GWERD QUALITY ASSURANCE PROJECT PLAN

TITLE: Ground-Water Investigation in Pavillion, Wyoming

TASK NO. 23993
QA ID NO. G-14478

QA CATEGORY: 1

DATE: ORIGINAL QAPP Submitted 4/19/2010

NUMBER OF PAGES: 89 (excluding Appendix A)

REVISION NO: 6 (submitted 2/2/2012) (see p. 89 for Revision History)

Dominic DiGiulio - Principal Investigator — Date 2/17/2012

Richard Wilkin - Co-Principal Investigator — Date 2/17/2012

APPROVALS:

David Jewett - Acting Division Director — Date 02/17/2012

Steve Vandegrift - GWERD QA Manager — Date 2/17/2012

Distribution List:

Steve Acree, EPA/ORD/NRMRL/GWERD
Junqi Huang, EPA/ORD/NRMRL/GWERD
Ken Jewell, EPA/ORD/NRMRL/GWERD
Tony Lee, EPA/ORD/NRMRL/GWERD
Gregory Oberley, EPA/Region VIII
Nathan Wiser, EPA/Region VIII
Sujith Kumar, Shaw Environmental
Patrick DeArmond, EPA/ORD/NERL
Randall Ross, EPA/ORD/NRMRL/GWERD
Kristie Hargrove, PA/ORD/NRMRL/GWERD
Russell Neill, EPA/ORD/NRMRL/GWERD
Christopher Ruybal, Student Contractor
Doug Beak, EPA/ORD/NRMRL/GWERD
Robert Parker, EPA/Region VIII
Jennifer Gundersen, EPA/Region III

EPAPAV0025493

1.0 Project Description and Objectives

1.1 Process and/or Environmental System to be Evaluated

This investigation is being conducted to provide technical support to EPA Region VIII to complete a ground-water investigation near Pavillion, Wyoming under authority of the Comprehensive Environmental Response, Compensation, and Liability Act. EPA Region VIII is lead organization of this investigation. The investigation by EPA Region VIII was initiated in response to complaints about odors and taste associated with water in domestic wells. Potential sources of ground-water contamination include activities associated with oil and gas production such as leaking or abandoned pits, gas well completion and enhancement techniques, improperly plugged and abandoned wells, as well as activities associated with residential or agricultural practices. EPA Region VIII has completed two phases of domestic well sampling in addition to collecting surface water and soil samples.

1.2 Purpose of the Project and Specific Project Objectives

To date, four sampling events (Phase I - IV) have been conducted starting in March 2009 and ending in April 2011. In March 2009 (Phase I), EPA collected water samples from 35 domestic wells in the area of investigation and 2 municipal wells in the town of Pavillion. Detection of methane and dissolved hydrocarbons in several domestic wells prompted collection of a second round of samples in January 2010 (Phase II). During this phase, EPA collected: (1) ground-water samples from 17 domestic wells (10 previously sampled), 4 stock wells, and 2 municipal wells; (2) a filter sample from a reverse osmosis system; (3) surface-water and sediment samples from 5 locations along Five-Mile Creek (a creek traversing the area of investigation); (4) gas and produced water/condensate samples (organic compounds only) from 5 production wells; and (5) ground-water samples from 3 shallow monitoring wells and soil samples near the perimeter of three known pit locations. Detection of elevated levels of methane and diesel range organics (DRO) in deep domestic wells located close to one or more gas production wells prompted EPA to install 2 deep monitoring wells in June 2010 to differentiate potential deep versus shallow sources of ground-water contamination. Monitoring wells MW01 and MW02 (referred to as *Type A* wells) are screened at 233-239 m and 293-299 m bgs, respectively. In September 2010 (Phase III), EPA collected gas samples from well casing from MW01 and MW02. In October 2010, EPA collected ground-water samples from MW01 and MW02 in addition to a previously unsampled domestic well and two previously sampled domestic wells. Finally, in April 2011 (Phase IV), EPA resampled the 2 deep monitoring wells to compare previous findings and expand the analyte list to include glycols, alcohols, and low molecular weight acids. Eight previously sampled domestic wells and three previously sampled stock/irrigation wells were also sampled at this time.

This revision No. 6 of the QAPP was prepared for the next sampling event (Phase V) anticipated for April 2012. Ground water will be collected from the deep monitoring wells, previously sampled domestic wells, and previously sampled shallow monitoring wells. Soil gas sampling will not be completed in Phase V.

NRMRL-Ada will assist EPA Region VIII in this investigation by: (1) installing and sampling two deep monitoring wells in two areas where contamination is suspected, (2) providing samples to the EPA Region VIII, Region III, and added in Phase V, ORD/NERL Las Vegas, ALS Environmental, and TestAmerica laboratories for analysis of organic compounds, (3) analyzing

EPAPAV0025494

ground-water samples for major ions, inorganic compounds, organic compounds, metals and dissolved gases at NRMRL-Ada's laboratory in Oklahoma, (4) collecting samples for tritium analysis (added in Phase V) and analysis of stable isotopes of methane and dissolved inorganic carbon at Isotech Laboratories, (5) conducting a soil-gas survey and screening samples in the field for fixed gases and total hydrocarbons using portable gas analyzers, and (6) installing dedicated soil-gas probes and collecting samples for analysis of fixed gases, light hydrocarbons, and isotopes at a Isotech Laboratories, and (6) sampling gas in domestic wells with analysis of fixed gases, light hydrocarbons, and isotopes at Isotech Laboratories. A schedule of field activities is provided in **Table 1**.

One objective of this study to evaluate and simulate the potential migration of fixed gases, light hydrocarbons, organic compounds, and inorganic constituents from deep subsurface media to overlying formations to support research associated with geologic sequestration of carbon dioxide. While carbon dioxide (CO_2) is not a gas of concern in the Pavillion area, potential migration of light hydrocarbons and organic compounds serves as an anthropogenic analogue to evaluate gas and brine migration relevant to the study of geologic sequestration. It is widely acknowledged that leakage through transmissive faults (and associated fractures) and well penetrations (operational, non-operational, and abandoned wells) are the most likely potential pathway for CO_2 and brine release from a storage formation at a properly selected site for geologic sequestration. Leakage through transmissive faults and well penetrations could result in intrusion of CO_2 or brine into underground sources of drinking water (USDWs), release of CO_2 to the vadose zone and the atmosphere, and intrusion of CO_2 into buildings. Release of CO_2 or brine into a USDW could be accompanied by measurable alteration in pH, major ions, and mobilization of hazardous inorganics. The area of investigation near Pavillion has a large number of well penetrations (production and abandoned wells). Stimulation of gas production wells may have resulted in fracture networks in deep subsurface media deposits similar to that which would occur near faults. If leakage from a storage unit occurs via well penetrations, the presence of multiple confining layers and intervening permeable formations would diminish fixed gas, light hydrocarbon, organic compound, and major ion migration into a USDW with upward vertical transport. The conceptual model for this migration pathway is illustrated in **Figure 1**. For the case of single-fluid flow, Norbotten et al. (2004) conducted simulations to show that for a layered system, leakage from an abandoned well that reached the surface was reduced by orders of magnitude compared to the case of a single thick overlying aquitard due to the availability of permeable layers along the vertical column. Nordbotten et al. (2005a,b) derived a semi-analytical solutions to estimate the radial spread of a plume of injected gas around an injection well and conducted similar simulations. The solutions analyzed the extent of the injected CO_2 plume, provided leakage rates through abandoned wells, and estimated the CO_2 plume extent into overlying formations into which the fluid leaks. LeNeveu (2008) examined the effect of multiple layers on leakage through a borehole and also showed that in the event of a wellbore leak, a significant amount of the carbon dioxide rising in and around wellbores can dissolve into the formation water above the caprock before reaching the biosphere. If fixed gases, light hydrocarbons, organic compounds, and major ions are migrating via well penetrations into permeable sandstone units, a similar pattern would be expected. A critical component of this research objective will be to evaluate well integrity (e.g., cement bond logs) of production wells.

A second objective of this study, which supports the first objective, is to develop purging and sampling methodologies that allow collection of ground-water samples approaching or in excess

EPAPAV0025495

of 300 meters below ground surface to maximize retention of fixed gases, light hydrocarbons, and volatile organic compounds. When the partial pressures of dissolved gases such as CH_4 and CO_2 in a formation exceed atmospheric pressure, bubble formation (foaming) and vigorous off gassing occurs at the surface during sample retrieval using conventional methodologies. When hydrostatic head is reduced in a borehole below the summation of partial pressures of dissolved gases in the surrounding formation, foaming and off gassing occurs in the borehole as well. Both mechanisms can result in significant loss of volatile organic compounds in addition to loss of dissolved fixed gases and light hydrocarbons during sample collection. This results in a negative bias (observed concentration less than actual concentration).

A third objective of this study is to evaluate the feasibility of using soil-gas measurements to detect the migration of gases from deep subsurface media. Release of light hydrocarbons into the vadose zone could be accompanied by compositional changes in soil gas and flux to the atmosphere. A conceptual model for this pathway is illustrated in **Figure 2**. Soil-gas anomalies generally occur as linear, fault-linked anomalies, as well as in irregularly shaped diffuse or halo anomalies and irregularly spaced plumes or spot anomalies (Ciotoli et al., 1999). Linear anomalies longer than several meters are commonly taken as strong evidence of gas migration along gas-bearing faults (Fridman, 1990; Ciotoli et al., 1998). Gas migration through production or abandoned wells would have a spot anomaly near the surface.

A fourth objective of this study, which supports the third objective, is to improve quality control measures (leak, purge, and gas permeability testing) associated with soil-gas sampling. Leakage in both dedicated and direct-push sampling systems will be evaluated in this study. Despite the long-term (over a century) use of soil-gas sampling to support resource exploration and hazardous waste investigations, quality assurance and measures are poorly documented or lacking. Improvement in quality control measures will improve delineation of spatial anomalies detectable in near surface unsaturated geologic media associated with gas migration via faults, fractures, and well penetrations.

2.0 Organization and Responsibilities

2.1 Identification of Key Personnel and Responsibilities

Dr. Dominic DiGiulio, Environmental Engineer, U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Robert S. Kerr Environmental Research Center, Ada, OK. Dr. DiGiulio is the principal investigator of this project and is responsible for ensuring completion of all aspects of this QAPP. He and the co-principal investigator are responsible for coordinating the efforts of all key personnel in this project and preparation of reports and documents resulting from this investigation. He will lead the collection, analysis, and interpretation of soil-gas samples. He is the work assignment manager for overseeing the installation of deep monitoring wells. His Contract Officer Representative (COR) certification is current. He is the Health and Safety Officer for soil-gas sampling activities carried out by NRMRL-Ada. His HAZWOPER certification is current.

Dr. Richard Wilkin, Geochemist, U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Robert S. Kerr Environmental Research Center, Ada, OK. Dr. Wilkin is a co-principal investigator for this project. He will lead all aspects of this investigation related to the collection, analysis, and interpretation of ground-water samples. He is the Health and Safety Officer for ground-water sampling activities carried

EPAPAV0025496

out by NRMRL-Ada. His HAZWOPER certification is current.

Dr. Carlyle Miller, Geophysicist, U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Robert S. Kerr Environmental Research Center, Ada, OK. Dr. Miller is responsible for interpretation of geophysical logs associated with production wells and construction of two-dimensional geologic cross-sections in the area of investigation. Dr. Miller is also responsible for assisting Dr, DiGiulio in interpretation of cement bond logs.

Dr. Randall Ross, Geologist, U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Robert S. Kerr Environmental Research Center, Ada, OK. Dr. Ross is responsible assisting Dr. Wilkin in designing the ground-water sample collection methodology and for assisting in the collection of ground-water samples. His HAZWOPER certification is current.

Mr. Steven Acree, Geologist, U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Robert S. Kerr Environmental Research Center, Ada, OK. Mr. Acree is responsible assisting Dr. Wilkin in designing the ground-water sample collection methodology and for assisting in the collection of ground-water samples. He is the co - work assignment manager for overseeing the installation of monitoring wells. His COR and HAZWOPER certifications are current.

Dr. Junqi Huang, Environmental Engineer, U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Robert S. Kerr Environmental Research Center, Ada, OK. Dr. Huang is responsible for simulating gas and fluid flow through well penetrations. His HAZWOPER certification is current.

Ms. Kristie Hargrove, Environmental Scientist, 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. Hargrove is responsible for assisting Dr. DiGiulio in collecting gas samples and maintaining, operating, and calibrating all portable gas analyzers used in the field. She is also responsible for conducting a study to evaluate the integrity of Cali-5 Bond gas sampling bags. She will conduct on-site analysis of light hydrocarbons using a portable gas chromatograph. Her HAZWOPER certification is current.

Mr. Ken Jewell, Environmental Scientist, U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Robert S. Kerr Environmental Research Center (RSKERC), Ada, OK. Mr. Jewell is responsible for operation of the Geoprobe rig during soil-gas sampling. His HAZWOPER certification is current.

Mr. Russell Neill, Environmental Scientist, U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Robert S. Kerr Environmental Research Center (RSKERC), Ada, OK. Mr. Neill is responsible for operation of the Geoprobe rig and assisting Dr. DiGiulio in overseeing installation of monitoring wells. His HAZWOPER certification is current.

Mr. Tony Lee, Environmental Scientist, 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. Lee is responsible for assisting in

EPAPAV0025497

the ground-water sampling. His HAZWOPER certification is current.

Dr. Doug Beak, Geochemist, 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. Beak is responsible for assisting in the ground-water sampling. His HAZWOPER certification is current.

Mr. Christopher Ruybal, Student Contractor, 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. Ruybal is responsible for assisting Dr. DiGiulio in the collection of soil-gas samples. His HAZWOPER certification is current.

Ms. Alexandra Kirkpatrick, Student Contractor, 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. Kirkpatrick is responsible for assisting Dr. Wilkin with the collection of ground-water samples. Her HAZWOPER certification is current.

Mr. Steve Vandegrift, Quality Assurance Manager, U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Robert S. Kerr Environmental Research Center (RSKERC), Ada, OK. Mr. Vandegrift is responsible for quality assurance review/approval of the Quality Assurance Project Plan (QAPP), conducting audits, and QA review/approval of the final report. His HAZWOPER certification is current.

Mr. Robert Parker, Environmental Scientist, U.S. Environmental Protection Agency - Region VIII, Denver, CO. Mr. Parker is the CERCLA project manager for the Pavillion investigation and is responsible for overall project coordination between EPA Region VIII and NRMRL-Ada including obtaining access agreements for monitoring well installation and soil-gas sampling. His HAZWOPER certification is current.

Mr. Gregory Oberley, Geologist, U.S. Environmental Protection Agency - Region VIII, Denver, CO. Mr. Oberley is responsible for coordinating technical discussion and activities between NRMRL-Ada and EPA Region VIII. He is also responsible for developing conceptual models of geology and hydrology in the area of investigation. His HAZWOPER certification is current.

Mr. Nathan Wiser, Geologist, U.S. Environmental Protection Agency - Region VIII, Denver, CO. Mr. Wiser is responsible for assisting Dr. DiGiulio and Dr. Miller in interpreting cement bond logs and well completion forms associated with production wells. His HAZWOPER certification is current.

Dr. Jennifer Gundersen, Analytical Chemist, U.S. Environmental Protection Agency - Region III, Ft. Meade, MD. Dr. Gundersen will analyze samples for glycols and 2-butoxyethanol.

Dr. Patrick DeArmond, Analytical Chemist, U.S. Environmental Protection Agency, Office of Research and Development, National Exposure Research Laboratory, Las Vegas, NV. Dr. DeArmond will analyze samples for ethoxylated alcohols, alkylphenol ethoxylates, alkylphenols, and acrylamide.

Dr. Sujith Kumar, On-Site Manager, Shaw Environmental, Ada, OK. Dr. Kumar is responsible

EPAPAV0025498

for overseeing all contracting and subcontracting of work related to installation of monitoring wells and analytical work conducted by Shaw Environmental -RSKERC's on site analytical contractor.

Mr. Steve Pelphrey, Isotech Laboratories, Inc. Champaign, IL. Mr. Pelphrey is responsible for overseeing the fixed-laboratory isotopic analysis of soil-gas samples and ground-water samples.

Mr. Bernard Kirkland, TestAmerica, Savannah, GA. Mr. Kirkland is responsible for overseeing laboratory analysis of Methylene Blue Active Substances in ground-water samples.

Mr. Tom Beamish, ALS Environmental, Holland, MI. Mr. Beamish is responsible for overseeing laboratory analysis of alcohols in ground water samples.

2.2 Lines of Communication Among Project Participants

Dr. DiGiulio is responsible for initiating contact with appropriate project participants as he deems necessary. Other project participants will keep Dr. DiGiulio 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. Both Drs. DiGiulio and Wilkin are responsible for oversight of 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.

2.3 Specialized Training or Certificates

HAZWOPER certification is required for on-site work and visits by personnel from all organizations or stakeholders, Ms. Hargrove is certified to ship "Dangerous Goods" according the U.S. Department of Transportation guidelines and has received training for shipping samples via UPS.

2.4 Process and Responsibilities to Ensure Project Participants Have Current QAPP

Each member of the research team (Dr. Wilkin, Dr. Ross, Mr. Acree, Mr. Jewell, Ms. Hargrove, Mr. Neill, Mr. Lee) will be provided the most current draft version of the QAPP for comment and will be provided updated versions if the QAPP is modified. The approved QAPP and any subsequent approved revisions shall be provided to those in the Distribution list on cover page. They will typically be distributed electronically via electronic mail. The original QAPP Revision number is “0.” Future revisions will be numbered incrementally.

3.0 Scientific Approach

3.1 Ground-Water Monitoring

The ground-water sampling component of this project is intended to provide a survey of water quality in the area of investigation. NRMRL-Ada and EPA Region VIII will survey the area and speak to landowners in late April 2010 to determine the location of monitoring wells. NRMRL-Ada will issue a contract through its on-site contractor, Shaw Inc., to install two deep (e.g., 800'-1000'), designated as *Type A* monitoring wells. Monitoring well installation and development

EPAPAV0025499

will occur in June through September 2010. Monitoring wells will be installed in locations where contamination is suspected based on previous sampling of domestic wells by EPA Region VIII. There is a shallower (600') domestic well, near the location of a planned deep monitoring well without a pump, that will be sampled. This is designated as a *Type B* monitoring well. Ground-water samples may also be collected from domestic wells via homeowner taps. These wells are designated as *Type C* wells. Most domestic wells are screened between 200' - 300' below ground surface. However, several domestic wells are shallow (e.g., 60') while others are fairly deep (e.g., 750'). *Type D* wells are shallow monitoring wells adjacent to pits used for storage/disposal of drilling wastes, produced water, and flow-back fluids from gas production. Several of these shallow monitoring wells were sampled by EPA Region VIII in January of 2010 (Phase II). Depending on accessibility, some of these previously sampled wells or unsampled pit monitoring wells may be sampled by NRMRL-Ada researchers in Phase V. During development of version 6 of this QAPP the timeframe of sampling and analysis has been expanded to track changes in contaminant concentrations in the *Type A* monitoring wells and selected domestic wells, and to expand the list of analyzed constituents for Phase V. Results from Phase III and Phase IV testing has prompted the analysis of additional parameters, including ethoxylated alcohols/alkylphenols, acrylamide, methylene blue active substances (MBAS), tritium, propylene and ethylene glycols, and methanol. The spacing of the ground-water sampling events will in part depend on weather conditions but is anticipated to start in October 2010 and continue in the spring and fall of 2012. Phase V sampling is anticipated in April 2012. The study area and locations of *Type A* and *Type B* monitoring wells are illustrated in **Figure 3**. The latitude, longitude, and elevation of monitoring wells will be recorded.

3.2 Soil-Gas Survey

A soil-gas survey using two direct-push systems, Geoprobe Post Run Tubing (PRT) and sampling directly through rods, will be conducted in July 2010. The Geoprobe rig will also be used to install 9 dedicated vapor probes at this time. Probing will be limited to areas where EPA Region VIII has signed access agreements with landowners. Probing on property will commence near potential source areas (e.g., pits and production wells) and then proceed radially outward increasing in distance between probed areas with distance from potential source areas. The latitude and longitude of each measurement location will be recorded.

If soil conditions are favorable (e.g., 5 or more meters of unsaturated unconsolidated deposits) oxygen (O_2), CO_2, methane (CH_4), hydrogen sulfide (H_2S), and total hydrocarbons will be measured at three depths using portable gas analyzers. Otherwise, soil-gas will be screened at only one or two depths. Gas permeability will also be measured. Upon attainment of maximum penetration depth or probe refusal whichever comes first. Leak testing will be conducted using a chamber, tracers, and portable gas analyzers.

3.3 Soil-Gas Sampling

Dedicated soil-gas probes installed in July 2010 will be sampled in September, 2010. Leak, purge, and gas permeability testing will precede collection of each soil-gas sample. A sample will not collected if leakage through the borehole exceeds 10%, a standard used by the State of New York (2006). Samples will be submitted to Isotech Laboratories for analysis of: (1) fixed gases - argon (Ar), helium (He), H_2, O_2, nitrogen (N_2), CO_2; (2) light hydrocarbons - CH_4, ethane (C_2H_6), ethylene (C_2H_4), propane (C_3H_8), isobutane (iC_4H_{10}), normal butane (C_4H_{10}), isopentane (iC_5H_{12}), normal pentane (nC_5H_{12}), and hexane plus (C_6+); (3) isotopes - stable isotopes of

carbon in CH_4, C_2H_6 and C_3H_8 ($\delta^{13}C$), stable isotopes of hydrogen in CH_4 (δD), and radiocarbon isotopes of CH_4 (¬ ^{14}C). A study will be conducted to evaluate the stability of gas concentrations in Cali-5 Bond sampling bags over a 30 day period.

