits are still being determined, most will be between 10 and 50 pbb. In June of 2012 RLs were 5  $\mu\text{g/L}$  for 2-butoxyethanol; 5  $\mu\text{g/L}$  for diethylene glycol, 10  $\mu\text{g/L}$  for triethylene glycol, and 10  $\mu\text{g/L}$  for tetraethylene glycol.

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

**Table 16. USGS laboratory QA/QC requirements for  $^{87}\text{Sr}/^{86}\text{Sr}$  analysis using TIMS\*.**

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

\*Thermal Ionization Mass Spectrometry

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

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

**Table 17. 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 $r \geq 0.998$ .   | Daily. Each time instrument is turned on or set up, after ICV or CCV failure, and after major instrument adjustment. The lowest non-blank standard shall be set at the RL for all analytes. |
| Initial Calibration Verification   | 90-110% Recovery   | Following instrument calibration for each mass used.  |
| Initial Calibration Blank  | $\leq RL$  | Following each instrument calibration, immediately after the ICV.   |
| Continuing Calibration Verification  | 90-110% Recovery   | For each mass used, at a frequency of at least after every 10 analytical runs, and at the end of each run.  |
| Low Level Initial Calibration Verification (LLICV) and Low Level Continuing Calibration Verification (LLCCV) at the RL (identified by lab as CRDL) | 70-130% Recovery   | LLICV, following each instrument calibration., and LLCCV analyzed at the end of each run.   |
| Continuing Calibration Blank   | $\leq RL$  | At a frequency of at least after every 10 analytical runs, and at the end of each run. Performed immediately after the last CCV.  |
| Interference Check Sample  | For solution AB, $\pm 20\%$ of the analyte's true value; for solution A $\pm 5$ ppb or $\pm 2$ 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.   |

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

**Table 18. 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   | $\leq$ RL  | Analyzed after the analytical standards, but not before analysis of the Initial Calibration Verification (ICV) during the initial calibration of the instrument. |
| Continuing Calibration Verification (IPC or Instrument Performance Check) | 90-110% Recovery   | At beginning and end of run; every 10 samples during analytical run.   |
| Continuing Calibration Blank  | $\leq$ RL  | Analyzed immediately after every Continuing Calibration Verification (CCV); at beginning and end of run and every 10 samples during an analytical run.           |
| Interference Check Sample (SIC or Spectral Interference Check)            | For solution AB, $\pm 20\%$ of the analyte's true value; for solution A $\pm 20\%$ of the interferent's true value, for all other analytes $\pm 5$ ppb or within $\pm 2$ times the RL of the analyte's true value, whichever is greater.               | At the beginning of the run after the ICB but before the CCV and at the end of the run.  |
| Serial Dilution   | If the analyte concentration is sufficiently high (minimally a factor of 50 above the MDL in the original sample), the serial dilution (a five-fold dilution) shall then agree within 10% of the original determination after correction for dilution. | Every 20 samples.  |
| Preparation Blank (LRB or Laboratory Reagent Blank)                       | $\leq$ RL  | Every 20 samples.  |
| Laboratory Control Sample (LFB or Laboratory Fortified Blank)             | 85-115% recovery   | Every 20 samples.  |

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

**Table 19. 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 $r \geq 0.995$ .                | Daily. Each time instrument is turned on or set up, after ICV or CCV failure, and after major instrument adjustment. The lowest non-blank standard shall be set at the RL. |
| Initial Calibration Verification (ICV, second source)                             | 90-110% Recovery  | Immediately after calibration.   |
| Initial Calibration Blank (ICB)   | $\leq RL$   | Analyzed after the analytical standards, but not before analysis of the Initial Calibration Verification (ICV) during the initial calibration of the instrument.           |
| Continuing Calibration Verification (CCV)   | 90-110% Recovery  | Every 10 samples and at the end of the run.  |
| Lower Limit of Quantitation Check (LLQC) (identified by lab as either CRI or CRA) | 70-130% Recovery  | Analyzed at beginning and the end of each run.   |
| Continuing Calibration Blank (CCB)  | $\leq RL$   | Analyzed immediately after every Continuing Calibration Verification (CCV); every 10 samples and at the end of the run.  |
| Method or Preparation Blank   | $\leq RL$   | Every 20 samples.  |
| Laboratory Control Sample   | 80-120% recovery  | Every 20 samples.  |
| Matrix Spike  | 75-125% Recovery (Recovery calculations are not required if the sample concentration is $>4x$ the spike added.) | Every 20 samples.  |
| Post-Digestion Spike  | 80-120% Recovery per Method 7000B as reference in 7470A (Note the lab sop uses 75-125% Recovery)                | If a MS and/or MSD are out of control.   |
| Duplicate Sample  | RPD $\leq 20\%$ for sample values $\geq 5x$ RL; for sample values $< 5x$ RL, control limit = RL                 | Every 20 samples.  |



| <b>QC Type</b>                           | <b>Acceptance Criteria</b> | <b>Frequency</b>                                |
|--|----------------------------|---|
| Determination of Method Detection Limits |                            | Annually and after major instrument adjustment. |