3.3.a. Rationale for Soil-Gas Sampling Strategy

In an extensive natural gas and petroleum exploration program carried out by the Gulf Oil Research Center between 1972 and 1983, Jones and Drozd (1983) observed that soil-gas measurements can be used to help locate natural gas and petroleum deposits and that soil-gas anomalies of light hydrocarbons often occur along faults and fractures. They also observed similarity between soil-gas and reservoir gas composition. These two observations indicate that transport of hydrocarbon vapors to the vadose zone and thus also to ground water is dominated by advection through faults and fractures rather than by diffusion through faults, fractures, and structured geologic media. Their observations are consistent with studies in volcanic or geothermal areas where magma degassing, thermo-metamorphic alteration of carbonates, and advective transport through faults and fractures results in high concentrations of CO_2, H_2, He, H_2S, and radon detected in soil-gas and ground water (Azzaro et al., 1998; Baubron et al., 2002; Ciotoli et al., 2007; Fountain and Jacobi, 2000; King et al., 1996; Lewicki and Brantley, 2000; Lewicki et al., 2003).

Soil-gas anomalies generally occur as linear, fault-linked anomalies, as well as in irregularly shaped diffuse or halo anomalies and irregularly spaced plumes or spot anomalies (Ciotoli et al., 1999). Linear anomalies longer than several meters are commonly taken as strong evidence of gas migration along gas-bearing faults (Fridman, 1990; Ciotoli et al., 1998). Most faulted zones are caused by fault intersections and have extensive associated fractures that allow gases to escape laterally and vertically producing halo or diffuse anomalies (Matthews, 1985). Gas emanation from faults is not always continuous (Ciotoli et al., 1998). Multiple spot anomalies occurring along a linear trend may indicate spatially discontinuous gas conduction (Lombardi et al., 1996; Ciotoli et al., 1998). Gas migration through production or abandoned wells would have a spot anomaly near the surface. The ultimate distribution in constituents in soil gas depends on the permeability of rocks, depth of origin, and the influence of near-surface conditions such as ground-water flow, weathering, etc. (Ciotoli et al., 2004).

There are a number of potential limitations to using soil-gas sampling to detect leakage. The reservoir may be underpressurized thereby reducing the driving force for advective transport of hydrocarbons toward the surface. Given the observation of a highly pressurized natural gas blowout during drilling of a domestic well, this limitation would not appear to be a factor at Pavillion. Second, spillage of hydrocarbons near petroleum or natural gas wells could complicate data interpretation (source of hydrocarbons and other gases may be from a near surface source). A vertical gas profile especially in thick unconsolidated unsaturated deposits could resolve this issue.

3.3.b Selection of Gas Monitoring Parameters

The following discussion provides a rationale for selection of gases to analyze during soil-gas sampling.

Carbon Dioxide and Oxygen

EPAPAV0025501

Depressed levels of O_2 and elevated levels of CO_2 in gas samples could be due to: (1) biodegradation of hydrocarbons from an anthropogenic source (e.g., spillage of petroleum) in the vicinity of measurement, (2) biodegradation of CH_4 and other light hydrocarbons seeping from a petroleum or natural gas reservoir, (3) oxidation of native organic matter in subsurface media, and (4) geochemical reactions in subsurface media and ground water. Since oxidation of organic matter and hydrocarbons is accompanied by reduced O_2 concentration, concentration ratios of CO_2 and O_2 could be used to examine oxidation of hydrocarbons or organic matter as a source of CO_2. In soil gas, observation of increased CO_2 concentration with depth could indicate migration from ground water or a deeper source as opposed to oxidation from near surface organic matter.

Light Hydrocarbons

Thermogenic light hydrocarbons detected in soil gas typically have a well-defined composition indicative of reservoir composition. The concentration of hydrocarbons almost always occur in the following order: $CH_4 > C_2H_6 > C_3H_8 > nC_4H_{10}$ (Jones et al., 1999). Methane dominates the light hydrocarbon fraction above natural gas reservoirs whereas significant concentrations of C_2H_6, C_3H_8, and nC_4H_{10} are found in soil gas overlying petroleum reservoirs. For soil-gas above dry-gas reservoir, ratios of CH_4 to light hydrocarbons typically plot as $CH_4/C_2H_6 < CH_4/ C_3H_8 < CH_4/nC_4H_{10} < CH_4/nC_5H_{12}$ with typical upper limits ratios of: $CH_4/C_2H_6 < 350$, $CH_4/ C_3H_8 < 900$, $CH_4/nC_4H_{10} < 1{,}500$, $CH_4/nC_5H_{12} < 4{,}500$. Biogenic gas and gas from coal bed deposits however typically have ratios of CH_4/C_2H_6 that exceed 1000 or 10,000 (Janezic, 1979). Also, C_2H_6, C_3H_8, and nC_4H_{10} are not produced by biological processes in near surface sediments (Jones and Pirkle, 2009). Only CH_4 and C_2H_4 are products of biodegradation. Thus, elevated levels of C_2H_6, C_3H_8, and nC_4H_{10} in soil gas are indicative of thermogenic origin.

Hydrogen Sulfide

Hydrogen sulfide is produced during the anaerobic decomposition of organic matter by sulfur bacteria. It is also found in varying amounts in unrefined natural gas and petroleum, in sulfur deposits, volcanic gases and sulfur springs. Thus, elevated levels of H_2S in gas samples may indicate natural gas migration.

Hydrogen and Helium

Because H_2 and He are chemically inert, physically stable, and highly insoluble in water, they are widely recognized as deep source or ~~good~~ fault and fracture indicators (Klusman, 1993; Ciotoli et al., 1999; Ciotoli et al., 2004). Helium and H_2 have been observed in soil gas at values up to 430 and 50 ppmv respectively over the San Andreas fault in California (Jones and Pirkle, 1981). Wakita et al. (1978) observed He at a maximum concentration of 350 ppmv along a nitrogen vent in Japan. Wakita et al. (1980) reported hydrogen anomalies ranging from 2 to 30,000 ppmv H_2 along the Yamasaki fault zone in Japan with ambient background values of 0.5 ppmv observed outside the influence of the fault. The atmospheric concentration of helium is 5220 ± 15 ppbv.

The presence of He in soil gas is often independent of the oil and gas deposits. However, since He is more soluble in oil than water, it is frequently found at elevated concentrations in soil gas above natural gas and petroleum reservoirs and hence may serve as a natural tracer for gas

EPAPAV0025502

migration.

Carbon and Hydrogen Isotopes

Carbon and hydrogen isotope analysis is very useful in determining the origin of CH_4, other light hydrocarbons, and CO_2 in soil gas. Isotopes are reported as the relative difference in the ratio of the less abundant heavier isotope to the more abundant lighter isotope of the sample with respect to a reference standard. Ratios are expressed in parts per thousand or permil (‰). Stable carbon isotope analysis of $\delta^{13}C$ is defined as:

$$\delta 13C(‰) = \left[\frac{\left(^{13}C/^{12}C\right)_{sample}}{\left(^{13}C/^{12}C\right)_{standard}} - 1 \right] x1000$$

where the standard is the Pee Dee Belemnite (PDB) reference standard. ¬ ^{14}C is defined as:

$$\Delta 14C(‰) = \left[\frac{\left(^{14}C/^{12}C\right)_{sample}}{\left(^{14}C/^{12}C\right)_{standard}} - 1 \right] x1000 .$$

The reference standard is oxalic acid decay corrected to 1950. δD is defined as

$$\delta D(‰) = \left[\frac{\left(^{2}H/^{1}H\right)_{sample}}{\left(^{2}H/^{1}H\right)_{standard}} - 1 \right] x1000$$

where the standard is the Vienna Standard Mean Ocean Water Standard.

Baldassare and Laughrey (1997), Schoell (1980, 1983), Kaplan (1997), Rowe and Muehlenbachs (1999), and others have summarized interpretation of values of $\delta^{13}C$ and δD for CH_4. As illustrated in **Figure 4**, it is often possible to distinguish CH_4 formed from microbial and thermogenic processes by plotting $\delta^{13}C$ for CH_4 versus δD for CH_4. For CH_4 found in near-surface environments due to acetate fermentation (marsh gas and landfill gas), values of $\delta^{13}C$ for CH_4 range from -40 to -62‰ and values of δD for CH_4 range from 270 to -350‰. For outwash deposits, values of δ13C for CH_4 range from -62 to -90‰ and values of δD for CH_4 range from about -180 to -240‰. For CH_4 of thermogenic origin, values of $\delta^{13}C$ for CH_4 range from -28 to -60‰ and values of δD for CH_4 range from -110 to -250‰. Values of $\delta^{13}C$ for CH_4 near -60‰ associated with values of δD for CH_4 in the -160 to -260‰ range are attributed to mixing of thermogenic and microbial methane.

Since radiocarbon has a half-life of 5730 years, ancient organic matter and fossil fuels such as natural gas are ^{14}C-free meaning that undiluted thermogenic CH_4 or CO_2 from degradation of thermogenic CH_4 will have a value of ¬ ^{14}C near -1000‰.

3.4 Analysis of Drilling Additives

In an attempt to identify all possible sources of inorganic and organic constituents identified in

EPAPAV0025503

ground water collected from the deep monitoring wells (*Type A* wells), commercial products used during installation and development of the wells were analyzed for chemical constituents. This analysis was conducted after anomalous chemical signatures were detected in MW01 and MW02 during Phase III and Phase IV sampling. Chemical extraction and analysis was conducted in a sequenced approach. First, analyses were completed for inorganic components (major and minor cations, anions) and for total organic carbon in March 2011. Products that showed elevated levels of total organic carbon were subsequently analyzed for organic compounds in July 2011. This type of analysis is a non-standard approach since it is generally assumed that products used during well drilling and completion do not remain in the subsurface and do not influence the results of subsequent water-quality testing. Products used at Pavillion for well installation and well development include: EZ-Mud Gold (Haliburton; clay stabilizer), Quik-Gel (Haliburton; bentonite), Dense Soda Ash (OCI Chemicals; sodium carbonate), Quik-Trol Gold (Haliburton; clarifier), Penetrol (Haliburton, mud removal), and Aqua-Clear PFD (Haliburton, mud removal). Material Safety Data Sheets for these products do not indicate the presence of volatile or semi-volatile contaminants of concern. Nevertheless, these products were extracted into water at a product/water ratio greater than or close to the ratio recommended by the manufacturer for product use in the field. At the time of well installation, samples of these products were collected into glass mason jars by the contractor in charge of the well installation. The samples with proper chain of custody were delivered to the NRMRL-Ada laboratory and stored in a refrigerator. Procedures used for the water extractions and analyses will be discussed in a following section.

4.0 Sampling Procedures

Samples will be retained by the laboratories until the principal investigators give permission for disposal.

4.1 Ground-Water Sampling

4.1.a Regional Geology and Geochemistry Background Hydrogeological Information

The USGS published a report entitled *"Monitoring-Well Network and Sampling Design for Ground-Water Quality, Wind River Indian Reservation, Wyoming (2005)"*. As illustrated in **Figure 5**, hydrostratigraphy in the area can be divided into local Quaternary age aquifers, 10 bedrock aquifers, and 11 confining layers. Quaternary age media include alluvium, colluvium, eolian, terrace, pediment, landslide, glacial, and travertine deposits. Quaternary age deposits are generally less than 50 ft thick yield 2 to 60 gallons per minute (gal/min), and have dissolved-solids concentrations range from 109 to 4,630 milligrams per liter (mg/L). Tertiary age deposits include the Wind River, Fort Union, and Indian Meadows Formations. In the Wind River basin trough, the Wind River and Fort Union have combined thickness in excess of 10,000 ft. However, thickness varies greatly throughout the basin. The Indian Meadows Formation lies between the Wind River and Fort Union Formations, but it is not differentiated in the subsurface of the Wind River Structural Basin. Domestic wells and many natural gas production wells in the Pavillion area are screened in the Wind River Formation. Water yields from wells in the Wind River Formation range from 0.1 to 350 gal/min, and dissolved-solids concentrations range from 211 to 5,110 mg/L. Thus, this formation is recognized by EPA as an Underground Source of Drinking Water (TDS<10,000 mg/L). These large ranges result in part from the varied lithology of the formation. Tertiary volcaniclastic rocks of the Wiggins, Tepee Trail, and Aycross Formations occur above the Wind River Formation. Water quality samples collected from

springs discharging from volcaniclastic rocks have dissolved-solids concentrations ranging from 197 to 244 mg/L. Discharges from the springs range from 8 to 37 gal/min. Mesozoic rocks consist mostly of siltstone, sandstone, and shale. Smaller amounts of claystone, conglomerate, coal, bentonite, limestone, dolomite, and gypsum also are present. These rocks are overlain by thick Tertiary deposits, except near the flanks of the mountains and around some of the structures in the basin. Water yields from wells in Mesozoic aquifers range from 0.5 to 90 gal/min, and dissolved-solids concentrations range from 182 to 6,060 mg/L. In general, the median values for dissolved-solids concentrations in the water samples from Mesozoic aquifers are about 1,000 mg/L, except in water samples from the Cody Shale, which has a median value of 2,540 mg/L. It is likely that most of the water samples from Mesozoic aquifers evaluated came from relatively shallow depths near recharge areas. Away from these areas, water from Mesozoic aquifers probably is saline to briny. Paleozoic rocks are composed mostly of sandstone, shale, limestone, and dolomite, with some chert. Well-yield and water-quality records are sparse for Paleozoic aquifers. Dissolved solids in Paleozoic aquifers range from less than 500 mg/L to more than 3,000 mg/L. Most of these water-quality samples probably came from shallow depths (less than a few thousand feet). In the central basin area where these rocks are deeply buried, the dissolved-solids content is probably much greater.

4.1.b Installation of Monitoring Wells

NRMRL-Ada's on-site contractor, Shaw Inc., will be tasked with drilling and installation of two deep monitoring well wells. A local driller, Mr. Louis Dickinson, states that a highly productive white coarse-grained sandstone aquifer exists at 800 - 1000' below ground surface in this area. The goal of drilling is to place monitoring wells in this deposit which is part of the Wind River Formation. An interview was conducted with Mr. Dickinson, to determine stratigraphy around and within the area of deep monitoring well installation. Domestic wells in the area were drilled with mud rotary. One deep well will be drilled on the Jeff [redacted] property and the other well will be drilled on the [redacted] property. In December 2005, Mr. Dickinson was contracted to drill a domestic well to replace an existing well screened at 210' on a property adjacent (0.5 miles east-northeast) to the [redacted] property owned by [redacted] Mr. [redacted] complained of "petroleum-like" odors and taste associated with the water. While drilling the well, Mr. Dickinson recorded deposits as a function of depth outlined below.

Depth (ft)	Deposit
0 - 15	top soil
15 - 75	brown sandstone
75 - 90	gray coarse-grained sandstone
90 - 140	red and green claystone
170 - 195	gray shale
195 - 210	gray fine-grained sandstone
210 - 445	gray shale
445 - 460	gray fine-grained sandstone
460 - 520	gray shale
520 - 540	gray medium-grained sandstone
540 - 550	gray shale

Mr. Dickinson states that while developing the well to remove drilling mud, a methane gas blowout occurred on 12/19/05. The well was shut-in on 12/22/05. When the well was shut-in, a

significant increase in gas production was noted in production well 14-2. Mr. [redacted] states that he began smelling gas at 160 - 180' during drilling.

Another deep monitoring well will be located on the Jeff [redacted] property. Dr. Dickinson installed a deep domestic well in a nearby location and recorded deposits as a function of depth outlined below.

Depth (ft)	Deposit
0 - 70	brown coarse-grained sandstone
70 - 170	gray shale
170 - 205	gray medium-grained sandstone
205 - 245	gray shale
245 - 335	gray medium-grained sandstone
335 - 420	gray shale
420 - 520	gray medium-grained sandstone
520 - 575	gray shale
575 - 595	gray fine-grained sandstone
595 - 840	gray shale
840 - 850	red and green claystone
850 - 875	white coarse-grained sandstone
875 - 940	red claystone
940 - 1000	green claystone
1000 - 1050	white coarse-grained sandstone
1050 - 1060	green claystone

Monitoring well installation and development will occur in June through September ~~August~~ 2010. Drilling and installation of deep wells will require the use of blowout protection (BOP) to ensure the safety of workers and prevent potential loss of commodity (natural gas). BOP is common when drilling in fields containing natural gas.

Shaw Inc. will provide the following tasks to support for drilling and monitoring well installation.

- Explore both the feasibility and cost of drilling deep wells using methods that include rotosonic, air rotary with casing advance, water rotary, and mud rotary.

- Compile a list of drillers capable of installing deep monitoring wells with BOP. This list does not have to be limited to the State of Wyoming. Since this is a CERCLA investigation, drilling permits are not required.

- Explore the costs associated with continuous coring of deep wells versus coring only screened intervals (20' for deep wells), versus no coring (just cuttings).

- Provide a geologist to log cuttings and/or core material during drilling.

- Provide a cost estimate for open hole logging of one or more deep wells during drilling. The primary purpose of logging is to assist in identification of lithology. Methods to consider include resistivity and density logging.

- Determine well screen and casing materials to ensure a minimum internal diameter of 4

inches. A 20 foot screen will be used for deep wells. The screen will be placed in the white coarse-grained sandstone.

- Survey the location and elevation of casing.

- Dispose of drilling cuttings including muds and drilling fluids as required by State law. Shaw may need to sample and analyze fluids as part of disposal.

- Develop monitoring wells and dispose of purge water as required by State law. Wells will be developed until the following conditions are met:
    - < 10 NTU
    - minimum of 3 purge volumes even if < 10 NTU if obtained prior to attainment of 3 purge volumes
    - attainment of at least 5 purge volumes if < 10 NTU is not achieved after 3 purge volumes.

- Ensure that drilling does not occur near buried utility lines. In the event that a buried line is punctured, the Contractor will be responsible for contacting the relevant utility company and repair of a utility line if necessary.

Shaw Inc. will develop a separate QAPP for drilling which will be reviewed independently of this document. Shaw Inc. will report on the completion of all TDs in the form of a letter, memo, or other written correspondence to completely address the particular work request. Such documentation shall be addressed to the PO/WAM. This documentation shall reference the TD number, the method(s) used, and comments on any problems or specifics.

Monitoring wells may be located within 100 feet of an existing production well. Wells however will be located off paved roads and on domestic property where EPA Region VIII has gained access. Expansion or improvement of roads will not be necessary to drill. There are no cultural sites or endangered species to be protected. There are no natural features (e.g., streams) that will need protection.

4.1.c Ground-Water Monitoring

A dedicated submersible pump (4-inch Franklin Electric 3HP) will be used to sample water from the two, deep *Type A* wells. The pump intake in both wells will be placed at the top of the 20-foot screened interval. A bomb sampler (**Figure 6**) will be used to sample water from the *Type B* monitoring well in order to insure that a representative sample is collected for pressure-sensitive dissolved gas analyses. In this way a comparison will be made of dissolved gas concentrations in ground water from the *Type B* well between samples in which pressure is maintained (using bomb sampler) and samples collected at ambient pressure. The bomb sampler will be deployed following well purging.

Based on the sampling efforts in Phase III and Phase IV, representative formation samples from MW01 and MW02 will be collected in Phase V using the following approach. In MW01 the initial pumping rate will be approximately 25 L/min. The initial pumping rate will be measured and the water level in the well casing will be tracked as a function of time. After approximately 30 minutes of purging, the pumping rate will be reduced using an in-line valve to approximately 8 L/min. Purging will continue for at least another 30 minutes while the water level in the well

casing is monitored. Based on previous testing, over this period of reduced pumping rate, the water level in the well casing is expected to rise on the order of 30 m. Given that the screen length is only 6.1 m (20 ft) and that the pump is set approximately 0.6 m (2 ft) above the screen, rising water level in the well casing will indicate that ground water is derived from the formation with no component of casing storage. The total volume of water purged at the start of sampling will be approximately 1200 L but will be dictated by relationships between pumping rate and water level change in the well casing.

For MW02, EPA will remove water from the well casing until pump cavitation forces purging to cease. Pump cavitation results from bubble formation due to reduction in hydrostatic head and high partial pressures of dissolved gases. -Water level in the well, rate of flow, and total volume of water removed from the casing will be recorded. At the cessation of purging, the water level in MW02 will be monitored over several (e.g., 4) days. Sampling will be initiated prior to full recovery to initial static elevation since full recovery requires a significant period of time (weeks). Prior to sampling, three casing volumes (40 gallons) of pipe associated with the submersible pump will be removed. This procedure will ensure that water collected for samples analysis originated from the formation with a casing storage time of four days or less.

The following methodology will be used for the *Type A* monitoring wells (to be sampled in Phase V).