**Table 20. Region 7 Contract Laboratory QA/QC requirements for VOCs by GC/MS.**

| QC Type  | Acceptance Criteria  | Frequency   |
|--|--|---|
| Instrument Calibration                           | The acceptance criterion for the initial calibration requires RSD $\leq 15\%$ or for alternate curve fits the correlation coefficient $r \geq 0.990$ .   | Each time instrument is turned on or set up, after ICV or CCV failure, and after major instrument adjustment. The lowest non-blank standard shall be set at the RL. |
| System Performance Check                         | BFB Tune must meet tuning criteria in Table 4 of 8260B.<br>Minimum average response factors for the SPC compounds* must meet criteria  | Prior to sample analysis; beginning of each 12 hour shift.  |
| Initial Calibration Verification (second source) | 75-125% Recovery   | Immediately after calibration.  |
| Continuing Calibration Verification (CCV)        | %D $\leq 20\%$ for analytes using RF;<br>80-120% Recovery for analytes using curve fitting   | Every 12 hours.   |
| Surrogates                                       | 70-130% Recovery   | All blanks, QC samples, and samples.  |
| Internal Standards                               | EICP area must not vary by more than a factor of 2 (-50 to +100%) of the mid-point calibration standard.<br>Retention time must not vary by more than 0.50 min of those in the mid-point calibration standard. | All blanks, QC samples, and samples.  |
| Method Blank                                     | $\leq RL$<br>$\leq 2 \times RL$ for methylene chloride, acetone, and 2-butanone  | After calibration standards. Every 12 hours.  |
| Laboratory Control Sample                        | 70-130% Recovery<br>60-140% Recovery for t-butyl alcohol, isopropyl alcohol, and ethanol   | Every 20 samples. Evaluated only when MS is outside control limit.  |
| Matrix Spike                                     | 70-130% Recovery<br>60-140% Recovery for t-butyl alcohol, isopropyl alcohol, and ethanol   | Every 20 samples.   |
| Duplicate Sample (MS/MSD)                        | RPD $\leq 30\%$  | Every 20 samples.   |
| Determination of Method Detection Limits         |  | Annually and after major instrument adjustment.   |

\*SPC compounds minimum response factors (RF):

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Chloromethane, min. RF = 0.10  
1,1-Dichloroethane, min. RF = 0.10  
Bromoform, min. RF = 0.10  
1,1,2,2-Tetrachloroethane, min. RF = 0.30  
Chlorobenzene, min. RF = 0.30

**Table 21. 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     |
| 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 22. Data qualifiers**

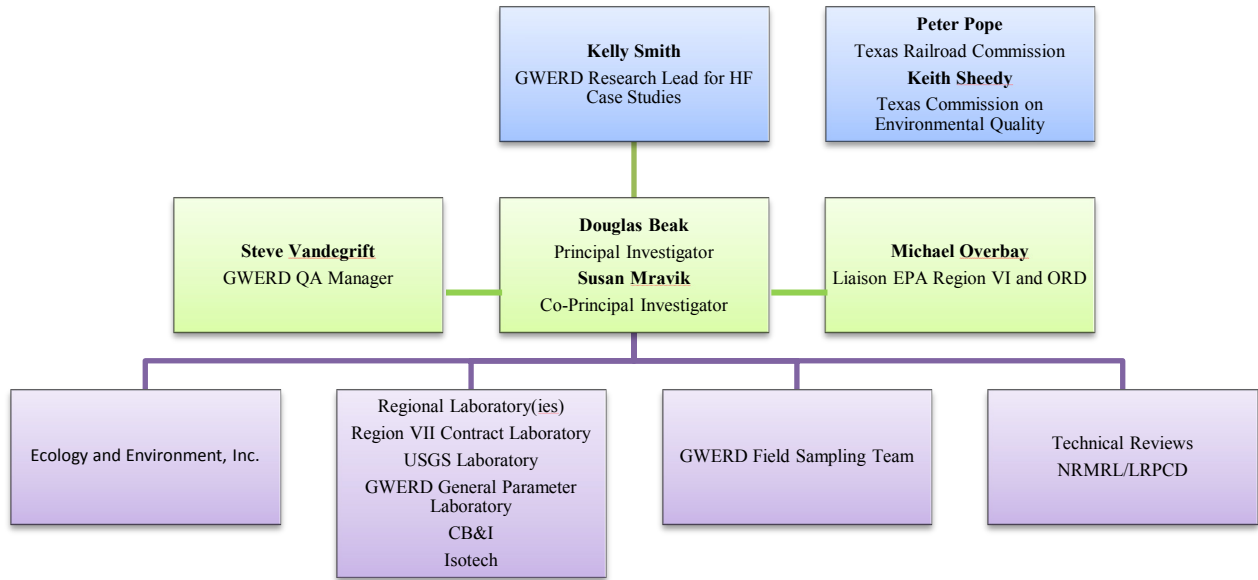
| <b>Data Qualifiers</b> |  |
|------------------------|--|
| <b>Qualifier</b>       | <b>Definition</b>  |
| U                      | The analyte was analyzed for, but was not detected above the reported quantitation limit (QL).   |
| J                      | The analyte was positively identified. The 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