1) The dedicated pump will be powered on. It is expected that the pump will yield an initial flow rate of approximately 1-7 gallons per minute (3.8 to 27 L/m). This total flow will be split, with one portion going to waste and the other portion will be valved through a flow cell equipped with a YSI 5600 multiparameter probe. Effluent from the YSI probe will be directed to a partially filled rectangular plexiglass chamber. Atmospheric air will be allowed to enter the chamber through a port on one side of the chamber. On the other side of the chamber airflow will be directed in line to a Landtec GEM2000 Plus portable gas analyzer and Thermo Scientific portable flame- and photoionization detector (FID/PID). This will enable measurement of measurement of oxygen, carbon dioxide, methane, hydrogen sulfide, carbon monoxide and total hydrocarbons in the air phase above water exiting the YSI probe. Since this is a flow through chamber, concentrations in the gas phase cannot be used to calculate aqueous phase concentrations. Thus, the chamber will be utilized as a qualitative screening tool to examine trends in gases evolving from the purge water, not actual aqueous concentrations. The rate of pumping will be measured using a Model TM0050 in-line turbine flow meter with associated Model FM0208 flow monitor manufactured by Turbines, Inc. The instantaneous flow rate will be recorded within the first five minutes after pumping is initiated and at intervals no greater than every 15 minutes during pumping. Alternatively, the rate of pumping may also be determined using a stop watch and 2 L graduated cylinder by measuring the water volume collected after approximately 5 seconds. The desirable pumping rate through the flow cell should be less than 2 L/min. Draw down of the water table during pumping will be measured with a sonic water level sensor obtained from Eno Scientific, Inc. (model WS2010 PRO, or equivalent water level indicator). This device emits a sonic pulse and calculates the distance to the water surface based on time delay of the reflected pulse. The listed resolution and accuracy of this device is 0.05 ft and 0.1 ft, respectively. Water level measurements will be made at a minimum of once every 10 minutes during well purging.

2) The YSI probe will be used to track the stabilization of pH, oxidation-reduction potential (ORP), specific conductance (SC), dissolved oxygen (DO), and temperature. In general, the following guidelines will be used to determine when parameters have stabilized: pH changes <0.02 standard units per minute, ORP changes <2 mV per minute, and specific conductance changes <1% per minute. These criteria are initial guidelines; professional judgment in the field will be used to determine on a well-by-well basis when stabilization occurs.
3) The final values for pH, ORP, specific conductance, dissolved oxygen, and temperature will be recorded. The amount of purge water necessary to achieve stabilization will be measured by recording the volume measured by the in-line flow meter at the end of pumping. Alternatively, the amount of purge water may be determined by recording the volume within the waste tank prior to and at the end of pumping. This volume will be determined on a well-by-well basis and used for subsequent sampling activities. At a minimum, however, a volume equivalent to 3-screen volumes will be pumped. For a 4-inch diameter well with a 20-foot screen, this is equivalent to 39 gallons of ground water.
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. Triplicate 1 L samples (amber glass) and four 40 mL vials (amber glass) will be collected for the Region VIII EPA lab. These samples are for analysis of semi-volatile organics, VOCs (EPA Method 8260), gasoline range organics, and diesel range organics. Samples for semi-volatile organics are collected unpreserved into 1 L amber glass bottles. Samples for VOCs will be collected into 40 mL amber glass bottles with sodium triphosphate added as a preservative. Samples for gasoline range organics will be collected into 40 mL amber glass bottles and preserved with HCl (Optima) to pH<2. Samples for diesel range organics will be collected into 1 L amber glass bottles and preserved with HCl (Optima) to pH<2. The samples will be stored and shipped on ice to the Golden (CO) facility for GC-MS analysis. Addition of preservatives for these samples is added in Phase V to increase sample holding time. All glass bottles will be Pre-cleaned Certified.
b. Two 40 mL vials (amber glass) will be collected for analysis of selected glycols (e.g., 2-butoxyethanol, diethylene glycol, triethylene glycol, tetraethylene glycol). These samples will be sent to the Region III EPA lab located in Fort Meade, Maryland. The samples will be stored and shipped on ice.
c. For Phase V, two 40 mL vials (amber glass) will be collected for analysis of methanol, propylene glycol, and ethylene glycol. The samples will be preserved by acidifying with HCl (Optima) to pH<2. These samples will be sent to ALS Environmental in Holland, MI. The samples will be stored and shipped on ice.
d. For Phase V, two 1 L (amber glass) bottles will be collected for the analysis of ethoxylated alcohols, alkylphenol ethoxylates, alkylphenols, and acrylamide. These samples will be sent to the ORD/NERL lab located in Las Vegas, Nevada. The samples will be stored and shipped on ice.
e. Two 40 mL vials (amber glass) will be collected for analysis of alcohols, volatile organic compounds, and aromatic hydrocarbons. The bottles will contain trisodium phosphate as a preservative and will be filled with no head space. Samples will be stored and shipped on ice.
f. Duplicate 60 mL serum bottles will be collected for dissolved gas analysis (e.g., hydrogen, carbon dioxide, ethane, methane, propane, n-butane). The bottles will contain trisodium phosphate as a preservative and will be filled with no head space and

sealed with a crimp cap. Dissolved gas samples will be stored and shipped on ice. The serum bottles will be filled underwater in a 5 gallon bucket.

g. Two 40 mL vials (amber glass) will be collected for analysis of low molecular weight organic acids. The bottles will be filled, preserved with 1 M NaOH, and stored and shipped on ice.

h. A 1 L plastic bottle containing a caplet of benzalkonium chloride will be filled underwater in a 5 gallon bucket and sealed and shipped to Isotech for $\delta^{13}C$ of C1-C5 dissolved gases and $\delta^{2}H$ of methane.

i. For Phase V, a 500 mL plastic bottle will be filled for analysis of tritium (^{3}H). The sample will be sent to Isotech for analysis (no preservative added, shipped on ice).

j. For Phase V a 500 mL plastic bottle will be filled for analysis of Methylene Blue Active Substances (MBAS). The sample will be sent to TestAmerica in Savannah, GA (no preservative, shipped on ice). Due to the 2 day holding time, this sample will be immediately packaged with appropriate chain of custody sheets and transported to a shipping facility for overnight delivery. If a sample is collected on a Friday, arrangements will be made with TestAmerica for weekend receipt and sample analysis.

k. A 1-liter plastic beaker will be filled for selected analyses to be conducted in the field. Field measurements will consist of alkalinity, ferrous iron, dissolved sulfide, and turbidity. Alkalinity will be measured by titrating ground water with 1.6N H_2SO_4 to the bromcresol green-methyl red endpoint using a HACH titrator (HACH method 8203, equivalent to Standard Method 2320B for alkalinity). Ferrous iron will be measured using the 1,10-phenanthroline colorimetric method (HACH DR/2010 spectrometer, HACH method 8146, equivalent to Standard Method 3500-Fe B for wastewater). Dissolved sulfide will be measured using the methylene blue colorimetric method (HACH DR/2010 spectrometer; HACH method 8131, equivalent to Standard Method 4500-S^{2-} D for wastewater). Turbidity will be measured using a turbidimeter calibrated prior to the sampling trip with certified standards.

l. A summary of QA/QC requirements from SOPs and ground-water sampling details are provided in Tables 2 and 3.

5) After the unfiltered samples have been collected a 4 L capacity vessel will be filled up with ground water. A peristaltic pump (Geopump) will be used pump water from the vessel through teflon-lined polyethylene tubing and through high-capacity ground-water filters into pre-labeled sample bottles. First, approximately 100 mL of ground water will be filtered and sent to waste and next the following series of samples will be collected:

   a. 125 mL plastic bottle for metals analysis by ICP-OES for Al, Ag, As, B, Be, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Sr, Ti, Tl, V, Zn, Si, and S; this sample will also be used for ICP-MS analysis for Cd, Cr, As, Cu, Pb, Ni, Se, Hg, U, Th, and Tl. This sample will be filtered and preserved by adding 5 drops of concentrated HNO_3 (Optima; pH test strips will be used to confirm that the sample pH is <2). Test strips for pH will be used on every sample to insure that a proper preservation pH is attained. This is especially important in case high alkalinity samples are encountered during the ground-water sampling.
   b. 30 mL amber plastic bottle for LC-ICP-MS analysis of arsenic speciation. The method of preservation for this sample will depend on the result of the dissolved sulfide measurement (step 4d above). If the dissolved sulfide concentration is <0.1 mg/L, then the sample will be preserved with 2 drops of concentrated hydrochloric acid (pH test strips will be used to confirm that the sample pH is <2;

see note above regarding use of pH test strips). If the dissolved sulfide concentration is >0.1 mg/L, then no acid will be added. The sample will be stored and transported on ice. This analysis may be dropped during later sampling rounds if elevated arsenic concentrations are not observed in Pavillion ground water. This analysis will not be conducted in Phase V.

c. 30 mL clear plastic bottle for CE (capillary electrophoresis) sulfate, chloride, bromide, and fluoride. This sample will be filtered, no preservative added.
d. 30 mL clear plastic bottle for FIA (flow injection analysis) for nitrate + nitrite and ammonium. This sample will be filtered, 2 drops of sulfuric acid added as preservative (pH test strips will be used to confirm that the sample pH is <2; see note above regarding use of pH test strips).
e. 40 mL glass VOA vial in duplicate for analysis of dissolved inorganic carbon (DIC) This sample will be filtered, no preservative added.
f. 40 mL glass VOA vial in duplicate for analysis of dissolved organic carbon (DOC) This sample will be filtered, phosphoric acid added as a preservative.
g. 60 mL plastic bottle for analysis of $\delta^{13}C$ of dissolved inorganic carbon. This sample will be filtered, no preservative added. Samples will be shipped on ice to Isotech Laboratories for isotopic analyses.
h. 20 mL glass VOA vial for analysis of $\delta^{18}O$ and $\delta^{2}H$ of water using IRMS or using a Picarro spectrometer (Picarro will be used for Phase V). This sample will be filtered, no preservative added.

Unless noted otherwise above, ground-water samples will be submitted to Shaw, NRMRL-Ada's on-site contractor, and the EPA General Parameters (GP) Laboratory, for fixed-laboratory analysis. Specific samples will be delivered to the Region VIII analytical facility, the Region III Fort Meade laboratory, the TestAmerica laboratory in Savannah, GA, the ORD/NERL laboratory, the ALS Environmental laboratory in Holland, MI, or to Isotech Laboratories for tritium analysis and isotopic analyses of dissolved inorganic carbon and dissolved gases.

It is possible that another state or federal agency will take the lead in sampling the deep monitoring wells at some point during the Phase V sampling effort. If this were to occur, NRMRL-Ada researchers would take follow-on samples after the lead sampling agency collects samples. In this case, well purging and monitoring of geochemical parameters would be governed by a separate sampling plan. That plan would be added to this QAPP by reference . Field data and purging details as they occur in the field would be recorded in field notebooks. Split samples would be taken as described above.

The following methodology will be used for the *Type B* monitoring well located on the [redacted] property. This well will not be sampled during Phase V.

1) Since the screen length is not known for this well, a caliper log will be conducted to ascertain the depth interval over which the casing is open. This is a 6-inch diameter well. Based upon the screen length, a calculation of 3-screen volumes will be made to determine a minimum pumping volume.
2) An Idronaut Ocean Seven 303 CTD Multiparameter Probe will be lowered down the well casing using a logging truck. The probe will be positioned approximately at the top of the screened interval of the well. The multiparameter probe will record geochemical parameters of interest, such as pH, oxidation-reduction potential, specific conductivity, dissolved oxygen concentration, and temperature. As a

contingency plan, a Century Geophysical Corporation E-log tool (model number 7044) will be used as a downhole probe to measure and track the stabilization of specific conductance and temperature.

3) Next, a Grundfos Redi-Flo2 (stainless steel) pump will be positioned in the monitoring well approximately 20 feet below the ambient ground-water level. Either a portable Honda EM2500 watt generator or equivalent generator will be used to power the pump. Polyethylene tubing will be used (OD=0.500 inch, ID=0.375 inch). Alternatively polyethylene tubing of OD 0.625 inch and ID 0.500 inch may be used. The initial expected pumping rate is 10 L/min; the higher pumping rate is needed because this is a 6-inch diameter well. The rate of pumping will be determined by measuring the water volume collected after approximately 15 seconds into a 4 L graduated cylinder. Drawdown in the well will be manually monitored using a Solinst Model 101 water level indicator before sampling and at a minimum frequency of once every 30 minutes during pumping.
4) Once pumping of ground water is initiated, geochemical parameters acquired with the multiparameter probe or the specific conductance probe will be monitored for stabilization. Geochemical parameters will be used to track and establish when representative formation water is accessed by the downhole probe. In general, the following guidelines will be used to determine when parameters have stabilized: pH changes <0.02 standard units per minute, ORP changes <2 mV per minute, and specific conductance changes <1% per minute. As noted before, these criteria are initial guidelines, and professional judgment in the field will be used to determine on a well-by-well basis when stabilization occurs.
5) Once stabilization occurs, the final values for pH, ORP, specific conductance, dissolved oxygen, and temperature will be recorded. The amount of purge water necessary to achieve stabilization will be measured from the accumulated volume in the waste container. The downhole probes (Idronaut or Century Geophysical Corporation E-log tool) are designed for use in deep sea or deep subsurface investigations. The probes are designed to provide accurate readouts at high pressure.
6) Next the Idronaut multiparameter probe or conductance probe and the pump will be retrieved from the well. The logging trailer will be used to lower the bomb sampler (Century Geophysical Corporation Fluid Sampler, 1 liter, 303 SS, model # 9751 plus a series of 304 SS vessels; **Figure 7**) through the well opening and to the desired depth within the screened interval. A series of valves will be used to attach 500 mL vessels and two 150 mL stainless steel sampling vessels (Swagelok, 150 mL, 304L SS, part #304L-HDF4-50a). This series of sampling vessels will used to collect ground water in one sampling pass, including pressurized samples for dissolved gas analyses. The pump will again be lowered to the same depth and the volume of water determined to attain stabilization will again be pumped. At that time, the bomb sampler will be activated from the surface and ground water will fill the bomb sampler and attached sample vessels. The downhole valve on the bomb sampler will be closed and next, the pump and sampling apparatus will be pulled from the well.
7) Each time the bomb sampler is deployed downhole, where duplicate or multiple samples are required, the monitoring wells will be re-purged to assure that representative formation water is acquired in the downhole sampler.

Once at the surface, the duplicate 150 mL sample vessels for dissolved gas analysis will be detached. The vessels will be stored on ice and returned to Shaw, NRMRL-Ada's on-site

contractor, for fixed-laboratory analysis. Shaw will measure dissolved gases in these samples (carbon dioxide, methane, ethane, propane, butane, and acetylene). Each time this well is sampled, separate 150 mL vessels will be used. These samples will not be acid preserved; therefore, lack of acid preservation will be noted on sample log-in sheets and on the final analytical report of concentration data.

Pressure-insensitive samples will be collected after first expelling the contents of the 1 L plus attached series of 500 mL vessels into a plastic reservoir. A peristaltic pump (Geopump) will be used to pump water from the reservoir through teflon-lined polyethylene tubing into pre-labeled sample bottles. The following samples will be collected:

a) Triplicate1 L samples (amber glass bottle) and quadruplicate 40 mL samples (amber VOA vials) will be collected for the Region 8 EPA lab (for trace organics, volatile organic compounds, gasoline range organics, and diesel range organics). No preservative will be added to the samples. The samples will be stored and shipped on ice to the Denver (CO) facility for GC-MS analysis. These samples will not be filtered.
b) Two 40 mL vials (amber glass) will be collected for analysis of selected glycols (e.g., 2-butoxyethanol, propylene glycol, ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol). These samples will be sent to Shaw, Inc. and the Region 3 EPA lab located in Fort Meade, Maryland. The samples will be stored and shipped on ice.
c) A 40 mL vial (amber glass) will be collected for analysis of alcohols, volatile organic compounds, and aromatic hydrocarbons. The bottle will contain trisodium phosphate as a preservative and will be filled with no head space. The samples will be stored and shipped on ice.
d) A 40 mL vial (amber glass) will be collected for analysis of low molecular weight organic acids. The bottles will be filled with no head space, preserved with trisodium phosphate, and stored and shipped on ice.
e) A 200 mL unfiltered sample will be collected for field measurements. Field measurements will consist of alkalinity, ferrous iron, and dissolved sulfide. Alkalinity will be measured by titrating ground water with 1.6N H_2SO_4 to the bromcresol green-methyl red endpoint using a HACH titrator (HACH method 8203, equivalent to Standard Method 2320B for alkalinity). Ferrous iron will be measured using the 1,10-phenanthroline colorimetric method (HACH DR/2010 spectrometer, HACH method 8146, equivalent to Standard Method 3500-Fe B for wastewater). Dissolved sulfide will be measured using the methylene blue colorimetric method (HACH DR/2010 spectrometer; HACH method 8131, equivalent to Standard Method 4500-S^{2-} D for wastewater). A portion of this sample will also be used to measure pH, specific conductance, ORP, and dissolved oxygen using the YSI meter and multiparmater probe.
f) Two 60 mL serum bottles will be filled with unfiltered water for dissolved gas analysis. One serum bottle will be unpreserved and the other bottle will be preserved with trisodium phosphate.
g) Next a high-capacity filter will be attached to the tubing and a series of filtered samples will be collected following wasting 100 mL through the filter.
h) 125 mL plastic bottle for metals analysis by ICP-OES for Al, Ag, As, B, Be, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Sr, Ti, Tl, V, Zn, Si, and S; this sample will also be used for ICP-MS analysis for Cd, Cr, As, Cu, Pb, Ni, Se, Hg, U, Th, and Tl. This sample will be filtered and preserved by adding 5 drops of concentrated HNO_3 (pH test strips will be used to confirm that the sample pH is <2). Test strips for pH will be used on every sample to insure that a proper preservation pH is attained. This is

especially important in case high alkalinity samples are encountered during the ground-water sampling.

i) 30 mL amber plastic bottle for LC-ICP-MS analysis of arsenic speciation. The method of preservation for this sample will depend on the result of the dissolved sulfide measurement (step 4d above). If the dissolved sulfide concentration is <0.1 mg/L, then the This sample will be filtered and preserved with 2 drops of concentrated hydrochloric acid (pH test strips will be used to confirm that the sample pH is <2; see note above regarding use of pH test strips). If the dissolved sulfide concentration is >0.1 mg/L, then no acid will be added. The sample will be stored and transported on ice. This analysis may be dropped during later sampling rounds if elevated arsenic concentrations are not observed in Pavillion ground water.
j) 30 mL clear plastic bottle for CE (capillary electrophoresis) sulfate, chloride, bromide, and fluoride. This sample will be filtered, no preservative added.
k) 30 mL clear plastic bottle for FIA (flow injection analysis) for nitrate + nitrite and ammonium. This sample will be filtered, sulfuric acid added as preservative.
l) 45 mL glass VOA vial in duplicate for analysis of dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC). This sample will be filtered, no preservative added.
m) 20 mL glass VOA vial for analysis of $\delta^{18}O$ and $\delta^{2}H$ of water using IRMS. This sample will be filtered, no preservative added.
n) 60 mL plastic bottle for analysis of $\delta^{13}C$ of dissolved inorganic carbon. This sample will be filtered, no preservative added. Samples will be shipped on ice to Isotech Laboratories for isotopic analyses.
o) The ground water remaining in the reservoir will be emptied unfiltered into a plastic bottle supplied by Isotech. The bottle will contain a caplet of benzalkonium chloride and will be submitted for analysis of $\delta^{13}C$ of C1-C5 dissolved gases and $\delta^{2}H$ of methane. The bottle will be stored and shipped upside down to prevent gas loss from the container.
p) Unless noted otherwise above, ground-water samples will be submitted to Shaw, NRMRL-Ada's on-site contractor, and the EPA General Parameters (GP) Laboratory, for fixed-laboratory analysis. Specific samples will be delivered to the Region 8 analytical facility, the Region 3 laboratory in Fort Meade, or to Isotech Laboratories for isotopic analyses of dissolved inorganic carbon.
q) A summary of QA/QC requirements from SOPs and ground-water sampling details are provided in Tables 2 and 3.

The same procedure described above for deploying the bomb-sampler may be used on the two deep monitoring wells, if arrangements can be made to pull and replace the dedicated pumps from these wells.

Type C ground-water samples will be collected from selected taps of local homeowners. These samples will *not* be filtered. Samples will be poured directly into sample containers as noted above with the exception that none of the samples will be filtered. It is understood that samples from *Type C* wells (and *Type A* wells) may be subject to degassing as they are pumped to the surface, leading to sample results that are probably not as representative as those taken with the sample bombs. Field measurements will also consist of turbidity, alkalinity, ferrous iron, and dissolved sulfide. In addition, pH, ORP, specific conductance, dissolved oxygen, and temperature will be measured with a YSI Model 5600 multiparameter probe. Water from the taps will be run until these parameters stabilize following the criteria described in section 3.1. Duplicate samples will collected at a frequency of one in every 10 taps sampled. Duplicate bottles for each parameter to be measured will be collected at the same time. *Type C* wells will be sampled during Phase V.

EPAPAV0025514

Type D wells are shallow monitoring wells adjacent to pits used for storage/disposal of drilling wastes, produced water, and flow-back fluids from gas production. Several of these shallow monitoring wells were sampled by EPA Region VIII in January of 2010 (Phase II). Depending on accessibility, some of these wells or unsampled pit monitoring wells may be sampled by NRMRL-Ada researchers. These wells will be sampled in the same way as the *Type A* wells with the exception that a peristaltic pump will be used in place of the dedicated downhole pump. In addition, filtered samples will be collected by attaching a capsule filter directly to the pump outflow tubing, i.e., a separate reservoir will not be used. It is anticipated that up to three *Type D* wells will be sampled during Phase V.

4.1.d Ground-Water Sample Collection

As part of this study, techniques are being developed to acquire representative samples from deep ground-water monitoring wells. The method described allows for sampling after the ground water flow regime in the vicinity of the monitoring well stabilizes, as in the standard low-flow sampling technique for minimal drawdown and minimal well disturbance. A downhole water quality indicator device (e.g., pH, specific conductance, ORP, dissolved oxygen) will be used to establish the extraction volume for sample collection. Some samples will be filtered with a high-capacity ground water filter. Samples for metals analysis by ICP-OES and ICP-MS will be collected into 125 mL clear plastic bottles and acidified to pH<2 with nitric acid (Optima). Samples for As speciation will be collected into 30 mL amber plastic bottles and acidified to pH<2 with hydrochloric acid (Optima). Samples for anion analysis will be collected into 30 mL clear plastic bottles. Samples for carbon analysis (concentrations of DOC and DIC) will be collected into 40 mL glass bottles. Samples for O and H stable isotope analysis of water will be collected into 20 mL VOA vials. Samples for dissolved gas analysis will be collected into 150 mL stainless steel vessels (*Type B* wells) or 60 mL serum bottles with crimp cap seals (*Type A, C, and D* wells). Samples for organic analytes will be collected into 1 L or 40 mL amber glass bottles.

Holding times for all analyses are specified in **Table 2**. Holding parameters have not been determined by Isotech for the carbon isotope measurements. This topic is outside of the scope of the current study. The minimum concentration of DIC and methane necessary for isotope measurements are 100 mg/L and 1 mg/L, respectively. All samples will be placed on ice immediately after collection and kept chilled until return to the laboratory. Duplicate samples will be collected on an average of every 10 ground-water wells sampled. Duplicates will be handled in an identical manner to the primary ground-water samples; separate bomb samples will be retrieved in order to collect duplicate samples. Every sample for analysis will be collected in duplicate. On every day of ground-water sampling campaigns, a blank sample will be collected using distilled water to evaluate contamination from the sampling equipment. The equipment blank will be distilled water poured into the 1 L bomb sampler, emptied into the plastic beaker, and then pumped into sampling bottles. Samples that are typically filtered (e.g., metals, anions) will be collected by pumping water from the plastic beaker through a ground water filter. At the same time a source blank will be prepared by pouring deionized water directly into the sampling bottles. A trip blank will be prepared and submitted for analysis. Blank samples will not be submitted for any of the isotope analyses.

Multiparameter probes used for the measurement of pH, ORP, specific conductance, and dissolved oxygen will be calibrated or checked in the field prior to use following the

EPAPAV0025515

recommendations provided by the equipment manufacturer. The pH electrode will be calibrated using a two-point calibration with pH 7 and 10 buffers (note: because of the unusually high pH measured in the deep monitoring wells in October 2010 and April 2011, a certified pH 12.5 buffer will be used as a spot check in the field for Phase V. It will be checked at the beginning of the day, mid-day, and end of the day to ensure it measures within 0.2 standard units). The ORP electrode will be checked by measuring an ORION ORP standard solution (200 ± 20 mV). The specific conductance electrode will be checked with a 1413 uS/cm standard solution (1413 uS/cm ±5%). The dissolved oxygen sensor will be calibrated to 100% atmospheric oxygen saturation. The electrode will be checked by reading a zero-oxygen solution. Performance of the pH probes will be checked at mid-day and the end of each day by measuring and recording the pH of a pH 7 (±0.1 standard units) buffer solution. The other probes shall be checked as well with criteria noted earlier in the paragraph).

Hach spectrophotometers (ferrous iron and sulfide) and turbidimeters (turbidity) will be inspected prior to going to the field and their function verified. These instruments are factory-calibrated and will be checked in the lab prior to going to the field per the manufacturer's instructions. For the Hach spectrophotometers this will consist of checking the accuracy and precision of iron measurements. The ferrous iron accuracy will be checked by measuring a 1 mg Fe/L standard (using Ferrover); the results should be between 0.90 - 1.10 mg Fe/L. The precision will be tested using the standard performing the measurement three times on this solution. The single operator standard deviation should be ±0.05 mg Fe/L. Turbidity will be checked against turbidity standards supplied by Hach (or equivalent). In addition, blanks (deionized water) will be run at the beginning of the day 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 analytes in the blanks. Turbidity blanks are expected to be <1.0 NTU. Alkalinity measurements will use a 1.6N H_2SO_4 solution to titrate samples and standards in the field. The titrator will be checked using a 100 mg/L standard made from Na_2CO_3 or $NaHCO_3$. The analyzed value should be in the range of 90-110 mg/L. Duplicates will be performed once a day or on every tenth sample. Duplicate acceptance criteria are RPD< 15. The values obtained for each duplicate sample will be recorded in the field notebook and RPD will be calculated 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.

Decontamination procedures will be used on the bomb sampler, pump and tubing, plastic reservoirs used for holding ground water, and the multiparameter probes. Note whenever possible, new tubing and plasticware will be used when moving to new sampling locations. After the completion of sampling activities at a well, the bomb sampler will be given an Alconox scrub and wash, followed by 2 potable water rinses, followed by 1 rinse with distilled water. The pump (non-submersible) and tubing used in the well will be cleaned by circulating 2 gallons of Alconox solution through the pump for 5 minutes, followed by a potable water recirculation for 5 minutes, followed by a 5 minute recirculation with distilled water. The multiparameter probe will be rinsed with potable water followed by a rinse with distilled water. Multiple sampling assemblies will be available to minimize the amount of decontamination required, i.e., cleaned vessels will be on-hand in the field. Any pump tubing used with the peristaltic pump for sample

EPAPAV0025516

filtration will be discarded and replaced for each new well sampled.

4.1.e Ground-Water Sampling Labeling

Each well will be uniquely labeled. Samples collected from each well will include the unique label, the date, the initials of the sampler, and designation of the sample type, e.g., "metals". This information will be recorded onto labeling tape, using water-insoluble ink, affixed to each sample bottle.

4.1.f Ground-Water Sample Packing and Shipping

Samples collected from each well will placed together in a sealed Ziploc plastic bag. The bags will be placed on ice in coolers. Glass bottles will be packed with bubble wrap to prevent breakage. The coolers will be sent via FedEx, overnight, to the appropriate lab with chain of custody forms (see **Figure 8)** and custody seal.

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

Isotech Laboratories, Inc.
1308 Parkland Court
Champaign, IL 61821
1-217-398-3490
ATTN: Steve Pelphrey

TestAmerica Savannah
5102 LaRoche Avenue
Savannah, GA 31404
1-912-354-7858
ATTN: Bernard Kirkland

EPA Region 8 Lab
16194 West 45th Drive
Golden, CO 80403
1-303-312-7775
ATTN: Mark Murphy

EPA Region 3 Lab
701 Mapes Road
Ft. Meade, MD 20755
1-410-305-2835
ATTN: Jennie Gundersen

EPA NERL Lab
944 East Harmon Avenue

Las Vegas, NV 89119
1-702-798-2102
ATTN: Patrick DeArmond

ALS Environmental
3352 128th Avenue
Holland, MI 49424
1-616-399-6070
ATTN: Tom Beamish

4.2 Soil-Gas Sampling

Prior to conducting the soil-gas survey, EPA Region VIII will contact landowners and prepare access agreements prior to selection of sampling locations. EPA Region VIII will also contact EnCana, owner of petroleum and natural gas wells, to request the presence of a representative during soil-gas sample location selection to ensure that probing does not occur near buried gas pipelines. Based on discussion with homeowners, NRMRL-Ada personnel will mark off additional areas around homes or on land owned by homeowners that should be avoided during probing. Prior to probing, NRMRL-Ada personnel will contact utility companies to review procedures to follow in the unlikely event that a buried utility line is damaged or severed.

4.2.a Geoprobe Post Run Tubing System (PRT)

An area-wide soil-gas survey will be conducted using the Geoprobe PRT system. A retractable probe and connecting rods will be pushed vertically into the ground until the desired depth is reached. The probe rods will be retracted approximately 6 cm. A metal rod will be used to extend the retractable probe to its full length. The probe creates a 2.5 cm (1") diameter, borehole upon retraction. A PRT adapter with low density polyethylene tubing (0.43 cm x 0.64 cm) will be inserted into the probe rods and turned counterclockwise to engage the adapter threads and an O-ring with the point holder. The tubing will be pulled up lightly to test engagement of the threads. The sample is drawn through the point holder, the adapter, and sample tubing. Since the retraction length is 6 cm (2.25") and the diameter of the retraction tube is 0.95 cm (3/8"), the interval volume of the open portion of the hole is approximated by 25 cm^3. The point holder adds another 24 cm^3 of internal volume. If 0.47 cm (3/16") internal diameter low density polyethylene tubing is used to connect the PRT adapter, the internal volume of tubing = 0.15 * length of tubing (cm^3). The tubing will be replaced after each sample eliminating sample carryover problems and the need to decontaminate the probe rods. Soil-gas samples will also be collected directly through the retractable tip and drive rods by attaching a threaded Geoprobe Gas Sampling Cap having a 1/4" barbed adapter.

4.2.b Installation of Dedicated Soil-Gas Probes

Prior to probing in a "new" (e.g., different property owner, near bedrock outcrop) area, an exploratory borehole will be cored to determine depth to water and variation of soil texture with depth. To create a borehole, a Geoprobe® rig will b e used to push and extract 2.25" O.D. 4' long steel Geoprobe® macrocore (MC) samplers to 3' below the water table surface or refusal whichever comes first. Each sampler will contain a 4' long clear polyvinylchloride (PVC) liner to collect soil cores. A MC core catcher will be used with each liner to avoid loss of soil during retrieval. Each core will be sliced open for manual inspection. Soil texture will be determined

using the Natural Resources Conservation Service Guide to Texture by Feel modified from S.J. Thien (1979).

It is expected that the water table will be very shallow (less than 5') in some areas, so soil-gas probes will be constructed using a 5' section of schedule-40 PVC 1" I.D. slotted screen and riser pipe. The screen will be set across the water table. This will allow measurement of depth to the water table prior to gas extraction to avoid extraction of water during soil-gas sampling. The probes will be sealed and locked using commercially available expandable well caps to ensure a gas-tight seal. All casing materials will be connected without use of solvents, glues, or materials which would induce contamination into the wells. O-rings will be placed between sections of riser pipe to ensure that the casing was water- and gas-tight.

The sandpack will extend 0.5' below and 0.5' above the screened interval. A 0.5' layer of bentonite chips will be placed above the sandpack to prevent intrusion of grout into the sandpack. A grout tremie pipe will be used to pump a bentonite slurry to the base of the rod string using a stainless-steel rod and 3/8" tubing to create an impervious watertight bond between the casing and the undisturbed formation surrounding the casing. The bentonite grout will extend to within 30.5 cm (1') of the surface. Probes will be encased in a 20.3 cm (8") diameter bolted metal box at the surface to protect the probes from surface traffic.

4.2.c Soil-Gas Sample Train

Leak, purge, and gas permeability testing will accompany each soil-gas sample collected from dedicated soil-gas probes for fixed laboratory analysis using a 36 cm (14") diameter 25 cm high (10") stainless-steel chamber designed at GWERD. A photograph of the soil-gas sample train is provided in **Figure 9**. Barbed brass 6.35 mm (1/4") fittings are used to inject and monitor a tracer gas mixture. Masterflex® Viton L/S 6.35 mm internal diameter tubing is used to connect the brass fitting used for injection to a 150-mm Cole-Parmer variable area flow meter (0 - 29 LPM) with a needle valve and to a pressurized canister of tracer gas mixture. Viton tubing is used to direct the tracer gas mixture inside or directly above a borehole or PRT tubing to maximize and monitor tracer concentration at potential location(s) of leakage during leak testing. Viton tubing is used to connect the other brass fitting to a portable gas analyzer for monitoring of tracer concentration inside the chamber at the point of injection.

There are four sampling ports on the chamber to allow gas extraction at a screened interval while monitoring and/or introducing tracers in three other screened intervals if desired. Two sample ports consist of stainless-steel Swagelok® quick connect bodies on the exterior and interior of the chamber. One sample port consists of a Swagelok® stainless-steel tee with a stainless-steel Swagelok® quick connect body on the interior of the chamber and two stainless-steel Swagelok® quick connect bodies on the exterior of the chamber. The centrally located port is equipped with a stainless-steel Swagelok® cross with a stainless-steel Swagelok® quick connect body on the interior of the chamber, two stainless-steel Swagelok® quick connect bodies on the exterior of the chamber, and a stainless-steel Swagelok® toggle valve which is then connected to another stainless-steel Swagelok® quick connect body. The configuration of the centrally located sample port allows for collection of samples in evacuated canisters (not used in this investigation) and placement of an inline 1.0 um polypropylene Whatman disposable filter for gas-water separation. Use of disposable filters eliminates the need to clean the gas-water separator in the event of water entrapment. The toggle valve allows the portion of the sample train upstream from the valve to be shut-in when sampling using evacuated

EPAPAV0025519

canisters. Stainless-steel Swagelok® single-end shu toff stem (SESO) are used to connect the port used for sampling (two external quick-connects) to the centrally located port. SESO stems remain open when uncoupled.

The toggle valve is connected to Swagelok® 6.35 mm stainless-steel flexible tubing, a stainless-steel Swagelok® barbed fitting, and 6.35 mm (1/4") Tygon Masterflex tubing. The Tygon tubing is feed into a Masterflex E/S Portable peristaltic pump which allows gas extraction at approximately 1 liter per minute (LPM). The tubing is then attached to Nafion® tubing to reduce the relative humidity of the gas stream and to ensure a condensing atmosphere in portable gas analyzers. If the relative humidity of atmospheric air is low (e.g, less than 50%), a Perm Pure moisture exchanger (exchanges water with atmospheri c air) will be used. If relative humidity is high (e.g., greater than 50%), a 48" Durridge® Drys tik (allows gas flow through an inner tube while removing water vapor via counter flow through an outer tube) will be used. Ambient air will be passed through a cylinder of Drierite and fed to the Drystik to flush water vapor from the tubing. Nafion® is a copolymer of perfluoro-3,6-dio xa-4-methyl-7octene-sulfonic acid and tetrafluoroethylene (Teflon®). Only three compound s or classes of compounds are normally removed directly by Nafion® tubes: water (H-OH), am monia (when water is present, NH_3 reacts to form NH_3-OH), and alcohols (R-OH, where R is any organic group). Thus, Nafion® tubing should not affect gas screening or laboratory analysis. Nevertheless, both standards and equipment blanks will be run through the Nafion® tu bing to ensure that this is the case.

Tygon Masterflex tubing will be used to connect Nafion® tubing to a 6.35 mm brass barb and the inlet of a 150 mm Gilmont Accucal flowmeter. Flow is measured in standard cubic centimeters per minute (sccm). The outlet of the flowmeter is connected to a stainless-steel Swagelok® cross equipped with two stainless-steel S wagelok® quick-connect bodies to allow duplicate collection of soil-gas samples in Cali-5 Bond gas sample bags for submittal to Isotech Laboratories. The cross is connected to a stainless-steel Swagelok® toggle valve to allow gas flow through the flowmeter to be shut-in while bypass gas flow from the leak chamber flows through another in line stainless-steel Swagelok® t oggle valve in route to portable gas analyzers. This toggle valve allows the use of one gas analyzer to measure gas tracer concentration in the sample train and chamber during leak testing.

A 6.35 mm brass barb on the flowmeter is used to connect the sample train to a GEM2000 Plus CES LandTec Gas Analyzer for continuous measurement of O_2, CO_2, CH_4, CO, H_2, and H_2S in the gas stream for purge testing and screening of soil-gas samples. The outlet of GEM2000 Plus LandTec Gas Analyzer is then fed into a Thermo Scientific TVA-1000B flame ionization detector (FID)/photoionization detector (PID) for continuous measurement of hydrocarbons.

Gas extraction occurs by connecting the quick-conne ct body on the inside of the chamber associated with the port containing two external quick-connect bodies to the quick-connect body of a soil-gas probe using a stainless-steel Swagelo k® double-end shutoff (DESO) stem, Swagelok® 6.35 mm stainless-steel flexible tubing, and a 316 stainless-steel tube-fitting single-end shutoff stem (SESO). A DESO stem has a valve that seals when uncoupled allowing vacuum testing of the entire sample train.

The stainless-steel chamber used for leak testing with dedicated vapor probes will allow approximately 20 cm clearance from the ground surface for soil-gas sampling using the PRT system. Another chamber will be constructed to increase ground clearance to 60 cm. In this case, ports for additional probes in a cluster will not be necessary since there is only one probe

per location.

4.2.d Leak Testing

During soil-gas sampling, ambient air may enter a sampling vessel through loose fittings in above ground components of the sampling train or through openings or cracks in and/or around concrete and bentonite seals used to isolate one or more screened intervals at discrete depths. Components of the above ground sampling train will be tested for leakage prior to soil-gas sampling by observing vacuum loss as a function of time. The Ideal Gas Law will be used to estimate flow of ambient air into above ground components of a sampling train as a function of vacuum. A peristaltic pump will be used to create a vacuum of greater than 75 kPa (atmospheric pressure = 101.325 kPa). Vacuum will be measured using a Sper Scientific manometer. Pressure will be recorded once per minute at three vacuums. Fittings will be inspected, tightened, or replaced as necessary if leakage exceeds 1 sccm. Given that sample flow varies from 300 to 1000 sccm, this contribution to overall leakage is negligible.

Evaluation of leakage in a borehole necessitates the use of non-degradable, non-reactive, and relatively conservative (little retention in soil or water) gases with low ambient and subsurface concentration that can be analyzed in real time in the field using portable gas analyzers. Helium, which has a dimensionless Henry's Law Constant (measured as air concentration/water concentration) of 110 at 20°C, is the most commonly used tracer for leak testing. Tracer gas, He, at 10% will be injected into the chamber during leak testing. The flow rate will be measured using a variable area flowmeter. Detection of He at a concentration of 25 ppmv provides leak detection sensitivity at 0.0025%. Helium is not a target analyte is this investigation. Migration of He in the sample train will not affect interpretation of sample results.

Carbon monoxide (CO) will also be used for leak testing. CO has a dimensionless Henry's Law constant of 43. For comparison, N_2, O_2 and CO_2 which is slightly soluble in water have dimensionless Henry's Law Constants of 61, 31, and 1.2 respectively. Soil-gas will be analyzed prior to tracer testing to check for background. If CO is detected at elevated background concentrations in soil-gas, 1,1-dichloro-2,2,2-trifluoroethane (R-123), which has a dimensionless Henry's Law Constant of 1.4, will be used for leak testing. Sulfur hexafluoride is the most commonly used halocarbon for leak testing but its use in this investigation was deemed inappropriate since it has an extremely high global warming potential of 10,000. R-123 has a global warming potential of only 90 (CO_2 = 1.0) and an ozone depletion factor of only 0.02 (R-11 = 1.0).

Tracer gas, CO, at 18,000 ppmv, will be injected into the chamber during leak testing. The flow rate will be measured using a variable area flowmeter. Leak testing of CO at a concentration of 18,000 ppmv and detection at 10 ppmv provides leak detection sensitivity at 0.055%. Leak testing at a concentration of 10,100 ppmv and detection at 25 ppmv provides leak detection sensitivity at 0.25%.

4.2.e Purge Testing

Tubing connected to an initially closed valve at the top of a dedicated vapor probe will have had direct contact with ambient air prior to sampling. Thus, some volume of gas must be extracted prior to sampling to eliminate the influence of ambient conditions. A simple mass balance equation can be utilized to demonstrate that when the initial concentration in a probe is zero, the

EPAPAV0025521

most conservative condition, extraction of 3 to 5 internal volumes ensures that vapor concentrations entering a sampling vessel are 95% to greater than 99%, respectively, of gas concentrations in the surrounding soils. However, the process of borehole creation and subsequent vapor probe installation likely perturbs vapor concentration some distance from a borehole. Thus, if vapor equilibration has not occurred prior to sampling, greater than 3 to 5 internal volume exchanges (including the internal volume of the sandpack) may be necessary to achieve a stable concentration. This has been observed during an ongoing investigation at another site.

Borehole installation methods such as air rotary, would be expected to impact vapor concentrations a significant distance from a borehole. Air rotary is often used in consolidated media. Rotosonic drilling is frequently used for borehole creation in glacial till where large cobbles are present and in semi-consolidated media and induces intense vibration and heating of soils adjacent to the casing. Direct-push sampling methods such as the Geoprobe PRT system used in this investigation likely results in the least disturbance since sampling is accomplished without removal of soil. However, direct-push techniques compress surrounding soil and may result in air restriction in plastic clayey soils. This has been observed during an ongoing investigation at another site.

A practical approach to evaluating nonequilibrium is to collect sequential samples or samples preceded by various extraction volumes (i.e. purging) until relative stability of vapor concentration is achieved. During soil-gas sampling, mass removed in the vicinity of a probe is replaced by mass drawn in by gas advection from surrounding soil and by partitioning from soil to water and water to air. If vapor nonequilibration exists, vapor concentration will increase with gas extraction volume as less contaminated disturbed soil gas is replaced by more contaminated less disturbed soil gas. Subsequent purging efforts then should result in achievement of steady-state concentrations at less purge volumes. This has been observed during an ongoing investigation at another site.

When evaluating the potential impact of excessive purging, concentration reduction during gas extraction will not occur until significant mass removal occurs at and above a probe as relatively clean atmospheric air replaces contaminated soil gas or when the rate-limited mass exchange occurs from high pore-gas velocities. Thus, attainment of a near constant concentration (± 1% of O_2, CO_2, and CH_4 readings) during purging ensures attainment of equilibrium and the absence of excessive purging. For instance, DiGiulio et al. (2006b) evaluated the effect of extracting a large volume of air from a relatively shallow vapor probe (screened interval 2.1 meters to 2.4 meters below grade). The internal volume of the probe was one liter. The probe had been sealed for at least three months prior to sampling. A total of 103 liters of air were extracted during this test. After the first internal exchange, sample concentration then remained relatively constant.

Readings will be recorded manually onto a spreadsheet illustrated in **Figure 10** and then input into an EXCEL spreadsheet.