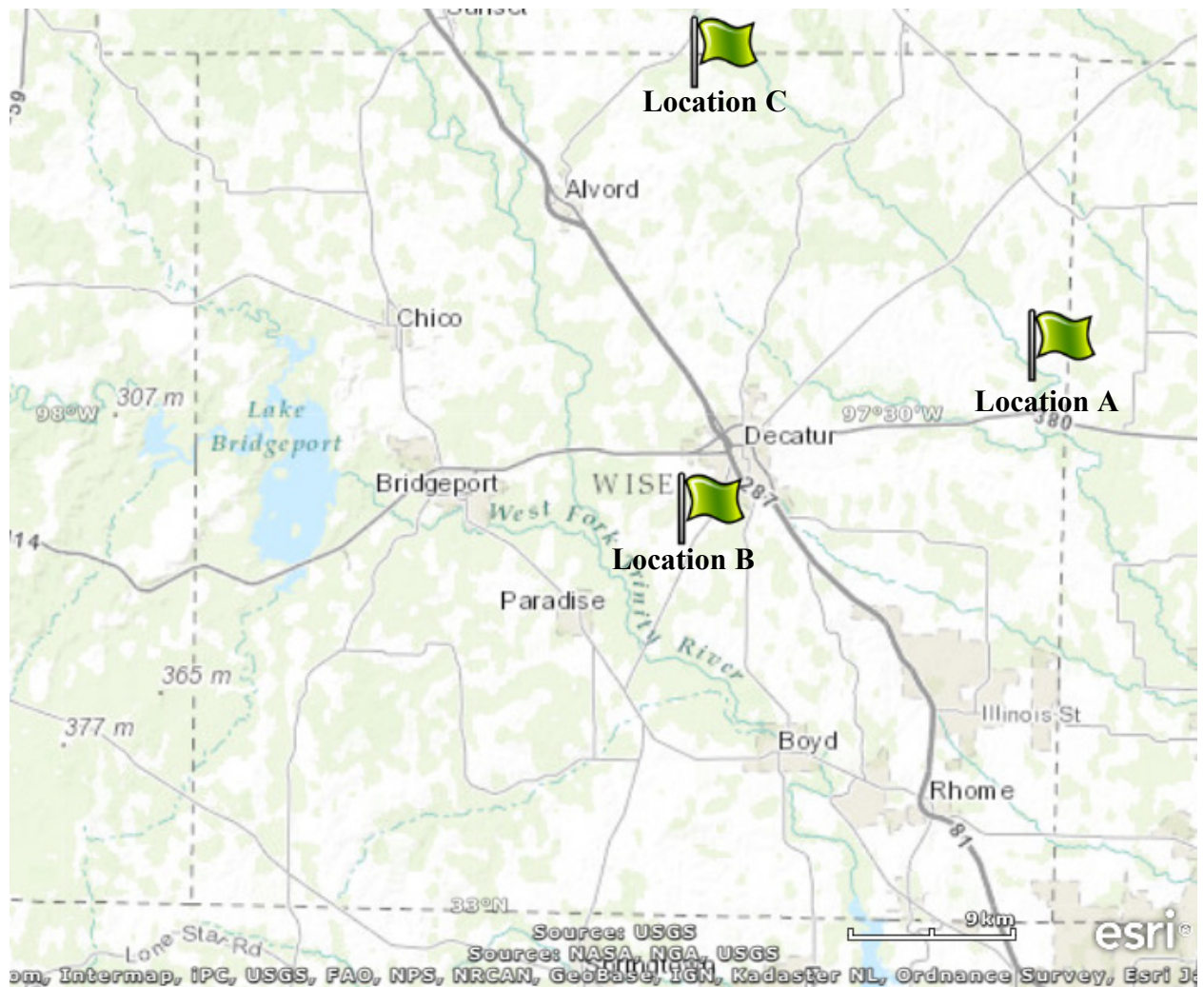
| Descriptor | Definition  |
|------------|---|
| NA         | Not Applicable (See QAPP)                         |
| NR         | Not Reported by Laboratory or Field Sampling Team |
| ND         | Not Detected                                      |
| NS         | Not Sampled                         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

**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, Wise Co., TX.**



**Figure 2. Map showing study locations in Wise Co. TX.**

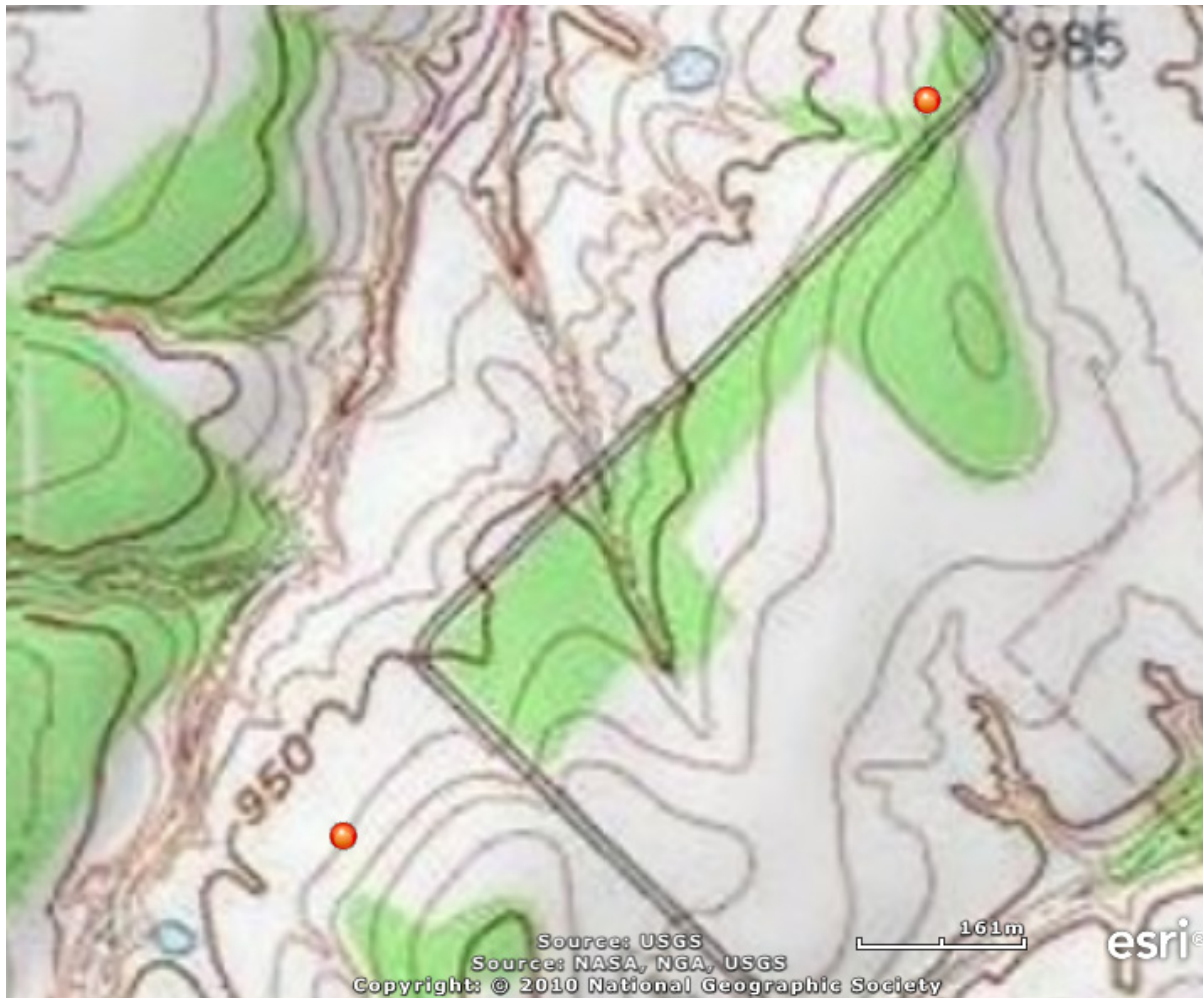




**Figure 3. Map showing location A sampling points in Wise Co. TX. Green circles are groundwater sampling locations; purple circles are surface water sampling locations.**



**Figure 4. Map showing location B sampling points in Wise Co. TX. Green circles are groundwater sampling locations.**



**Figure 5. Map showing Location C sampling points in Wise Co. TX. Red circles are groundwater sampling locations.**



## Appendix A

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

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

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

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

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

- 1 A high precision  $^{87}\text{Sr}/^{86}\text{Sr}$  analysis with a 2-sigma uncertainty of  $\pm 0.00002$ .
- 2 ICPMS analysis of Sr concentration (coefficient of variation of  $\pm 5$  percent).