4.2.f Gas Permeability Testing

Gas permeability determination is necessary to simulate gas flow in soil during soil-gas sampling. Gas flow modeling is useful in evaluating the volume from which gas is extracted during purging and sampling and the potential for interaction with atmospheric air. This analysis

becomes critical when sampling at shallow (e.g., < 1 meter) depths.

There are a number of publications describing field-scale gas permeability tests. These tests however typically involve extraction or injection from a gas well or probe at flow rates exceeding 30 LPM with measurement of pressure in nearby probes. Estimates of radial and vertical permeability represent integrated values over the field of measurement. During soil-gas sampling, gas permeability testing is conducted at much lower flow rates (e.g., < 1 LPM) with measurement of pressure at point of extraction or injection (i.e., single-interval testing). Single-interval testing provides permeability estimation over a relatively small volume of subsurface media thereby providing a mechanism for assessing physical heterogeneity or spatial variability in permeability on a scale much smaller than full field-scale tests.

In highly permeable media such as sand, steady-state conditions are typically achieved in seconds. In silt or media of less permeability, steady-state is typically achieved in tens of minutes. In low permeability media, transient gas permeability testing eliminates the need to wait for attainment of steady state and allows estimation of gas-filled porosity in a formation.

Line-source/sink analytical solutions are commonly used transient gas flow analysis and parameter estimation. The implicit assumption in use of these solutions is that borehole storage effects are insignificant. Varadhan and DiGiulio (unpublished) derived an analytical solution for two-dimensional axisymmetric anisotropic transient gas flow from a well having a finite radius and borehole storage. The analytical solution is described by DiGiulio and Varadhan (2001). DiGiulio and Varadhan (2001) compared the line-source/sink and finite-radius solutions at the radius of the sandpack during air injection. The line-source/sink solution simulated a more rapid rise in normalized (observed pressure/initial pressure) pressure at early time and a lower normalized pressure at late time compared to the finite-radius solution. The former effect is due to a delayed response from borehole storage. The latter effect is due to simulation at some distance in the formation itself for the line-source/sink solution compared to simulation at the sandpack -formation boundary for the finite-radius solution. Thus, neglecting borehole storage can result in a source of error in estimating gas permeability when conducting single-interval tests.

In this investigation, the analytical solution developed by Varadhan and DiGiulio (unpublished) will be used to interpret single-interval transient gas permeability tests. Pressure readings will be recorded every second using a Sper Scientific manometer and stored in a PC using a RS-232 cable and software provided by the manufacturer. Pressure measurement will occur prior to entry into the gas/water separator to avoid measurement of head loss associated with most above ground fittings. Head loss associated with tubing and quick-connects prior to the point of pressure measurement will be determined at flow rates used for testing and subtracted from pressure differential readings used for analysis. A Gilmont 150 mm variable area Accual flowmeter with a range of 0 to 2100 sccm and a needle valve to control flow will be used to measure flow. The accuracy and precision of the flowmeter is 2% and 1% respectively.

4.2.g Cali-5 Bond Sample Bag Study

Soil-gas and gas samples from domestic wells will be collected in 0.5 liter Cali-5-Bond® evacuated gas sample bags equipped with a Leur-Fit Valve™. A Leur-taper Quick-Mate™ connector with a 4 mm barb fitting will be used to connect flexible tubing to the sampling bag. Cali-5-bond™ gas sampling bags are constructed from inert 5.5 mil thick material made from

EPAPAV0025523

five layers of film. The layers are comprised of an inner layer of high-density polyethylene, followed by polyamide, an aluminum foil barrier, a polyvinylidene chloride layer and an outer layer of polyester.

A defined holding time is not known for the Cali-5 Bond sample bags. Non-published internal data provided by Isotech Laboratories suggests stability in excess of 105 days for many of the target analytes. However, neither hydrogen nor helium were included, which may be more apt to be lost by diffusion. Attempts to locate published data on holding times for these sample bags was unsuccessful. To ensure data are not compromised or to identify data that may have been affected by holding times, a study will be done to identify holding times for the target analytes in the Cali-5 Bond sample bags. If it is determined that gas data may be compromised by exceeding the holding time determined in this study, such data shall be identified with appropriate qualifiers.

The stability of fixed gases and light hydrocarbons in 0.5 liter Cali-5 Bond gas sampling bags equipped with a Leur-Fit Valve™ will be evaluated. Gas samples will be analyzed for fixed gases and light hydrocarbons. Fixed gases include Ar, He, H_2, O_2, N_2, CO_2, CH_4, C_2H_6, C_2H_4, C_3H_6, C_3H_8, iC_4H_{10}, nC_4H_{10}, iC_5H_{12}, nC_5H_{12}, and C_6+. Helium will be eliminated from analysis if it is used as a carrier gas for the GC. A commercially prepared gas mixture will be used that will allow concentration versus time measurement of gases. Samples will be analyzed at 0, 5, 15, and 30 days after sample collection. A duplicate sample will be collected once every two samples.

Fixed gases and hydrocarbons will be analyzed by gas chromatography using a method based upon RSKSOP-194v4. Sample reporting units will be mol% or ppmv.

Check or reference standards will be analyzed every tenth analysis, ensuring that sample runs are always bracketed by standards. Blanks will be analyzed prior to samples to determine presence of background. Presence of background that would interfere with sample analysis will be corrected prior to sample analysis.

Accuracy of gas component analysis shall be will be within +/-15%, i.e., the measured value of standards compared to their known or certified value. Precision of the analyses will be determined by duplicate sample analysis with a Relative Percent Difference (RPD)* not to exceed 15%.

Full data packages shall be provided in electronic form for all sample analyses to allow for reconstruction of analysis: calibration documentation, QA/QC results, raw data, data reduction, data qualifiers, quantitation and detection limits, deviations from method requirements, deviations from QC acceptance criteria, and these deviations' impact to reported results.

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

Where a = sample measurement
b = duplicate sample measurement

4.2 h <u>Soil-Gas Sample Labeling</u>

All soil-gas samples will have a unique identifier, with the date and time of collection, and the initials of the sampler. Labeling tape will be affixed to each Cali-5 Bond sample bag. Water insoluble ink will be used to record sample information. Sample collection identification, date adn time of collection, and the sampler will be noted in the field notebook as well as the chain of custody.

4.2i Soil-Gas Sample Packing and Shipping

Isotech Laboratories will provide UN approved one gallon metal cans for shipment of Cali-5 Bond sample bags. Up to three 0.5 liter 6" x 8" bags can fit into each can when properly filled. Care will be taken to not compress the sample bags while packing. After packing, the lid will be placed on top of the can sealed by pounding on a plastic ring provided with the can. Metal cans will be placed in fiberboard boxes provided by Isotech Laboratories according to the general instructions included with the box. Samples will be shipped overnight through UPS. If soil-gas samples contain less than 5% methane (or other hydrocarbons), they are not considered flammable nor hazardous for shipping purposes. The Chain of Custody form that will accompany soil-gas samples is illustrated in **Figure 11**. See Section 4.1.f for Isotech's shipping address.

If needed, Isotech Laboratories provides instructions on labeling and shipping boxes containing flammable soil-gas samples which are based on the IATA Dangerous Goods Regulations 48th Edition, 2007". The following labels will be affixed to the outside of the box all on the same side: (1) FLAMMABLE GAS, (2) UN3167, and (3) DANGER DO NOT LOAD IN PASSENGER AIRCRAFT. Labels will not be folded or affixed in such a manner that parts of the same label appear on different faces of the package. A "SHIPPERS DECLARATION FOR DANGEROUS GOODS" obtained from UPS will accompany soil-gas samples. The information that may be needed on this form is given below.

Proper Shipping Name: Gas Samples, non-pressurized , flammable, n.o.s. (Natural Gas)
Class or Division: 2.1
UN or ID Number: UN3167
Subsidiary Risk: None (leave blank)
Packaging Group: None (leave blank)
Quantity& Type of Packaging:
Fiberboard boxes box X 4L
Packing Instructions: 206
Shipment Type: Non-Radioactive
Prepared per: ICAO/IATA
Additional Information:
NRMRL-Ada emergency response telephone number
Limitations: Cargo Aircraft Only

As required by the Department of Transportation (49 CFR - Part 172, Subpart G, §172.604) a person who offers a hazardous material for transportation must provide an emergency response telephone number, including the area code or international access code, for use in the event of an emergency involving the hazardous material. A Materials Safety Data Sheet (MSDS), illustrated **Figure 12**, will accompany soil-gas samples exceeding 5% methane.

4.3 Analysis of Drilling Additives

In an attempt to evaluate all possible sources of inorganic and organic constituents identified in ground water collected from the deep monitoring wells (*Type A* wells), commercial products used during installation and development of the wells were analyzed in March 2011 and July 2011. This type of analysis is a non-standard approach since it is generally assumed that products used for well drilling and completion do not remain in the subsurface and do not influence the results of subsequent water-quality testing. Products used at Pavillion for well installation and well development include: EZ-Mud Gold (Haliburton; clay stabilizer), Quik-Gel (Haliburton; bentonite), Dense Soda Ash (OCI Chemicals; sodium carbonate), Quik-Trol Gold (Haliburton; clarifier), Penetrol (Haliburton, mud removal), and Aqua-Clear PFD (Haliburton, mud removal). Material Safety Data Sheets for these products do not indicate the presence of volatile or semi-volatile contaminants of concern.

In the laboratory, these products were separately diluted with tap water at a weight ratio of approximately 1:20 to 1:100. This dilution range is typically more concentrated than the recommended product mixture and therefore concentrations measured in the water extracts would represent maximum values that could be observed in the case that a pure product mixture was pulled through the well screens. All dilutions were completed in clean 1 L plastic beakers. A laboratory balance was used to measure a weight of a) the product and b) the final weight of the product plus water mixture. The product plus water mixture was stirred thoroughly. Solid products (EZ-Mud Gold, Dense Soda Ash, Quik-Gel, Quik-Trol Gold) were allowed to completely dissolve into tap water. After complete mixing, a 5 mL subsample was collected from the 1 L beaker and measured for pH using a benchtop pH meter and electrode calibrated with pH 7.0 and 10.0 buffer solutions. A 1 mL sample was pulled and measured for specific conductivity using a portable probe calibrated with 1413 uS/cm solution.

Samples were pulled and submitted for analysis as follows. A 30 mL sample was collected for anion analysis (chloride, sulfate) using RSKSOP-276 v3. A 60 mL sample was collected, acidified with nitric acid, and analyzed for metals by ICP-OES using RSKSOP-213v4. A 45 mL sample was collected for the analysis of total organic carbon by RSKSOP-330v0. The sample was preserved by acidifying with phosphoric acid. Alcohols, aromatic, and chlorinated hydrocarbons were analyzed by GC-MS using RSKSOP259 v1. The sample was poured to completely fill with no head space glass VOA vials containing trisodium phosphate. A 45 mL sample was collected for glycol ether analysis by direct aqueous injection/GC-FID using a method in development by Shaw (following EPA 8015). Tap water used to prepare the water extracts was submitted for the same set of analyses. One of the prepared extracts was selected for duplicate samples, which were collected and submitted to the respective analytical laboratory.

5.0 MEASUREMENT PROCEDURES

5.1 Ground Water

Ground-water samples will be collected and analyzed using standard operating procedures. Analysis includes inductively coupled plasma - optical emission spectroscopy (ICP-OES; for cations), inductively coupled plasma - mass spectroscopy (ICP-MS; for trace metals), liquid chromatography - inductively coupled plasma - mass spectroscopy (LC-ICP-MS; for arsenic speciation), capillary electrophoresis (CE, anions), carbon analysis using infrared detection,

isotope ratio mass spectroscopy for isotope ratios in water, and gas chromatography (GC, for dissolved gas analysis). These analytical methods and accompanying QA/QC practices (e.g., blanks, calibration checks, duplicates, second source standards, matrix spikes) are described in various in-house Standard Operating Procedures RSKSOP-112v6, RSKSOP-259v1, RSKSOP-299v1, RSKSOP-213v4, RSKSOP-175v5, RSKSOP-194v4, RSKSOP-214v5, RSKSOP-257v2, RSKSOP-276v3, RSKSOP-296v0, RSKSOP-330v1, and RSKSOP-297v1 or RSKSOP-298v1). 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. An SOP has been developed by Shaw as part of this study for samples collected from deep wells with the sample bombs. This SOP (RSKSOP-327) addresses analysis procedures for pressurized samples and procedures for carrying out calculations. Shaw worked on developing an SOP (direct aqueous injection/GC-FID, based on EPA Method 8015) for analysis of glycols in water (2-butoxyethanol, ethylene, propylene, diethylene, triethylene, and tetraethylene glycols), but was discontinued due to inability to achieve the detection limits needed and a potential for false positives at low levels.

Samples will be submitted to Isotech Laboratories for analysis of tritium and stable isotope ratios ($\delta^{13}C$) of dissolved inorganic carbon by gas-stripping and IRMS. A general discussion of QA/QC for Isotech Laboratories is provided in their QAP attached in **Appendix A**. However, acceptance criteria are not included. An inquiry will be made of Isotech for this information.

For Phase V, samples will be submitted to TestAmerica for analysis of Methylene Blue Active Substances (MBAS) using EPA Method 425.1. This method is used to estimate the concentration of detergents and anionic-type surfactants in water samples. Linear alkyl sulfonate (LAS) is used as a proxy compound and concentrations are reported as mg/L LAS.

For Phase V, samples will be submitted to ALS Environmental for analysis of methanol, propylene glycol, and ethylene glycol by EPA Method 8015M (GC/FID). ALS Environmental uses their in-house SOP titled "Nonhalogenated Organic Analysis by GC/FID".

For Phase V, samples for ethoxylated alcohols, alkylphenols, and acrylamides will be analyzed by the ORD/NERL-Las Vegas laboratory using a method in development as follows. Water samples are extracted using an automated Autotrace SPE workstation. The ethoxylated alcohols, alkylphenols, and alkylphenol ethoxylates are extracted using Waters Oasis HLB SPE cartridges (6cc, 200 mg), however, any polystyrene-divinylbenzene SPE cartridge that has been demonstrated to show sufficient recovery can be used. Additionally, acrylamide is extracted using activated carbon (500 mg) cartridges from Biotage. Because highly polar acrylamide is not retained by HLB cartridges, the flowthrough from the HLB cartridge sample loading is collected for the acrylamide extraction, which is subsequently extracted using activated carbon cartridges. The HLB extraction method begins by conditioning the SPE cartridges with 5 mL MeOH, followed by 5 mL H_2O. Next, 500 mL sample is loaded onto the cartridges. The volumetric flasks that contained the samples are then rinsed with 50 mL water, which is also loaded onto the cartridges. The SPE cartridges are rinsed with 2 mL water, and then they are dried for 30 min with N_2. The analytes are eluted off the cartridge by eluting 2 times with 3 mL of 2:2:1 MeOH/acetone/ethyl acetate, containing 0.1% formic acid. This eluate should contain the ethoxylated alcohols, alkylphenols, and alkylphenol ethoxylates, and it is concentrated to 0.5 mL using a TurboVap Concentrator. After concentration, samples may be filtered using 0.2 micron syringe filters. The flowthrough that was collected during sample loading of the HLB SPE is then extracted for acrylamide using activated carbon. The activated carbon SPE cartridge is first

EPAPAV0025527

conditioned with 8 mL MeOH and then 8 mL H_2O. The samples are then loaded onto the cartridges. The volumetric flasks that contained the samples are then rinsed with 50 mL water, which is also loaded onto the cartridges. The SPE cartridges are rinsed with 2 mL water, and then they are dried for 30 min with N_2. The analytes are eluted off the cartridge by eluting with 10 mL of MeOH. The eluates are concentrated with a TurboVap Concentrator.
The extracted samples are then analyzed by LC-MS. Positive ionization mode is used for the ethoxylated alcohols, alkyphenol ethoxylates, and acrylamide. Negative ionization mode is used for the alkylphenols. Full scan mode is used for the ethoxylated alcohols, alkylphenols and alkylphenol ethoxylates. Multiple reaction monitoring MS/MS is used for the acrylamide.

Samples will be submitted to Region III and Region VIII laboratories for analysis of organic compounds. Region III and VIII are responsible for the laboratory QA/QC for these samples.

5.2 Soil-Gas

5.2.a Field Screening During Soil-Gas Survey

A summary of instruments to be used in this investigation, method of measurement (standard operating procedures), concentration range of measurement, concentrations for calibration, and concentrations of gas standards to be used to check the accuracy of instruments is summarized in **Table 5**. The methods to be used are listed in **Table 6**. The accuracy of the instruments will be checked using criteria listed in **Table 6** from the SOPS cited in this table. Gas standards for calibration will be introduced into five-liter SKC Flex Foil sampling bags and feed directly to portable gas analyzers. Check standards will be introduced into ten-liter SKC Flex Foil sampling bags and feed into the sampling train to ensure the absence of flow and material (e.g., tubing, filters, etc) effects.

The Thermo Scientific TVA-1000B will be calibrated at all concentrations listed. Other portable gas analyzers will be calibrated at the concentration specified or at a concentration closest to expected soil-gas concentration. Calibration will occur at the beginning of each work day and when deviation from a check standard at the calibration concentration(s) at the relevant accuracy occurs. The concentration selected for calibration will be that closest to the expected soil-gas concentration. A check standard at the calibration concentration and a method blank will be measured prior to and at the end each sample event and at all concentrations during calibration. "Accuracy" in **Table 5** is per the manufacturer's specifications and may not reflect project requirements.

Carbon monoxide (tracer) will be supplied using gas cylinders (103 liter) obtained from Air Liquide in Plumsteadville, PA using certified gas mixture concentrations with balance air. R-123 (alternative tracer) will be supplied using gas cylinders (221 liter) obtained from Air Liquide America Specialty Gases, LLC from Plumsteadville, PA using certified gas mixtures with balance argon. Two gas standards (103 liter cylinders): (1) 2.5% CH_4, 5% CO_2, 10% O_2, balance N_2 and (2) 2.5% CH_4, 20% CO_2, 10% O_2, balance N_2 will be obtained from Ideal Gas Inc. in Southgate, MI and two gas standards (103 liter cylinders): (1) 50% CH_4, 35% CO_2, balance N_2 and (2) 4% O_2, balance N_2 obtained from James Supply and Rental in Ada, Oklahoma will be used for calibration and concentration checks for O_2, CO_2, and CH_4. Gas standards for H_2S and H_2 will be obtained from CES-LANDTEC from Colton, CA.

Carbon dioxide and CH_4 are measured in the GEM2000 Plus using IRGAs. The CO_2 reading is

EPAPAV0025528

filtered to an infrared absorption frequency of 4.29 μm (nominal), the frequency specific to CO_2. Therefore, other gases typically detected in soil gas will not affect the CO_2 reading. The CH_4 reading is filtered to an infrared absorption frequency of 3.41um (nominal), the frequency specific to hydrocarbon bonds. The presence of other light hydrocarbons (e.g. ethane, propane, butane) will result in a higher reading of CH_4 than actually present. Oxygen, H_2S, and CO are measured in the GEM2000 Plus using internal electrochemical cells. The O_2 sensor is a galvanic cell type with no influence from CO_2, CO, H_2S, SO_2 or H_2. The electrochemical cell for CO is susceptible to interference from H_2 and H_2S giving an artificially high reading of CO in the presence of these gases. The GEM2000 Plus uses a 'hydrogen compensated' CO cell to counteract the interference of H_2 and an internal H_2S filter to eliminate H_2S cross gas interference.

A Thermo Scientific TVA-1000B will be used to screen for total hydrocarbons using a portable flame ionization detector (FID) and photo ionization detector (PID) according to RSKSOP-320v1 - *Determination of Organic and Inorganic Vapors using the TVA-1000B Toxic Vapor Analyzer*.

5.2.b Fixed-Laboratory Analysis of Gas Samples

Nine shallow (< 15') soil-gas probes were installed in July 2010 and screened for O_2, CO_2, CH_4, H_2S, CO, and total hydrocarbons using portable gas analyzers (IRGAs, electrochemical cells, PID, FID). Levels of O_2 varied from 11 to 19%. Levels of CO_2 varied from 1 to 7%. CH_4 and total hydrocarbons were not detected (greater than 10 ppmv). H_2S and CO were not detected (detection limit of 1 ppmv). Preliminary screening of soil-gas samples indicates insufficient concentration of methane (> 0.5%) to allow stable and radiocarbon isotope analysis. Two deep (drilled to near 1000' below ground surface) ground-water monitoring wells were installed and developed in the area. Screening of gas inside one well currently being developed revealed a reading of close to 5000 ppmv (0.5%) with a FID indicating a high concentration of CH_4. Screening of headspace of water from four domestic wells indicated readings of approximately 100 ppmv with a FID. However, gas above water at one well ignited on one instance indicating CH_4 above the LEL or 5%.

Gas samples will be collected from 9 soil-gas probes, 2 deep wells, and 4 domestic wells. Gas exiting probes and wells will be monitored for O_2, CO_2, CH_4, CO, H_2S, and total hydrocarbons using IRGAs, electrochemical cells, a FID, and PID prior to sample collection. These results will be reported on Chain of Custody forms to assist Isotech Laboratories with analysis. With the exception of radiocarbon analysis, turnaround time should be less than 10 days or less from date of sampling.

Soil-Gas Sampling

Soil-gas sampling will include 11 samples (includes 2 duplicate samples), 2 equipment blanks, and 2 transportation blanks collected in 0.5 liter Cali-5 Bond gas sampling bags equipped with a Leur-Fit Valve™. All samples will be analyzed for fixed gases (Ar, He, H_2, O_2, N_2, CO_2) and light hydrocarbons (CH_4, C_2H_6, C_2H_4, C_3H_6, C_3H_8, iC_4H_{10}, nC_4H_{10}, iC_5H_{12}, nC_5H_{12}, C_6+). The equipment blanks will consist of ultrapure N_2 circulated through the sample train. The quality of nitrogen gas used will be documented in the field notebook. The transportation blanks will consist of ultrapure N_2 introduced directly into a sample bag.

Gas Sampling from Domestic Wells

One-quarter inch outside diameter HDPE tubing will be inserted into the top of caps of domestic wells and connected to a TVA-1000B portable FID to determine the viability of collecting gas samples for fixed laboratory analysis. Since the detection limit of methane for fixed laboratory analysis is 10 ppmv, this concentration will serve as a cutoff for screening. A maximum of five samples (including 1 duplicate sample) will be collected in 0.5 liter Cali-5 Bond gas sampling bags equipped with a Leur-Fit Valve™. Samples will be analyzed for fixed gases, light hydrocarbons, stable isotopes of carbon (^{12}C, ^{13}C) and hydrogen (^{1}H, ^{2}H) for CH_4, C_2H_6, and C_3H_8, and radiocarbon (^{14}C) for CH_4. Sample collection will include 1 equipment and 1 transportation blanks for fixed gases and light hydrocarbons. The equipment blanks will consist of ultrapure N_2 circulated through the sample train. The transportation blanks will consist of ultrapure N_2 introduced into a sample bag.

The aqueous concentration of fixed gases and light hydrocarbons will be estimated during purging of domestic wells. A commercial faucet to hose adapter will attached to a faucet or other sampling point. A section of 1/4-inch internal diameter Altafluor 200-E high performance fluorinated ethylene propylene (FEP) will be connected to the adapter. The tubing will be connected to a stainless-steel barbed fitting which will be threaded to a stainless-steel tee. One end of the tee will be threaded to a stainless-steel Swagelok quick-connect body. The other two ends of the tee will be threaded to stainless-steel Nupro valves. One of the valves will be connected to a stainless-steel barbed fitting which will be connected to a 0.5 L Cali-5 Bond gas sampling bag equipped with a Leur-Fit Valve™ via 3/16" internal diameter Altafluor 200-E FEP tubing. The other Nupro valve will be connected to a stainless-steel barbed fitting which will be connect to ⅜-inch internal volume Altafluor 200-E FEP tubing. The tubing will be connected to a brass barbed fitting which will serve as an entry point into a 5 liter plexiglass cylinder. Atmospheric air will be introduced at the base if the cylinder at a flow rate of 1 LPM using a peristaltic pump. Air in the cylinder will exit at an outlet at the top of the cylinder through a brass barbed fitting. Air will flow via ⅜-inch Altafluor 200-E FEP tubing to a TVA-1000B portable flame ionization detector calibrated in accordance with RSKSOP-320v1. Another outlet at the base of the cylinder will be connected to Teflon tubing for disposal of water. Prior to purging, connections will be leak tested by applying a vacuum using a 0.5 L Hamilton gas-tight syringe. A digital manometer will be connected to the quick-connect to test vacuum. Readings on the portable FID will be recorded every 30 seconds until FID readings stabilize (± 10 ppmv). If only gas is present in the gas sampling bag, samples will be submitted to Isotech Laboratories for stable carbon and hydrogen isotope analysis of methane, ethane, and propane, stable carbon analysis of carbon dioxide, light hydrocarbons, and fixed gases. If only water or a combination of gas and water is present in the sampling bag, light hydrocarbons and fixed gases will be analyzed using an Agilent Micro 3000 portable gas chromatograph in accordance with RSKSOP-194v4. Calculations to support estimation of aqueous concentration in gas sampling bags are as follows.

By mass balance, aqueous concentration in a gas sampling bag can be estimated by:

$$C_w = C_g K_H \left[\frac{V_g + V_{g(carrier)} + K_H V_w}{V_g + K_H V_w} \right]$$

where

C_w = concentration in aqueous phase (mg L^{-1})

C_g = concentration in gas phase (mg L^{-1})
K_H = dimensionless Henry's Law Constant at temperature of interest (mg L^{-1} (aq)/mg L^{-1} gas)
V_g = volume of gas phase in sample bag prior to addition of carrier gas (L)
$V_{g(carrier)}$ = volume of carrier gas added to sample bag (L)
V_w = volume of water in sample bag (L).

If $V_{g(carrier)}$ = 0 (gas only or no addition of carrier gas necessary), then

$$C_w = C_g K_H$$

If V_g = 0 (water only), then,

$$C_w = C_g \left(\frac{V_{g(carrier)}}{V_w} + K_H \right).$$

Henry's Law can be estimated at a temperature of interest by:

$$k_H = k_H^* \exp\left[-\frac{\Delta_{soln} H}{R} \left(\frac{1}{T} - \frac{1}{T^*} \right) \right]$$

where

k_H = Henry's Law Constant at temperature of interest (mol L^{-1} atm^{-1})
k^*_H = Henry's Law Constant at 298.15°K (mol L^{-1} atm^{-1})
$\Delta_{soln}H$ = Enthalpy of solution (J mol^{-1})
R = Ideal Gas Constant (8.314 J mol^{-1} K^{-1})
T = temperature of interest (°K)
T* = 298.15°K.

Sandler (1999) provides a comprehensive list of Henry's Law Constants and $\Delta_{soln}H/R$ for inorganic and organic compounds.

Henry's Law Constant can then be converted to a dimensionless form by:

$$K_H = k_H RT$$

where

R = Ideal Gas Constant (8.206E-02 L atm mol^{-1} K^{-1})
T = temperature of interest (°K).

A gas concentration in parts per million volume (ppmv) can be expressed in mg/l by:

$$C_g(mg/l) = C_g(ppmv)\frac{MP}{10^3 RT}$$

where:

EPAPAV0025531

M = molecular weight (g mol-1)
P = gas pressure inside bag (atm)
R = Ideal Gas Constant (8.206E-02 L atm mol^{-1} K^{-1})
T = temperature of interest (°K)

Since the gas sampling bag is flexible, atmospheric pressure can be used to estimate gas pressure inside the gas sampling bag. Assuming negligible addition of mass from the gas phase, then by mass balance the volume of water in a sampling bag can be estimated by:

$$V_w \approx \frac{M_T - M_{tare}}{\rho_w}$$

where

M_T = Total mass of sample bag (g)
M_{tare} = tare (empty) mass of sample bag (g)
ρ_w = density of water (g/L).

Initial gas volume in the sample bag can then be estimated by:

$$V_g = V_T - V_{tare} - V_w$$

where

V_T = total initial volume of bag prior to addition of carrier gas sampling (L)
V_{tare} = tare (empty) volume of bag (L).

Volumes will be estimated by immersing gas 0.5 L Cali-5 Bond gas sampling bags in a 2 L graduated cylinder partially filled with water. The volume of water displaced will determine the volume. Mass will be determined by weighing 0.5 L Cali-5 Bond gas sampling bags using a precision balance (EPA# 785522). The balance will be verified by weighing certified weights (certified 1/21/2011) and recording the results in the precision balance instrument log book. Temperature will be determined using a traceable digital thermometer (Cole Parmer Cat. No. 94460-74, calibration certification No. 4227-328519 3). Samples will equilibrate to room temperature for at least one hour.

Gas Sampling from Deep Monitoring Wells

Gas Sampling from two deep monitoring wells will include collection of 3 samples (includes 1 duplicate sample) for fixed gases, light hydrocarbons, stable isotopes of carbon and hydrogen for CH_4, C_2H_6, and C_3H_8, and radiocarbon for CH_4. Sample collection will include 1 equipment and 1 transportation blank for fixed gases and light hydrocarbons. The equipment blank will consist of ultrapure N_2 circulated through the sample train. The transportation blank will consist of ultrapure N_2 introduced into a sample vessel. If gas pressure in the well casing is low (< 2 psig), the sample train used for soil-gas sampling will be utilized to collect gas samples in 0.5 liter Cali-5 Bond gas sampling bags equipped with a Leur-Fit Valve™. A Schematics of the two deep wells are provided in **Figures 13a** and **13b**. Connection to the casing is through a 1/2" female NPT fitting associated with a 1/2" ball valve. If the soil-gas sampling train is used for gas

EPAPAV0025532

sampling, pipe fittings will be used to reduce from a 1/2" male NPT fitting to a 1/8" female NPT fitting. A Swagelok quick-connect body will then be used to seal the system . If pressure in the well casing is high (≥ 2 psig), an Isotech wellhead manifold system will be used for sampling. Connection to the wellhead manifold is through a 1/4" male NPT fitting. If the wellhead manifold is used for sampling, pipe fittings will be used to reduce from a 1/2" male NPT to 1/4" female NPT.

5.3 Evaluation of Cement Bond Logs

Cement bond/variable density (CBL/VDL) logs, available for less than half of production wells, were obtained online from the Wyoming Oil and Gas Conservation Commission (WOGCC) to evaluate well integrity. Sporadic bonding is defined as an interval having an amplitude (mV) greater than A80 (EPA 1994) where

$$A_{80} = 10^{0.2\log A_0 + 0.8\log A_{100}}$$

and A80, A0, and A100 = amplitude at 80%, 0%, and 100% bond respectively. A0 typically corresponds to amplitude in free pipe whereas A100 corresponds to the best-bonded interval on the CBL.

CBL/VDLs provide an average volumetric assessment of the cement in the casing-to-formation annular space and are considered low resolution tools compared to ultrasonic imaging tool logs which provide a high-resolution 360° scan of the co ndition of the casing-to-cement bond (Bybee 2007). Acoustic imaging tools do not directly measure cement seal. Communication of fluids between intervals has been observed to occur despite indication of "good to excellent" cement bond on acoustic logs (Boyd et al. 2006). All CBL/VDLs available from WOGCC reflect pre-hydraulic fracturing conditions.

5.4 Review of Borehole Geophysical Logs

Borehole geophysical logs from 32 oil and gas wells were downloaded from the WOGCC website and utilized to map lithology in the vicinity of the two deep monitoring wells. Depending upon the specific production well, various combinations of natural gamma, resistivity, self-potential, density, and neutron porosity logs were used. The natural gamma log measures the natural radioactivity of the formation surrounding a wellbore. Shales and clays are responsible for most natural radioactivity, so the gamma ray log can be useful for determining which intervals contain these types of rocks. The resistivity log measures the formation resistance to electrical current flow. Shales and brine-filled sandstones have lower resistivity than sandstones containing fresh water. Sandstones containing hydrocarbons are typically very resistive. The spontaneous potential (SP) log measures the difference in electrical potential between a fixed electrode at the surface and an electrode in a borehole. Readings opposite shales or clays are relatively constant and form the shale baseline, or "shale line." The SP curve typically deflects to the left or right opposite permeable formations depending on the salinity of the drilling mud. The gamma-gamma or density log measures the response of the formation to bombardment by gamma radiation. Strata with high bulk densities impede the source gamma rays more than low density strata and produce correspondingly lower counts at the detector.
The neutron log measures the response of the formation to bombardment by neutron radiation. A high concentration of hydrogen atoms near the source captures a greater number of neutrons

EPAPAV0025533

and produces a smaller counting rate at the detector. In saturated materials, the neutron log can be an indicator of porosity.

Using these geophysical logs, sandstone and shale intervals were selected for each well. Since distinguishing grain size from the geophysical logs is not possible, all sandstones were assigned to a single category. This designation was maintained for consistency for near surface deposits where fine-, medium-, and coarse-grained sandstones can be differentiated from driller's logs No gradational/intermediate values between the two lithologies (e.g. 80% shale, 20% sandstone) were used although they are known to exist throughout the Wind river Formation. It will be generally clear from the various logs whether a specific interval contained sandstone or shale, but not clear where each layer started or ended. Assignment of boundaries is therefore subjective. Each sandstone or shale layer were represented as having at least one meter in thickness since log resolution is insufficient to discern individual layers less than this resolution.

The scattered borehole data was used to populate a 3D lithology model using a commercial software package Rockware15. Lithology cross-sections represent slices taken through this 3D model. Since the majority of geophysical logs from the oil and gas wells were run after installation of surface casing, the shallow lithology structure (i.e. the upper 150-200 meters) in the model will be dominated by information from the two EPA installed monitoring wells. Lithology of this site is likely highly variable and will be difficult to correlate from borehole to borehole, even for boreholes in close proximity to one another consistent with other observations in the Wind River Formation (Osiensky 1984). Thus, various sandstone and shale layers may be represented as very thin and of limited lateral extent again consistent with previous observations of lithology in the Wind River Formation (Single 1969, Flores and Keighin 1993).

6.0 Quality Metrics (QA/QC Checks)

6.1 Quality Metrics (QA/QC Checks) for Field Screening Gas Analysis

QA/QC requirements for field screening of gas samples are provided in **Table 6**.

6.2 Quality Metrics for Fixed Laboratory Gas Analysis

QA/QC requirements for fixed laboratory analysis of gas samples are provided in **Table 7**.

A summary of field-based QC samples, purpose, method, and frequency for soil-gas sampling is provided in **Table 8**. This is exclusive of QC samples required at Isotech Laboratories.

Isotech Laboratories must demonstrate proficiency in conducting analyses for the determination of concentration of gas components and stable isotope analyses of carbon in methane and carbon dioxide. This may be demonstrated by accreditation through a recognized authority, such as ISO (International Organization for Standardization), and/or by providing documentation of successful analyses of reference standards. The laboratory shall provide documentation for their QA program (e.g., Quality Management Plan or Quality Assurance Plan).

Fixed gases and hydrocarbons shall be analyzed by gas chromatography using a method based upon ASTM D1945-03. A combination of TCD/FID detectors shall be used to be able to provide

the detection limits needed and to accommodate detection limits and a concentration range of the gases as required by ASTM D1945-03. Sample reporting units may be mol% or ppmv. Stable isotopes of carbon ($\delta^{13}C$) for methane and carbon dioxide (~0.5%) will be analyzed by isotope ratio mass spectrometry. Radiocarbon will be analyzed by accelerator mass spectrometry. It is understood that the instrumentation for ^{14}C analysis is unique and therefore these analyses may be sub-contracted to another laboratory. Method documentation with QC acceptance criteria shall be provided by the laboratory.

Primary standards for $\delta^{13}C$ and δD analyses shall originate from the International Atomic Energy Agency, Vienna, Austria, and certified by National Institute of Standards and Technology (NIST). Secondary and/or working standards shall be calibrated against the primary standards. Standards for the gas component analysis shall be certified and traceable to NIST. Instruments shall be calibrated or confirmed to be calibrated prior to sample analysis. Standards for ^{14}C analysis shall be traceable to NIST. Calibration shall be linear within the range of use. Initial calibration shall be verified by using a second source standard (standard from source different than those used for initial calibration).

Accuracy of stable carbon and hydrogen isotope analyses shall be within 0.5 per mil or less for $\delta^{13}C$ and 3 permil for δD, i.e, the measured value of check or reference standards compared to their known or certified value. The difference between duplicate sample analysis shall be within 1 permil for $\delta^{13}C$ and 3 permil for δD . At least every tenth analysis shall be a sample duplicate.* Check or reference standards shall be analyzed every tenth analysis, ensuring that sample runs are always bracketed by standards.

Accuracy and precision of ^{14}C analysis shall be within 1 pMC (percent modern concentration). Analysis should be capable of detecting to 2.0 pMC with a precision of +/- 5‰. Standards of known and documented uncertainty shall be analyzed at a frequency according to the laboratory's QA requirements and acceptance limits, such that sample runs are bracketed by standards. Blanks shall be analyzed prior to samples to determine presence of background.

Presence of background that would interfere with sample analysis shall be corrected prior to sample analysis.

Accuracy of gas component analysis shall be within +/-15%, i.e., the measured value of standards compared to their known or certified value. Precision of the analyses shall be determined by duplicate sample analysis with a Relative Percent Difference (RPD)** not to exceed 15%. At least every tenth analysis shall be a sample duplicate.* Check or reference standards shall be analyzed every tenth analysis, ensuring that sample runs are always bracketed by standards. Blanks shall be analyzed prior to samples to determine presence of background. Presence of background that would interfere with sample analysis shall be corrected prior to sample analysis.

If any of the laboratory's standard QA/QC criteria are stricter than those delineated here, then it is expected that the laboratory shall default to their criteria for these sample analyses.

Full data packages shall be provided on CD for all sample analyses to allow for reconstruction of analysis: Chain-of-custody forms, calibration documentation, QA/QC results, raw data, data reduction, data qualifiers, quantitation and detection limits, deviations from method requirements, deviations from QC acceptance criteria, and these deviations' impact to reported

EPAPAV0025535

results.

*Sample duplicates shall be performed on our samples submitted for this work, i.e., sample duplicate results for samples from other sources (for analytical runs that may include samples from other sources) shall not be considered for meeting these QC requirements.

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

Where a = sample measurement
b = duplicate sample measurement

6.3 Quality Metrics (QA/QC Checks) for Aqueous Analysis

QA/QC requirements (e.g., blanks, calibration checks, duplicates, second source standards, matrix spikes) are described in various in-house Standard Operating Procedures and summarized in **Table 3**. 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.

RPD calculations on field duplicates will be made for aqueous analytes present at concentrations greater than 5 times the Quantitation Level (QL) or the method Reporting Level (RL). RPDs are expecting to be less than or equal to 30%. If RPDs are greater than 30%, actions will be taken to better understand the reason. Analytes detected in various blank samples will be evaluated and flagged in presentations of data. Generally, blank contamination will be considered to be significant when blank contaminants are found at a level within 3 times that found in applicable field samples.

Samples will be submitted to Isotech Laboratories for analysis tritium and stable isotope ratios ($\delta^{13}C$) of dissolved inorganic carbon and $\delta^{13}C$ of dissolved gases, C1-C5, as well as $\delta^{2}H$ of methane. A general discussion of their QA/QC is provided in their QAP attached in Appendix A. Isotech has provided input on their acceptance criteria (see Tables 10,11, and 12). In addition, a Statement of Work was provided to Isotech with relevant information presented here:

> Samples will be provided from two separate ground-water monitoring wells. One well will be sampled in duplicate. A total of three samples will be submitted in total. In addition to the field duplicate, it is expected that the vendor will select one sample for a laboratory duplicate analysis to fulfill QA/QC requirements. This sample needs to be from this sample set and not from another site or sample queue. For this reason, we have added the cost of an additional analysis to cover the laboratory duplicate. The samples will be provided in 1 L bottles provided by Isotech Laboratories. The bottles will be filled with about 400 mL of ground water. It is expected that the concentration of DIC and dissolved gases will be high enough in the samples so that this volume will be adequate for the analyses. The sample bottles will already contain the preservative (2% benzalkoniumchloride). Samples for DIC will collected filtered into 60 mL plastic bottles. The bottles will be transported so that the aqueous solution will be on top of the bottle closure, i.e., the bottles will be transported upside down. Analyses of the laboratory duplicates will agree within 1 permil $\delta^{13}C$ and within 2 permil $\delta^{2}H$*, or less. The measured value of the stable carbon and hydrogen isotope ratio in calibration standards

EPAPAV0025536

will be within 0.5 permil* or less of the nominal value in the calibration standards. Isotech Laboratories will submit a final report at completion of analysis which includes: (1) statements outlining analytical procedures, (2) pretreatments applied, and (3) calibration information. Full data packages shall be provided on CD for all sample analyses to allow for reconstruction of analysis: Chain-of-custody forms, calibration documentation, QA/QC results, raw data, data reduction, data qualifiers, quantitation and detection limits, deviations from method requirements, deviations from QC acceptance criteria, and these deviations' impact to reported results. Results of the analysis will be reported to Rick Wilkin via e-mail at wilkin.rick@epa.gov within four weeks of the receipt of the samples.

*Isotech cannot meet criterion of 0.5 permil for H. Their criterion is 2 permil.

For the April 2011 sampling, a Statement of Work was provided to Isotech with relevant information and QC limits updated, supersedes that above:

Samples of ground water will be provided from field sites for isotopic analyses of dissolved inorganic carbon (DIC) and dissolved gases. The vendor will not be required to determine the concentration of inorganic carbon or dissolved gases in the samples. The isotope analyses are intended to provide information about the carbon cycle in the systems. The measurements will be for $\delta^{13}C$ of dissolved inorganic carbon, the $\delta^{13}C$ value of C1-C5 gases, and the $\delta^{2}H$ of hydrogen in methane.

Samples will be provided from ground-water monitoring wells located around Pavillion, WY. The wells will be sampled during April 2011. The vendor will be notified one week in advance of the sample collection activities. Duplicate samples will be collected in 10% of the wells, or as otherwise indicated in approved QAPPs. A total of 15 samples will be submitted for $\delta^{13}C$ of dissolved inorganic carbon and a total of 15 samples are planned for dissolved gas analysis. In addition to field duplicates, it is expected that the vendor will select one sample for a laboratory duplicate analysis in each submitted set to fulfill QA/QC requirements. This sample needs to be from our submitted sample sets and not from another site or sample queue.

The inorganic carbon samples will be collected into 60 mL plastic bottles (filtered, unpreserved); the dissolved gas samples will be sampled into 1 L plastic bottles provided by Isotech Laboratories. The bottles will be filled with ground water and those for dissolved gas analysis will be preserved with a caplet of benzalkonium chloride. It is expected that the concentration of DIC and dissolved gases will be high enough in the samples so that these volumes will be adequate for the analyses. For the dissolved gas samples, the bottles will be transported so that the aqueous solution will be on top of the bottle closure, i.e., the bottles will be transported upside down. All samples will be transported on ice. The vendor will determine the stable carbon isotope ratio of DIC and dissolved gases and hydrogen in methane in the water samples as described above.