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

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

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

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

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

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

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

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

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

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

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

Quattrocchi, F., Barbieri, M., Bencini, R., Cinti, D., Durocher, K., Galli, G., Pizzino, L., Shevalier, M., and Voltorni, N., 2006, Strontium isotope ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) chemistry in produced oil

field waters: The IEA CO<sub>2</sub> monitoring and storage project: Advance in the Geological Storage of Carbon Dioxide, Springer, The Netherlands, p. 243-259.

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

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

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

One form of the basic decay equation follows:

$$(^{87}\text{Sr}/^{86}\text{Sr})_p = (^{87}\text{Sr}/^{86}\text{Sr})_i + (^{87}\text{Rb}/^{86}\text{Sr})_p * (e^t - 1)$$

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

For geochronologic applications, the above equation is solved for “t” which is the interval of time since the rock or mineral system formed with an initial Sr isotopic composition of  $(^{87}\text{Sr}/^{86}\text{Sr})_i$  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  $(^{87}\text{Sr}/^{86}\text{Sr})_i$  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  $(^{87}\text{Rb}/^{86}\text{Sr})_p$  must be known so that  $(^{87}\text{Sr}/^{86}\text{Sr})_p$  can be corrected for the ingrowth of radiogenic  $^{87}\text{Sr}$ . 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

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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 ( $18 \times 10^6$  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  $^{84}\text{Sr}$  and  $^{87}\text{Rb}$ . Sample dissolution is accomplished through a combination of small amounts of concentrated  $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$ ,  $\text{HClO}_4$ , or  $\text{HNO}_3$  with concentrated  $\text{HF}$ . After refluxing on a hot plate to dryness the resultant precipitate is brought into solution with  $\text{HCl}$  or  $\text{HNO}_3$  and centrifuged. The supernatant solution is pipetted in small volumes onto an ion-exchange resin column pretreated with  $\text{HCl}$  or  $\text{HNO}_3$ . After washing with a measured volume of  $\text{HCl}$  or  $\text{HNO}_3$  acid, the final solution containing the purified Sr is collected in a Teflon beaker and dried on low heat. The sample is transferred to the mass spectrometer laboratory for isotopic analysis.

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

6.1.2.2 Carbonate Samples: Carbonate samples are typically weighed and dissolved in weak  $\text{HCl}$  or  $\text{HNO}_3$  leaving admixed silicates intact. Other methods of leaching include, but are not limited to 10 percent  $\text{CH}_3\text{COOH}$  (acetic acid), or 10 percent disodium EDTA (ethylenedinitrilotetraacetate). For isotope dilution determination, a weighed amount of Sr spike is added to the sample before dissolution. The leachate is separated from the insoluble material by centrifuging and the supernatant liquid is transferred to separate container. After drying the

leachate with low heat, the residual is dissolved in a small amount of HNO<sub>3</sub> acid. To estimate the proportion of carbonate in the original sample, the acid-leached residue is washed with ultra high purity (UHP) H<sub>2</sub>O, dried and weighed. Ion exchange procedures to isolate Sr from the solution are similar to those described above in Para. 6.1.2.1 for the silicate samples.

6.1.2.3 Water Samples: Water samples are weighed and spiked with Sr isotope (if necessary) then evaporated to dryness in Pyrex or Teflon beakers in an environmental hood. The dried sample is brought up in HNO<sub>3</sub> 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  $4 \times 10^{-7}$  mm of Hg, an ion beam is generated by heating the sample filaments with the ionizing filament operating at approximately  $1.8 \times 10^3$  C. When a stable Sr beam of approximately 0.5-5 volts of <sup>88</sup>Sr is attained, data collection is started. Five or more blocks of data are to be taken until an average <sup>87</sup>Sr/<sup>86</sup>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 <sup>86</sup>Sr/<sup>88</sup>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  $1.5 \times 10^3$  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 <sup>87</sup>Rb/<sup>86</sup>Sr and <sup>87</sup>Sr/<sup>86</sup>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