Analyses of the laboratory duplicates will agree within 1 permil ^{13}C and within 3 permil ^{2}H, or less. The measured value of the stable carbon and hydrogen isotope ratio in calibration standards will be within 0.5 permil or less and 3 permil or less, respectively, of the nominal value in the calibration standards.

EPAPAV0025537

Isotech Laboratories will submit a final report at completion of analysis which includes: (1) statements outlining analytical procedures, (2) pretreatments applied, and (3) calibration information. Full data packages shall be provided on CD for all sample analyses to allow for reconstruction of analysis: Chain-of-custody forms, calibration documentation, QA/QC results, raw data, data reduction, data qualifiers, quantitation and detection limits, deviations from method requirements, deviations from QC acceptance criteria, and these deviations' impact to reported results. Results of the analysis will be reported to Rick Wilkin via e-mail at wilkin.rick@epa.gov within five weeks of the receipt of the samples.

For the planned Phase V April 2012 sampling, a Statement of Work will be provided to Isotech with relevant information and QC limits updated, supersedes that above:

Samples of ground water will be provided from field sites for tritium analysis and isotopic analyses of dissolved inorganic carbon (DIC) and dissolved gases. The vendor will not be required to determine the concentration of inorganic carbon or dissolved gases in the samples. The isotope analyses are intended to provide information age of ground water and the carbon cycle in the system. The measurements will be for ^{3}H, $\delta^{13}C$ of dissolved inorganic carbon, the $\delta^{13}C$ value of C1-C5 gases, and the $\delta^{2}H$ of hydrogen in methane.

Samples will be provided from ground-water monitoring wells located around Pavillion, WY. The wells will be sampled during April 2012. The vendor will be notified one week in advance of the sample collection activities. Duplicate samples will be collected in 10% of the wells, or as otherwise indicated in approved QAPPs. A total of up to 10 samples will be submitted for ^{3}H, $\delta^{13}C$ of dissolved inorganic carbon, and a total of up to 10 samples are planned for dissolved gas analysis. In addition to field duplicates, it is expected that the vendor will select one sample for a laboratory duplicate analysis in each submitted set to fulfill QA/QC requirements. This sample needs to be from our submitted sample sets and not from another site or sample queue.

The samples for tritium analysis will be collected in 500 mL plastic bottles (unfiltered, unpreserved). The inorganic carbon samples will be collected into 60 mL plastic bottles (filtered, unpreserved); the dissolved gas samples will be sampled into 1 L plastic bottles provided by Isotech Laboratories. The bottles will be filled with ground water and those for dissolved gas analysis will be preserved with a caplet of benzalkonium chloride. It is expected that the concentration of DIC and dissolved gases will be high enough in the samples so that these volumes will be adequate for the analyses. For the dissolved gas samples, the bottles will be transported so that the aqueous solution will be on top of the bottle closure, i.e., the bottles will be transported upside down. All samples will be transported on ice.

The vendor will determine the stable carbon isotope ratio of DIC and dissolved gases and hydrogen in methane in the water samples as described above. Analyses of the laboratory duplicates will agree within 1 permil $^{13}\delta C$ and within 3 permil $^{2}\delta H$, or less. The measured value of the stable carbon and hydrogen isotope ratio in calibration standards will be within 0.5 permil or less and 3 permil or less, respectively, of the nominal value in the calibration standards. See Tables 10, 11, and 12 for summary of Isotech's QA/QC requirements.

Isotech Laboratories will submit a final report at completion of analysis which includes: tabulation of final results, list of SOPs used (title and SOP #), and full data packages. Full data packages (can be provided at a later data, within 30 days pf issuing final reports) shall be provided on CD for all sample analyses to allow for reconstruction of analysis: Chain-of-custody forms, calibration data , QA/QC data , raw data, data reduction, data qualifiers, , deviations from method requirements, deviations from QC acceptance criteria, and these deviations' impact to reported results. Results of the analysis will be reported to Rick Wilkin via e-mail at wilkin.rick@epa.gov within five weeks of the receipt of the samples.

For samples submitted to TestAmerica for analysis of Methylene Blue Active Substances (MBAS) using EPA Method 425.1, QA/QC requirements are included in Table 3. See Table 2 for sample requirements, preservation, and holding times.

For samples submitted to ALS Environmental for analysis of methanol, propylene and ethylene glycols by EPA Method 8015M (GC/FID), QA/QC requirements are included in Table 3. See Table 2 for sample requirements, preservation, and holding times.

For samples submitted to ORD/NERL-Las Vegas laboratory analysis of ethoxylated alcohols, alkylphenols, and acrylamides, QA/QC requirements are included in Table 4. See Table 2 for sample requirements, preservation, and holding times.

6.3.a Measured and Calculated Solute Concentration Data Evaluation

The computer program AqQA (RockWare Inc., version 1.1.1) will be used as a check on the quality of solute concentration data. Two methods will be used. First, the specific conductance values measured in the field will be compared to a calculated value that is based on anion- and cation-specific resistivity constants and the measured concentrations of anions and cations in specific ground-water samples. The agreement between the measured and calculated values should be within 15%. The second method will be to calculate the charge balance for each solution. This is done by summing and comparing the net positive and negative charge from the measured concentrations of anions and cations. The agreement should be within 10%. Poor agreement would suggest that some major solute(s) is not accounted for in the analytical measurements. At the discretion of the PI, discrepancies in this manner will be either flagged or the identity of other sample components and/or reason(s) for poor agreement will be investigated.

6.3.b Detection Limits

Detection limits for the various analytes are listed in the Standard Operating Procedures for these methods and are not repeated here. They are adequate for project objectives.

6.3.c QA/QC Calculations

% Recovery or Accuracy

%REC = $(m/n) \times 100$
Where m = measurement result

EPAPAV0025539

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:

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

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

Matrix Spike Recovery

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

$$\%\ Recovery = \frac{spiked\ sample\ conc - native\ sample\ conc}{spiked\ sample\ conc}100$$

7. Data Analysis, Interpretation, and Management

Data validation will consist of initial and final review of data. Initial review will include continuous oversight during field collection of data by the principal investigator to avoid common transcription errors associated with recording of data. Final review will include evaluation of all collected data for suitability in data interpretation. It will include but is not limited to the following activities: (1) assessment of data completeness, (2) review of log books and forms used for data logging, and (3) review of calibration and standard checks.

A summary of the data verification and validation approach is as follows:

- Laboratories will verify data prior to reporting data to the PIs
    - This includes evaluating data with respect to QC criteria of the method used and flagging data with appropriate qualifiers, if needed
- Data reports are reviewed by PIs for completeness, correctness, and conformance with QAPP requirements
    - All sample results are verified by the PIs to ensure they met project requirements as defined in the QAPP and any data not meeting these requirements are appropriately qualified
    - The Contract Laboratory Program guidelines on organic methods data review, USEPA (2008), are used for guidance in application of data qualifiers
- Audits of Data Quality (ADQs) is conducted on the majority of the data reports by a party independent of the data collection (performed or overseen by the QA Manager)
    - Typical results were to require further qualification of data

EPAPAV0025540

- PIs use the information from all these data verification/validation activities to assist in making the final determination of data usability
    - For example, one outcome may be to discard some data as unusable

Data results from methods under development (Region 3 and ORD/NERL laboratories) will be flagged as estimated. Ethylene and propylene glycols data (ALS Environmental) will also be considered as screening data due to potential for false positives using EPA Method 8015. Analysis of volatile organic compounds will be conducted at both the Region VIII laboratory and at the Shaw laboratory. The method used by the Shaw laboratory provides for analysis of a suite of alcohols which is not included in the Region VIII method. Both laboratories use EPA Method 8260 but have differing sample introduction procedures. In cases where analytes overlap, and in particular for the BTEX compounds, concentration data will be compared and reported in publication appendices. Because the Region VIII laboratory has consistently provided VOC data in Phases I through IV, data tabulations will generally rely on the Region VIII data for the purpose of maintaining consistency.

Data generated by another federal agency (e.g. USGS) may be utilized (in a manner similar to other data generated under this QAPP) if the agency used comparable sampling and analytical methods and subjects their data to a comparable quality assurance process (e.g., audits of data quality). Otherwise data generated from another federal agency will be referenced but not reported.

Data will not be released outside of RSKERC until all study data have been reviewed, verified, and validated. The PIs of this project are responsible for deciding when project data can be shared with interested stakeholders in conjunction with the approval from GWERD's Division Director.

7.1 Data Recording

7.1.a Soil Gas

To ensure collection of all relevant data during each purging event, a spreadsheet, illustrated in **Figure 10**, will be used to manually record readings from the GEM2000 CES LandTec Gas Analyzer. The data will be collected by a technician during testing and reviewed in the field by the principal investigator during and at the cessation of each test. The principal investigator will then convert purging data to an EXCEL spreadsheet for electronic storage and data manipulation. Calibrations and calibration checks will be recorded on the same spreadsheet used to record readings with the unit of measurement and the analyst's initials or name. For gas permeability testing, pressure readings will be recorded every second and stored in a file in a PC using a RS232 cable.

7.1.b Water

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

7.2 Data Storage

EPAPAV0025541

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. This discussion of data and records includes raw data, both electronic and paper-based. If the project records are archived, Dr. DiGiulio will coordinate with Dr. Wilkin the compiling of all data and records.

7.3 Analysis of Data

All data collected associated with ground-water and soil-gas sampling will be summarized in EXCEL spreadsheets. Data in spreadsheets will be spot-checked against original data reports by selecting random data points for comparison to verify accuracy of data transfer. When possible, data sets will be graphically displayed using EXCEL, Sigma Plot, and Origin to reveal important trends.

8.0 Assessment and Oversight

8.1 Assessments

Technical Systems Audits (TSAs) and Audits of Data Quality (ADQs) 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. Detailed checklists, based on the procedures and requirements specified in this QAPP and related SOPs, will be prepared and used during these TSAs. Two field TSAs will be done; one on the soil gas sampling and the other on the ground water sampling. It is anticipated these will take place in late September to October, 2010. The GWERD QA Manager (QAM), Steve Vandegrift, will take the lead on these audits with contract support from Neptune and Co.

Laboratory TSAs will focus on the critical target analytes (Table 9) and will be conducted on-site at GWERD (involves both EPA and contractor-operator labs) and at an off-site contract laboratory which will do the gas and isotope analysis. It is anticipated these will take place in late September to October, 2010. (At the time the original QAPP was prepared, Isotech Laboratories, Inc., in Champaign, IL, was anticipated to be the only off-site contract lab.) The GWERD QA Manager will take the lead on the TSA with contract support from Neptune and Co. for the off-site contract lab. The on-site lab TSA will be conducted by the GWERD QAM, with assistance from the NRMRL Director of QA, Lauren Drees in the preparation of checklists.

ADQs will be conducted on a representative sample of data for the critical target analytes. These will be performed by the GWERD QAM with assistance from the NRMRL Director of QA. These will begin with the first data sets (October, 2010) to ensure there are no issues with the data and to allow for appropriate corrective actions on subsequent data sets if needed.

ADQs (data verification and validation) will be conducted on data collected previously by Region 8. An ADQ will be performed on the data generated by Region 3 on their analysis of ground water samples for glycols. These will be performed by Neptune and Co. Data shall be submitted electronically to the GWERD QAM who will then forward the data to Neptune.

EPAPAV0025542

For Phase V, another state or federal agency may take the lead in sampling. At the time this QAPP was being revised, it was not yet determined how QA oversight would be implemented by this agency. However, it is expected that they would conform to our QA Category 1 requirements, i.e, they would prepare a Sampling and Analysis Plan equivalent to our QAPP, perform a field TSA and laboratory TSAs on the laboratories conducting analysis for critical target analytes, and conduct ADQs on the data they collect.

In addition, PE samples will be provided by the EPA to be analyzed by the laboratories used by both the EPA and the other agency for the critical target analytes (Table 9). TSAs by will not be done by the EPA on the laboratories conducting analyses for critical target analytes as they have been audited within the past two years by the EPA. The EPA will perform ADQs on laboratory data they collect during Phase V, at a minimum on the critical target analytes, and possibly all of their laboratory data.

8.2 Assessment Results

Assessment results will be documented in reports to the PIs and the GWERD Division Director. 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 PIs are responsible for responding to the reports as well as implementing corrective actions, if needed, in a timely manner to ensure that quality impacts to project results are minimal.

8.3 Informing Management

Meetings will be held at least once per month between NRMRL-Ada staff and EPA Region VIII management to keep Region VIII management informed of technical activities.

9.0 Reporting

The principal investigator and co-principal investigator will summarize and interpret data collected for EPA Region VIII to allow incorporation into a comprehensive report being developed by the principal investigators. The final product(s) for NRMRL-Ada could be one or more journal articles or an EPA Report describing activities and findings at the site. However, these publications would have to be cleared through both ORD and EPA Region VIII.

As part of the data validation and reporting process, synthesis of data and conclusions drawn from the data will be formulated by the PIs and project participants prior to release of this information or data to entities outside of RSKERC. Once all project data have been reviewed by the PIs, in coordination with the GWERD Director, the GWERD Director will approve its release for appropriate ORD and Region VIII clearance, and QA review and approval.

10.0 References

Azzaro, R., S. Branca, S. Giammanco, S. Gurrieri, R. Rasa, and M. Valenza. 1998. New evidence for the form and extent of the Pernicana Fault System (Mt. Etna) from structural and soil-gas surveying. *Journal of Volcanology and Geochemical Research*, 84:143-152.

EPAPAV0025543

Baldassare, F.J., and C.D. Laughrey. 1997. Identifying the sources of stray methane by using geochemical and isotopic fingerprinting. *Environmental Geosciences*, v. 4, no. 2, p. 85-94.

Baubron, J.C., A. Rigo, and J.P. Toutain. 2002. Soil gas profiles as a tool to characterize active tectonic areas: the Jaut Pass example (Pyrenees, France). *Earth and Planetary Science Letters*, 196:69-81.

Boyd, D., Al-Kubti, S., Khedr, O., N. Khan, and K. Al-Nayadi, prepared for the 2006 SPE Abu Dhabi International Petroleum Exhibition and Conference, Abu Dhabi, UAE, 5-8 November.

Bybee, K. (2007). Cement-bond-log interpretation reliability. *Journal of Petroleum Technology*, Feb. 2007, p. 64-66.Ciotoli, G., S. Lombardi, A. Annunziatellis. 2007. Geostatistical analysis of soil gas data in a high seismic intermontane basin: the Fucino Plain, central Italy. *Journal of Geophysical Research*, 112(B05407), doi:10.1029/2005JB004044.

Ciotoli, G., S. Lombardi, S. Morandi, and F. Zarlenga. 2004. A multidisciplinary statistical approach to study the relationships between helium leakage and neotectonic activity in a gas province: The Vasto basin, Abruzzo-Molise (central Italy). *The American Association of Petroleum Geologists Bulletin*, 88(3):355-372.

Ciotoli, G., M. Guerra, S. Lombardi, and E. Vittori. 1998. Soil gas survey for tracing seismogenic faults: A case study the Fucino basin (central Italy). *Journal of Geophysical Research*, 103(B10):23, 781-783, 794.

Ciotoli, G., G. Etiope, M. Guerra, and S. Lombardi. 1999. The detection of concealed faults in the Ofanto basin using the correlation between soil-gas fracture surveys. *Tectonophysics*, 299(3-4):321-332.

DiGiulio, D.C. and R. Varadhan. 2001. Development of recommendations and methods to support assessment of soil venting performance and closure. EPA/600/R-01/070. (http://www.epa.gov/ada/pubs/reports.html)

Fountain, J.C. and R.D. Jacobi. 2000. Detection of buried faults and fractures using soil gas analysis. *Environmental and Engineering Geoscience*, 6(3):201-208.

Fridman, A.I., 1990. Application of naturally occurring gases as geochemical pathfinders in prospecting for endogenetic deposits. *Journal of Geochemical Exploration*, 38(1-2):1-11.

Janezic, G.G. 1979. Biogenic light hydrocarbon production related to near-surface geochemical prospecting for petroleum. *The American Association of Petroleum Geologists Bulletin*, 63:403.

Jones, V.T. and R.J. Dozd. 1983. Predictions of oil and gas potential by near-surface geochemistry. *The American Association of Petroleum Geologists Bulletin*, 67(6):932-952.

Jones, V.T., and R.J. Pirkle. 1981. Helium and hydrogen soil gas anomalies associated with deep or active faults. Presented to the American Chemical Society, March 29 - April 3, 1981, Atlanta, Georgia

Jones, V.T. and Pirkle. 2009. Application of Exploration Geochemical Methodology to CO2

EPAPAV0025544

Monitoring, Lawrence Berkeley National Laboratory, BNL Subcontract No. 6804108.

Kaplan, I.R., Y. Galperin, S. Lu, and R. Lee. 1997. forensic environmental geochemistry-Differential of fuel-types, their sources, and release time, *Organic Geochemistry*, v. 27, no. 5/6, p.289-317.

King, C.Y., B.S. King, W.C. Evans, and W. Zang. 1996. Spatial radon anomalies on active faults in California. *Applied Geochemistry*, 11:497-510.

LeNeveu, D.M. 2008. CQUESTRA, A risk and performance assessment code for geological sequestration of carbon dioxide. *Energy Conversation & Management*, 49:32-46.

Lewicki, J.L. and S.L. Brantley. 2000. CO2 degassing along the San Andreas fault, Parkfield, California. *Geophysical Research Letters*, 27(1):5-8.

Lewicki, J.L., W.C. Evans, G.E. Hilley, M.L. Sorey, J. Rogie, and S.L. Brantley. 2003. Shallow soil CO2 flow along the San Andreas and Calaveras Faults, California. *Journal of Geophysical Research,* 108(B4):2187, doi:10.1029/2002JB002141.

New York State Department of Health, Center for Environmental Health, Bureau of Environmental Exposure Investigation. Guidance for Evaluating Soil Vapor Intrusion in the State of New York, October, 2006.

Nordbotten, J.M., M.A. Celia, and S. Bachu. 2004. Analytical solutions for leakage rates through abandoned wells. *Water Resources Research*, 40, W04204, doi:1-29/2003WR002997.

Nordbotten, J.M., M.A. Celia, and S. Bachu. 2005a. Injection and storage of CO2 in deep saline aquifers: Analytical solution for CO2 plume evolution during injection. *Transport Porous Media*, 58:339-360.

Nordbotten, J.M., M.A. Celia, S. Bachu, and H.K. Dahle. 2005b. Semianalytical solution for CO2 leakage through an abandoned well. *Environmental Science & Technology*, 39:602-611.

Rowe, D. adn K. Muehlenbachs. 1999. Isotopic fingerprinting of shallow gases in the Western Canadian sedimentary basin-Tools for remediation of leaking heavy oil wells. *Organic Geochemistry*, v. 30, p. 861-871.

Sandler, R. 1999. Compilation of Henry's Law Constants for Inorganic and Organic Species of Potential Importance in Environmental Chemistry, Max-Planck Institute of Chemistry, Mainz, Germany, http://www.mpch-mainz.mpg.de/~sander/res/h enry.html

Schoell, M. 1980. The hydrogen and carbon isotopic composition of methane from natural gases of various origin. *Geochimica et Cosmochimica Acta*, v. 44, p. 649-661.

Schoell, M. 1983. Genetic characteristics of natural gases. *American Association of Petroleum Geologists Bulletin*, v. 67, no. 12, p. 2225-2238.

Thien, S.J. 1979. A flow diagram for teaching texture by feel analysis. Journal of Agronomic Education. 8:54-55.

EPAPAV0025545

U.S. Environmental Protection Agency - Region VIII, Ground Water Section Guidance No. 34 - March 31, 1994.

Wakita, H., et al., 1980. Hydrogen release: New indicator of fault activity. *Science*, 210:188-190.

Wakita, H., et al., 1978. Helium spots: Caused by diapiric magma from the upper mantle. *Science*, 200:430-432.

Standard Operating Procedures

RSKSOP-112v6 - Standard Operating Procedure for Quantitative Analysis of Low Molecular Weight Acids in Aqueous Samples by HPLC, 22 p.

RSKSOP-175v5 - Sample Preparation and Calculations for Dissolved Gas Analysis in Water Samples Using a GC Headspace Equilibration Technique, 16 p.

RSKSOP-194v4 - Gas Analysis by Micro Gas Chromatographs (Agilent MIcro 3000), 13 p.

RSKSOP-213v4 - Standard operating procedure for operation of Perkin Elmer Optima 3300 DV ICP-OES, 21 p.

RSKSOP-214v5 - Quality control procedures for general parameters analysis using Lachat Flow Injection analysis (FIA), 10 p.

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

RSKSOP-257v2 - Standard operating procedure for elemental analysis by ICP-MS, 16 p.

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

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

RSKSOP-296v0 - Determination of hydrogen and oxygen isotope ratios in water samples using high temperature conversion elemental analyzer (TC/EA), a continuous flow unit, and an isotope ratio mass spectrometer (IRMS), 8 p.

RSKSOP-297v1 - Metals Speciation Determination by LC/ICP-MS, 21 p.

RSKSOP-298v1 - Arsenic Speciation Determination by LC/ICP-MS with Anion Suppression and NaOH Mobile Phase, 21 p.

RSKSOP-313v1 - Determination of R-123 using the H25-IR Infrared Refrigerant Gas Leak Detector, 12 p.

EPAPAV0025546

RSKSOP-314v1 - Determination of Fixed Gases using the GEM2000 and GEM2000 Plus Gas Analyzers & Extraction Monitors, 13 p.