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

#### 6.2.2 Chemical Dissolution:

- Ultra-high purity (UPH) H<sub>2</sub>O (18.2 x 10<sup>6</sup> ohms resistivity)
- Ultrex, Baker Analyzed, C Star Suprapur (EM Science) and/or reagents of equivalent or higher purity of the following: H<sub>2</sub>SO<sub>4</sub> (concentrated) HF (concentrated) HClO<sub>4</sub> (concentrated) HNO<sub>3</sub> (concentrated) HCl (concentrated) CH<sub>3</sub>COOH (acetic acid) Disodium EDTA (ethylenedinitrilotetraacetate)
- Platinum dishes
- Teflon covers, jars, beakers, tubes and other equipment
- Electronic analytical balance
- NIST traceable weights
- <sup>87</sup>Rb spike solution
- NIST SRM-607 Rb standard
- <sup>84</sup>Sr spike solution
- NIST SRM-610 or 611 Sr standard
- Hot plate
- Centrifuge
- Ion-exchange resins and columns
- Parafilm
- Environmental hood or laminaire flow hoods
- Appropriate standard laboratory equipment including, but not limited to: quartz, Teflon, and Pyrex beakers; graduated cylinders; and glass and plastic centrifuge tubes (accuracies in all ranges to ±5 percent)
- NIST glass and rock standards such as, but not limited to, SRM-610, SRM-611 and SRM-987 for strontium and SRM-607 for rubidium.

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

- Rhenium ribbon
- Tantalum ribbon
- EN-1 standard carbonate
- Biotite or K-feldspar mineral samples
- NIST SRM-987 (for strontium)

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- NIST SRM-727 (for rubidium)
- BCR-1 standard rock sample
- High purity elemental standard solutions
- NIST 1643 and 1640 water standards
- Liquid N<sub>2</sub>

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 <sup>87</sup>Rb/<sup>85</sup>Rb ratio is constant in nature, rubidium isotopic measurements are checked by analyzing Rb from an unspiked biotite or K-feldspar. These operational checks of the chemistry and mass spectrometry laboratories shall incorporate components that measure and/or regulate volume, vacuum, filament current/temperature, accelerating voltage, and ion-beam current. If the results of these operational checks are not within acceptable limits per Para. 11 of this procedure, mass spectrometer and/or laboratory operations are suspended until the problem(s) is (are) identified and rectified. If elemental concentrations of the standards indicate a significant change in the spike solution concentration then the affected spikes are re-determined with NIST standards. These checks will be documented in the mass spectrometer logbook.

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

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

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

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

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

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

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

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

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

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

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

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

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

**10. SOFTWARE**. Software 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  $^{87}\text{Rb}$  and shelf life is not applicable.

### **13. HANDLING, STORAGE AND SHIPPING OF EQUIPMENT AND CONSUMABLES.**

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

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

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

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

- Table of Sr Data
- Record of Mass Spectrometer Run



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

#### 15.1.2 Supporting Information:

- Calibration documentation identified in Para. 11.1 shall be submitted as supporting information.
- 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

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17. **ATTACHMENTS.** None.

18. **HISTORY OF CHANGES.**

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

## Revision History

| Revision Number | Date Approved | Revision  |
|-----------------|---------------|---|
| 0               | 6/20/11       | New document  |
| 1               | 2/27/12       | <p>Added <math>^{87}\text{Sr}/^{86}\text{Sr}</math> isotopes and O,H stable isotopes of water to analyte list to ascertain if the water is from a different source or is mixture of aquifer water and source water. (Sections 2.2.1.1, 2.4.1, 2.5.1, and Tables 6, 8, 9, and 13)</p> <p>Added USGS Laboratory contact information (2.3.3)</p> <p>Added Appendix A for Sr isotope methodology used by USGS</p> <p>Revised Project /Task organization (Section 1.1) to reflect change in personnel</p> <p>Revised location information (1.2.4 and 1.2.5)</p> <p>Updated Region VIII accreditation status and text to 2<sup>nd</sup> paragraph to provide clarification (1.5)</p> <p>Added geophysical measurements and methods to help identify the source of contamination and determine the extent of contamination (2.1.3 and 2.2.2)</p> <p>Added USGS sample shipping information (2.3.3)</p> <p>Section 2.2.1.1, #4o, made corrections to cited methods</p> <p>Section 2.5.1, for Region VIII, #5, indicated that Region VIII has provided their results for performance evaluations</p> <p>Section 2.7, provided clarification of steps taken to check performance of field measurements for sulfide, ferrous iron, alkalinity, and turbidity</p> <p>Sec. 3.1, provided clarification that ADQs are performed on the first data sets</p> <p>Sec. 3.1.2 and 3.2, corrected to whom audit reports are submitted</p> <p>Sec. 4.2, added text to clarify data verification/validation process as well as addition of new Table 18 on Data Qualifiers</p> <p>Added references for geophysical measurements, stable isotopes, data review, low molecular weight acids, microwave digestion for unfiltered metals samples</p> <p>Revised Table 2 Field Activities Schedule</p> |

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|   |         | <p>Made corrections to methods in Table 5 (methods for ferrous iron and sulfide are not EPA); replaced alkalinity method # with correct #; added pH, DO, ORP, and specific conductance</p> <p>Added bromide analysis by RSKSOP-288v3 in Tables 6 and 11; this method can analyze for Br in samples with high chloride concentrations</p> <p>Revised Region VIII SVOC, Table 12 with updated limits</p> <p>Table 13, corrections were made for DIC/DOC</p> <p>Table 14, replaced with updated/corrected version from Region VIII</p> <p>Added Table 16 showing USGS QA/QC requirements for Sr isotopes</p> <p>Revised Figure 1 and Sec. 1.1 to reflect current project organization (replaced Puls with Jewett; added Peterman, Costantino, Groves, and McElmurry)</p>   |
| 2 | 5/25/12 | <ul style="list-style-type: none"> <li>• Section 1.1, added new data management duties for Susan Mravik.</li> <li>• Updated section 1.2.2 Tier III Investigations to reflect how Tier III GW sampling will be done</li> <li>• Updated section 2.2.1.1 Domestic wells to reflect how sampling will occur for Tier III GW sampling</li> <li>• Updated Section 2.3.3. Replaced CB&amp;I lab contact person due to departure of employee</li> <li>• Updated 2.4.1. Modified first sentence for clarification.</li> <li>• Updated Section 2.5.3. Added text on isotope analysis and detection limits</li> <li>• Updated Section 2.5.4. Added language describing process for evaluating field duplicates and blanks</li> <li>• Updated Section 3.1.1. Added text clarifying that PE samples are not available or needed for isotope analysis</li> <li>• Revised Table 2 Field Activities Schedule to reflect modified sampling frequency and ceasing of sampling at Locations A and C</li> <li>• Table 6, replaced EPA Method 200.7 with 6010C; both are ICP-MS methods, but 6010C is the more appropriate method</li> </ul> |

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|   |         | <p>based on SW846 inherent method flexibility</p> <ul style="list-style-type: none"> <li>• Table 13, replaced metals QC criteria with revised criteria to make them more consistent with 6010C</li> <li>• Revised Table 18 to clarify qualifiers and add new ones</li> </ul>  |
| 3 | 9/10/12 | <ul style="list-style-type: none"> <li>• Title changed to reflect we are not doing any investigations in Denton Co., TX and to identify the special sampling event in September 2012</li> <li>• Distribution list changed to reflect additional personnel involved with the study</li> <li>• Section 1.1 changed to reflect update to David Jewett's responsibilities</li> <li>• Section 1.2, Denton Co., TX removed, no longer part of project</li> <li>• Section 1.2.1, added description of this sampling event</li> <li>• Section 1.2.2, changed sampling date for Tier III from May 2012 to November-December 2012</li> <li>• Section 1.2.3, deleted Ra because at this time no evidence suggests this to be important parameter in Wise Co.</li> <li>• Section 1.2.6, added information supplied to us by the homeowner and TRRC.</li> <li>• Section 1.3, added information on March 2012 sampling; added strontium and stable water isotopes to analyte list; added statement on the September 2012 sampling event</li> <li>• Section 1.3, deleted DRO and GRO. Data from previous sampling events indicated that these have limited utility for the study.</li> <li>• Section 2.2, added information for sampling production wells and scope of sampling for this sampling event, including samples for metals analysis by a CLP lab and samples for iodide</li> <li>• Section 2.3.2, added information for CLP lab</li> <li>• Section 2.3.3, added information for CLP lab</li> <li>• Section 2.4.1, changed title from "Ground Water" to "Ground, Surface, and Produced Waters" to reflect scope of samples to</li> </ul> |

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|                         |          | <p>be analyzed; added analysis of iodide for this sampling event; added analysis of samples for metals by CLP lab</p> <ul style="list-style-type: none"> <li>• Section 2.5.1, added information for CLP lab analysis of metals</li> <li>• Section 4.2, added data validation of metals data from CLP lab</li> <li>• Table 2, added the September 2012 sampling event</li> <li>• Table 6; replaced EPA Method 6010C with 200.7 (ICP-OES analysis for metals). 200.7 was referenced in QAPP Revisions 0 and 1. It was changed in Revision 2 to 6010C but since then it was determined by QA staff that use of 200.7 as the “base” method was appropriate as 200.7 incorporates 6010C by reference. Added volume and bottle requirements for metals analysis by CLP lab. Added Iodide analysis to table.</li> <li>• Table 7, all instances of RL were replaced with QL; criteria for blanks were updated to be consistent with data qualifier table.</li> <li>• Table 9, replaced EPA Method 6010C with 200.7 (see above); added footnotes to indicate the SOPs that implement specific EPA Methods</li> <li>• Table 10, added table of CLP CRQLs for metals</li> <li>• Table 12, added Laboratory Control Sample and information for iodide</li> <li>• Table 16, added CLP lab QA/QC requirements</li> <li>• Table 18, table replaced with most recent version; U, U1, D, and T removed as they will not be used; J10 has been added as well as Descriptors.</li> </ul> |
| 3,<br>Addendum          | 11/30/12 | <ul style="list-style-type: none"> <li>• Title changed to reflect the focus of this addendum</li> <li>• Scope of addendum is limited to the CLP metals reanalysis</li> </ul>  |
| 3,<br>Addendum<br>No. 2 | 1/10/13  | <ul style="list-style-type: none"> <li>• Title changed to reflect the focus of this addendum</li> <li>• Scope of addendum is limited to the SwRI analysis of samples for metals, mercury, and VOC analysis</li> </ul>   |
| 4                       | 4/24/13  | <ul style="list-style-type: none"> <li>• Section 1.1 updated to reflect new personnel and their roles</li> <li>• Replaced Phase 1 and Phase 2 with Tier II and Tier III</li> </ul>  |

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|  |  | <p>throughout the document</p> <ul style="list-style-type: none"> <li>• Section 1.2.1- provided updates for Tier II investigations and for Battelle comments</li> <li>• Section 1.2.2 updated for Tier III investigations and address Battelle comments</li> <li>• Section 1.4 updated to address Battelle comments</li> <li>• Section 1.5 updated to address Battelle comments and address USGS and Region VII Contract Laboratory analysis</li> <li>• Section 2.2, and 2.2.1.1- modified to address Battelle comments</li> <li>• Section 2.2.1 updated sample collection information, including samples for Region 7 contract laboratory</li> <li>• Section 2.2.1.3 updated to give more accurate description of how the sampling occurred</li> <li>• Section 2.3 updated to include Region 7 contract laboratory</li> <li>• Sections 2.4.1, and 2.10 updated to address Battelle comments</li> <li>• Sections 2.4.1 and 2.5.1 updated to include Region 7 contract laboratory information</li> <li>• Sections 2.6 and 2.7 updated to address Battelle comments</li> <li>• Sections 2.7 and 2.8 updated to include Region 7 contract laboratory</li> <li>• Section 2.10.3 updated information on data transcription check</li> <li>• Section 3.1 modified to address Battelle comments and reflect the current TSA procedure</li> <li>• Section 3.1.1 updated to include TSA for SwRI</li> <li>• Section 4.1 and 4.2 updated to reflect the current data validation procedure and address Battelle comments</li> <li>• Table 2 update Tier II sampling and removed reference to potential Tier III sampling</li> <li>• Table 1 updated laboratory information and modified critical analyte list</li> <li>• Table 2 updated schedule</li> <li>• Table 4 updated information for metals and VOCs</li> <li>• Table 7, footnote changed 12<sup>0</sup>C to 6<sup>0</sup>C to be consistent with</li> </ul> |
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|   |         | <p>Table 4</p> <ul style="list-style-type: none"> <li>• Table 9 updated with current information</li> <li>• Table 10 updated with current information</li> <li>• Tables 11 and 12, replaced previous table for CLP laboratory with these for Region 7 contract laboratory</li> <li>• Table 13, updated RSKSOP-276v3 to v4, most recent version</li> <li>• Tables 17-20, replaced previous table for CLP laboratory QA/QC requirements with those for the Region 7 contract laboratory</li> <li>• Table 22, replaced previous Data Qualifier table with most current version</li> <li>• Figure 1, replaced David Jewett with Kelly Smith</li> </ul> |
| 5 | 9/18/13 | <ul style="list-style-type: none"> <li>• Section 1.1 was updated to add individuals who may provide technical assistance</li> <li>• Section 2.9 was updated for the use of available databases for historical data, QA requirements, and evaluation of data.</li> <li>• Section 2.10 was updated to discuss additional data analysis needs and software packages</li> <li>• Figure 1 was updated to include Ecology and Environment and NRMRL/LRPCD in the organizational chart.</li> <li>• References were updated.</li> </ul>  |