RSKSOP-315v1 - Determination of Carbon Monoxide Using the Bacharach PCA2 Portable Combustion Analyzer, 13 p.

RSKSOP-320v1 - Determination of Organic and Inorganic Vapors Using the TVA-1000B Toxic Vapor Analyzer, 18 p.

Draft RSKSOP-327 - Creating Equilibrated Headspace Utilizing High Pressure Sample Cylinders.

RSKSOP-330v0 - Determination of Various Fractions of Carbon in Aqueous Samples Using the Shimadzu TOC-VCPH Analyzer, 16 p.

RSKSOP-334 - Determination of Stable Hydrogen and Oxygen Isotope Ratios in Water Samples Using a Picarro L2120i Cavity Ring-Down Spectrometer (CRDS), 30 p.

TestAmerica SOP SA-GE-160 rev.5: Methylene Blue Active Substances (MBAS).

Isotech SOP-117Rev0 - Low Level Tritium Analysis of Water.

ALS Environmental SOP HN-GC-004-R02 - Nonhalogenated Organic Anaysis by GC/FID.

USEPA-540-R-08-01. 2008. USEPA Contract Laboratory Program National Functional Guidelines for Superfund Organic Methods Data Review. Office of Superfund Remediation and Technology Innovation.

EPAPAV0025547

Table 1. Schedule of field activities at Pavillion, WY.

Field Activity	**06/10**	**07/10**	**08/10**	**9/10**	**10/10 Phase III**	**4/11 Phase IV**	**4/12 Phase V**
Monitoring Well installation and Development	**X**	**X**	**X**	**X**			
Ground-Water Sampling					**X**	**X**	**X**
Cali-5 Bond Sample Bag Study						**X**	
Soil-Gas Survey/ Installation of Probes		**X**					
Soil-Gas Sampling (probes)				**X**			
Gas sampling domestic wells				**X**		**X**	

Table 2. Ground water sample collection.

Measurement	Analysis Method	Sample Container	Preservation/ Storage	Holding Time(s)
Dissolved gases	RSKSOP-194v4 &-175v5*/** RSKSOP-327 draft; no EPA Method	150 mL stainless steel (SS) sampling vessel for deep wells & 60 mL serum bottles for tap water samples	Spare tap water samples preserved with/TSP† to compare w/unpreserved; Refrigerate at ≤6°C	14 days**
Metals	RSKSOP-213v4 &-257v2; EPA Methods 200.7 and 6020	125 mL Plastic bottle	HNO_3 pH<2	6 months (Hg 28 days)
As speciation	RSKSOP-298v1 or RSKSOP-297v1***	30 mL amber plastic	HCl pH<2; refrigerate at ≤6°C	8 days
SO_4, Cl, Br, F	RSKSOP-276v3; EPA Method 6500	30 mL clear plastic	Refrigerate at <6°C	28 days
NO_3 + NO_2, NH_4	RSKSOP-214v5; EPA Method 350.1 and 353.1	30 mL clear plastic	H_2SO_4 pH<2; refrigerate at ≤6°C	28 days
Dissolved DIC/DOC	RSKSOP-330v0; EPA Method 9060A	40 mL glass VOA vial (2 each for DIC and DOC)	H_3PO_4 to pH<2 (DOC only) No headspace; refrigerate at ≤6°C	DIC:14 days DOC: 28 days
$\delta^{13}C$ of dissolved inorganic carbon	Isotech: gas stripping & IRMS; no EPA Method	60 mL plastic bottle	Refrigerate at ≤6°C	No information
$\delta^{13}C$ of dissolved gases and $\delta^{2}H$ of methane	Isotech: gas stripping & IRMS; no EPA Method	1 L plastic bottle	Caplet of benzalkonium chloride; refrigerate at ≤6°C	No information
O, H stable isotopes of water	RSKSOP-296v1 or RSKSOP-334 in Phase V; no EPA Method	20 mL glass VOA vial	Refrigerate at ≤6°C	Stable
Tritium (added in Phase V)	Isotech: electrolytic enrichment and radiometric analysis of ^{3}H	500 mL plastic bottle	Refrigerate at ≤6°C	6 months
Methylene Blue Active Substances (added in Phase V)	TestAmerica, SOP SA-GE-160v5; EPA Method 425.1	500 mL plastic bottle	Refrigerate at ≤6°C	2 days

EPAPAV0025549

Alcohols, aromatic, and chlorinated hydrocarbons	RSKSOP-299v1 Or RSKSOP-259v1; EPA Method 5021A plus 8260C	40 mL glass VOA vial	Preserved with TSP; refrigerate at ≤6°C	14 days
Methanol, propylene glycol, ethylene glycol (added in Phase V)	ALS Environmental EPA Method 8015M	40 mL glass VOA vial	Preserved with HCl; Refrigerate at ≤6°C	14 days
Low Molecular Weight Acids	RSKSOP-112v6; no EPA Method	40 mL glass VOA vial	Preserved with 1 M NaOH; refrigerate at ≤6°C	30 days
Glycols (Region 3)	HPLC-MS-MS (Method under development)	40 mL glass VOA vial	Refrigerate at ≤6°C	14 days
Organics (Region 8)	EPA Method 8270D; EPA Method 5035 plus 8260C; EPA Method 8015D	1L amber glass bottles and 40 mL amber glass vials	Refrigerate at ≤6°C Trisodium phosphate added to VOC bottles; GRO/DRO samples preserved with HCl pH<2	VOCs & GRO-14 days; SVOCs-7 days until extraction, 30 days after extraction; DRO-7 days until extraction, 40 days after extraction
Acrylamide (added in Phase V)	SPE and LC-MS (Method under development)	1L amber glass bottle/2 and for every 10 samples of ground water need 2 more bottles for one selected sample, or if <10 samples collected, collect 2 more bottles for one select sample	Refrigerate ≤6°C	30 days
Alkylphenols (added in Phase V)	SPE and LC-MS (Method under development)	1L amber glass bottle/2 and for every 10 samples of ground water need 2 more bottles for one selected sample, or if <10 samples collected, collect 2 more bottles for one select sample	Refrigerate ≤6°C	30 days
Ethoxylated alcohols/ ethoxylated alkylphenols	SPE and LC-MS (Method under development)	1L amber glass bottle/2 and for every 10 samples of ground water need 2 more	Refrigerate ≤6°C	30 days

EPAPAV0025550

(added in Phase V)		bottles for one selected sample, or if <10 samples collected, collect 2 more bottles for one select sample		

*RSKSOP-175v5 appropriate for samples in serum bottles, not the SS sample vessels.
**14 days w/acid or trisodium phosphate preservation; holding time not established w/o preservation; comparison will be made between preserved and unpreserved tap water samples.
† trisodium phosphate
*** Method RSKSOP-297v1 will be used as the default method. However, if dissolved sulfide is present at levels >0.1 mg/L, then RSKSOP-298v1 will be used. In this case, samples will not be acidified.
**** A method and SOP will be developed as part of this study.
***** A holding time/preservative analysis will be conducted by collecting multiple samples from 2 wells with suspected glycols. Samples will be collected unpreserved and preserved with trisodium phosphate. Glycol analysis will be carried out over a period of two months on these samples to evaluate changes in concentrations and to provide information with which to determine appropriate preservation and holding time requirements.

EPAPAV0025551

Table 3. Groundwater laboratory QA/QC requirements summary* from SOPs.

Measurement	Analysis Method	Blanks (Frequency)	Calibration Checks (Frequency)	Second Source (Frequency)	Duplicates (Frequency)	Matrix Spikes (Frequency)
Dissolved gases	RSKSOP-194v4 &-175v5*	≤MDL (He/Ar blank, first and last in sample queue; water blank before samples)	85-115% of known value (After He/Ar blank at first of analysis queue, before He/Ar blank at end of sample set, and every 15 samples)	85-115% of known value (After first calibration check)	RPD≤20 (Every 15 samples)	NA
Metals	RSKSOP-213v4	<QL for 80% of metals (Beginning and end of each sample queue, 10-15 samples)	90-110% of known value (Beginning and end of each sample queue, 10-15 samples)	PE sample acceptance limits or 90-110% of known value (Immediately after calibration check)	RPD<10 for 80% of metals; for results <5xQL, difference of ≤QL (Every 15 samples)	90-110% Rec. for 80% of metals w/ no individual exceeding 50-150% Rec. (one per sample set, 10-15 samples)
Metals	RSKSOP-257v3	<QL for 80% of metals; none >10x MDL (Beginning and end of each sample queue)	90-110% of known value (Beginning and end of each sample queue, 10-15 samples)	PE sample acceptance limits or 90-110% of known value (Immediately after first calibration check)	RPD<10 for 80% of metals; for results <5xQL, difference of ≤QL (Every 15 samples)	90-110% Rec. for 80% of metals w/ no individual exceeding 70-130% Rec. (one per sample set, 10-15 samples)
As speciation	RSKSOP-298v1 and RSKSOP-297v1	<ΩQL (after initial calib., every 10-15 samples, and at end)	80-120% of known value (after initial calib., every 10-15 samples, and at end)	80-120% of known value (Immediately after calibration)	RPD<20; for results <5xQL, difference of ≤QL (Every 15 samples)	80-120% Rec. (one per 20 or every set)
SO_4, Cl, F, Br	RSKSOP-276v3	<MDL (Beginning and end of each sample queue)	90-110% Rec. (Beginning, end, and every 10 samples)	PE sample acceptance limits (One per sample set)	RPD<10 (every 15 samples)	80-120% Rec. (one per every 20 samples)

$NO_3 + NO_2$, NH_4	RSKSOP-214v5	<Ω lowest calib. std. (Beginning and end of each sample queue)	90-110% Rec. (Beginning, end, and every 10 samples)	PE sample acceptance limits (One per sample set)	RPD<10 (every 10 samples)	80-120% Rec. (one per every 20 samples)
Dissolved DIC/DOC (NPDOC)	RSKSOP-330	<MDL (beginning and end of each sample set)	90-110% of known value (Beginning, every 10 samples, and at end)	PE sample acceptance limits 90-110% of known value for others (One per sample set)	RPD≤10 (every 10 samples)	80-120% Rec. (one per 20 or every set
O, H stable isotopes of water	RSKSOP-296v0; RSKSOP-334 (334 used for Phase V)	NA	RSKSOP-296v0: Difference of calibrated/true < 1‰ for δ^2H & < 0.2‰ for $\delta^{18}O$ (Beginning, end and every tenth sample) RSKSOP-334v0: Difference of calibrated/true < 1.5‰ for δ^2H & < 0.3‰ for $\delta^{18}O$ (Beginning, end and every twenty samples)	RSKSOP-296v0: Working stds calibrated against IAEA stds. (Beginning, end, and every tenth sample) RSKSOP-334v0: Working stds calibrated against IAEA stds.† (Beginning, end, and every twenty samples)	RSKSOP296v0: Standard deviation ≤ 1‰ for δ^2H and < 0.2‰ for $\delta^{18}O$ (every sample) RSKSOP-334v0: Standard deviation ≤ 1.5‰ for δ^2H and < 0.3‰ for $\delta^{18}O$ (every twenty samples)	NA
Methylene Blue Active Substances (added in Phase V)	Test America; EPA Method 425.1	Method Blank, 1 per batch, result <0.5 RL of 0.2 mg/L	At beginning and end of analysis and after every 10 samples, 90-110%	After initial calibration, 90-110% of known value	RPD<10	One per 20 samples, or every set, 80-120% Rec.
Alcohols, aromatic, and chlorinated hydrocarbons	RSKSOP-299v1 or RSKSOP-259v1	<MDL (Beginning and end of each daily run)	80-120% of known value (after calibration, every 20 samples, at end)	80-120% of known value (Immediately after calibration)	RPD<20	70-130% Rec. (one per 20 or every set)
Methanol, propylene glycol, ethylene glycol (added in Phase V)	ALS Environ.; EPA Method 8015M	<1/2QL (1 per batch of 20 or less samples)	85-115% of known value (after calibration, every 20 samples, end)	85-115% of known value (Each new calibration)	RPD≤50 For MS/MSD pair (every 20 samples or less)	50-150% recovery (One per 20 samples, or less),

Low Molecular Weight Acids	RSKSOP-112v6	<MDL (Beginning and end of sample set, every 10 samples)	85-115% of known value (Prior to sample analysis, every 10 samples, end of sample set)	85-115% of known value (Prior to sample analysis)	RPD<15 (Every 20 samples)	80-120% Rec. (Every 20 samples)

*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

**RSKSOP-174v5 will need to be modified to accommodate samples collected from deep wells in the sample bombs. RSKSOP-327 was developed to address this issue.

***Although our SOW specified ≤ 0.5 ‰ for δ^2H, Isotech indicated that their lab criterion is as listed in the table.

Table 4. Data quality indicators for measurement data at the ORD/NERL laboratory.

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

[a]Batch of samples not to exceed 20
[b]PQL=practical quantitation limit, 5 times the MDL

EPAPAV0025555

Table 5. Summary of analytes, instruments, use, calibration, and check standards for portable gas analyzers and gas chromatograph.

Analyte	Instrument (Detector)	Method	Range	Calibration	Check Standard	Accuracy
O_2	GEM-2000 Plus CES-LANDTEC (EC Cell)	RSKSOP-314v1	0 - 21%	4%, 10%, or 20.9%	4% 10%, 20.9%	±1.0% (0-5%) ±1.0% (5-21%)
CH_4	GEM-2000 Plus CES-LANDTEC (IRGA)	RSKSOP-314v1	0 - 100%	2.5% or 50%	2.5%, 50%	±0.3% (0-5%) ±1% (5-15%) ±3% (15-100%)
CO_2	GEM-2000 Plus CES-LANDTEC (IRGA)	RSKSOP-314v1	0 - 100%	5%, 20%, or 35%	5%, 20%, 35%	±0.3% (0-5%) ±1.0% (5-15%) ±3.0% (15-50%)
H_2S	GEM-2000 Plus CES-LANDTEC (EC Cell)	RSKSOP-314v1	0 – 500 ppmv	25 ppmv	25,100 ppmv	±10% (0-500 ppmv)
CO (tracer)	GEM-2000 Plus CES-LANDTEC (EC Cell)	RSKSOP-314v1	0 – 2000 ppmv	100 ppmv	100, 500, 1000 ppmv	±10% (0-2000 ppmv)
CO (tracer)	Bacharach PCA2 Portable Combustion Analyzer (IRGA)	RSKSOP-315v1	0 – 20,000 ppmv	4,000 ppmv	4,000, 18,000 ppmv	±5% or ± 10 ppmv whichever is greater (0-2000 ppmv) ±10% (2,000-10,000 ppmv)
He (tracer)	Laco Technologies LHHLD-2002 Helium Underground Leak Detector	RSKSOP-321v0	25 ppmv - 100%	Factory calibration	25, 100, 500 ppmv, 10%	±10.0%
R-123 (tracer)	Bacharach H25-IR Industrial Refrigerant Leak Detector (IRGA)	RSKSOP-313v1	0 – 10,000 ppmv	Internal source (25.3 ppmv)	200, 1000 ppmv	±10% (0-1000 ppmv)
VOCs	Thermo Scientific TVA-1000B (FID)	RSKSOP-320v1	1.0 – 10,000 ppmv	0.0, 10, 100, 1000, 9000 ppmv CH_4	10, 100, 1000, 9000 ppmv CH_4	±25% or ±2.5 ppmv, whichever is greater, from 1.0 to 10,000 ppmv.
VOCs	Thermo Scientific TVA-1000B (PID)	RSKSOP-320v1	0.5 – 500 ppmv	0.0, 250, 475 ppmv	250, 475 ppmv Isobutylene	±25% or ±2.5 ppmv, whichever is greater, from 0.5 to 500 ppmv.
O2, CO2, N2, H2, He,CO, C1-C9	Agilent Micro 3000 Gas Chromatograph (TCD)	RSKSOP-194 rev. 4	~0.001-100 MOLE% determined by calibration	Refinery Gas Standards #7 & #5 and Natural Gas Standard #1	Refinery Gas Standards #7 & #5 and Natural Gas Standard #1	± 85-115%

EPAPAV0025556

Table 6. Soil gas sample field screening methods and QA/QC requirements* from SOPs.

Measurement	Analysis Method	Blanks** (Frequency)	Calibration Check Standards (Frequency)	Second Source Standards (Frequency)
O_2, CO_2, CH_4,	RSKSOP-314v1	0 (beginning & end of each sample event)	+/-1% of reading (beginning & end of each sample event)	+/-1% of reading (after each calibration, optional for this project)
CO, H_2S	RSKSOP-314v1	0 (beginning & end of each sample event)	+/-1% of reading (beginning & end of each sample event)	NA
CO	RSKSOP-315v1	0 (beginning & end of each sample event)	90-110% of known value (after calibration, beginning & end of each sample event)	NA
R-123	RSKSOP-313v1	0 (beginning & end of each sample event)	90-110% of known value (after calibration, beginning & end of each sample event; every 2 hours)	NA
Total Hydrocarbons	RSKSOP-320v1	0 (beginning & end of each sample event)	90-110% of known value for FID and 80-120% for PID (after calibration, beginning & end of each sample event)	NA
He	RSKSOP-321v0	0 (beginning & end of each sample event)	90-110% of known value (after calibration, beginning & end of each sample event)	NA

Corrective actions are detailed in the SOPs.
*Duplicate sample not appropriate for measurements from a sample train.
**Meter readings

EPAPAV0025557

Table 7. Soil gas sample fixed laboratory methods and QA/QC requirements.

Measurement	Analysis Method	Blanks (Frequency)	Calibration Checks (Frequency)	Second Source (Frequency)	Duplicates (Frequency)	Matrix Spikes (Frequency)
Ar, He, H_2, O_2, N_2, CO_2, CH_4, C_2H_6, C_2H_4, C_3H_6, C_3H_8, iC_4H_{10}, nC_4H_{10}, iC_5H_{12}, nC_5H_{12}, C_6+	Modification of ASTM D1945-03	None Detected (beginning every 10 samples, end of run)	85-115% (beginning every 10 samples, end of run)	85-115% (after each calibration)	RPD <15% (every 10 samples)	NA
$\delta^{13}C$ and δD of CH_4 , C_2H_6, C_3H_8	Gas stripping and IRMS	Will obtain from Isotech (after calibration)	Difference of calibrated/true <0.5 ‰ for δ13C and < 2.0‰ for δD* (Beginning and every tenth)	Working stds calibrated against IAEA std "LSVEC" for C and "SMOW" and "SLAP" for H (Beginning and every tenth)	Difference of <0.5 ‰ for δ13C and < 2.0‰ for δD* (every 10 samples)	NA
┐ ^{14}C for CH_4	Will obtain from Isotech	< 0.35 pMC Will obtain from Isotech	+/- 1 pMC Will obtain from Isotech	+/- 1 pMC Will obtain from Isotech	+/- 1 pMC Duplicates are not analyzed unless paid for as an additional analysis	NA

* Although the SOW specified < 0.5‰ for δD, Isotech Laboratories has indicated that their criterion is as listed in the table.

Table 8. Summary of quality control samples, purpose, method, and frequency to support gas analysis at a fixed laboratory.

QC Sample	Purpose	Method	Frequency	Acceptance Criteria
Equipment Blanks	Ensure that construction materials in gas sample bags and the sample train are not a source of vapors or gases of concern	Fill sample bags with ultrapure N_2 gas via the sample train.	One sample per day	< Detection limit
Travel Blanks	Ensure that cross-contamination does not occur during sampling or transport to the laboratory	Fill sample bags with ultrapure N_2 gas and place in shipping container with other samples.	One sample per shipment	< Detection limit
Duplicates	Check precision of sampling method and analysis	Use a tee to collect two samples simultaneously.	One sample every 10 samples	RPD < 20%

EPAPAV0025559

Table 9. Critical analytes.

Analyte	Laboratory Performing the Analysis
Gasoline Range Organics (GRO)	EPA Region VIII Laboratory
Diesel Range Organics (DRO)	EPA Region VIII Laboratory
Volatile Organic Compounds (VOC)*	Shaw Environmental and Region VIII Laboratory
Semivolatile Organic Compounds (SVOC)	EPA Region VIII Laboratory
Major Cations (K)	Shaw Environmental
Major Anions (Cl)	RSKERC general parameters lab

*Ethanol, isopropyl alcohol, tert-butyl alcohol, naphthalene, BTEX compounds.
Only those SVOC compounds that have DL, RL, and Control Limits may be used as critical analytes; all others will be used only as screening data.
Both VOC and SVOC have many target analytes and initially all are considered critical (with exception for SVOC noted above). GRO analysis provides data for not only TPH as gasoline, but several other compounds. Only TPH as gasoline will be considered critical from this analysis.

EPAPAV0025560

Table 10. Isotech Laboratory QA/QC Requirements for $\delta^{13}C$ of dissolved methane (and >C1) and δD of dissolved methane.

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

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

EPAPAV0025561

Table 11. Isotech laboratory QA/QC Requirements for $\delta^{13}C$ of DIC (Dissolved Inorganic Carbon).

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

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

EPAPAV0025562

Table 12. Isotech Laboratory QA/QC Requirements for Tritium.

QC Type	Performance Criteria	Frequency
Calibration Check	Accuracy criteria based on 1 sigma limits of existing data	Dead water blank in every set or minimum of 1 per 12 samples; calibrated with NIST 4361C, 1 per every 12 samples
Lab Duplicates	Precision based on 1 sigma limits of existing data	1 per every 10 samples
Preparation System Check/Reference Standards	Accuracy criteria based on 1 sigma limits of existing data	One per every 12 samples, checks against prepared dilutions of NIST 4361C

EPAPAV0025563

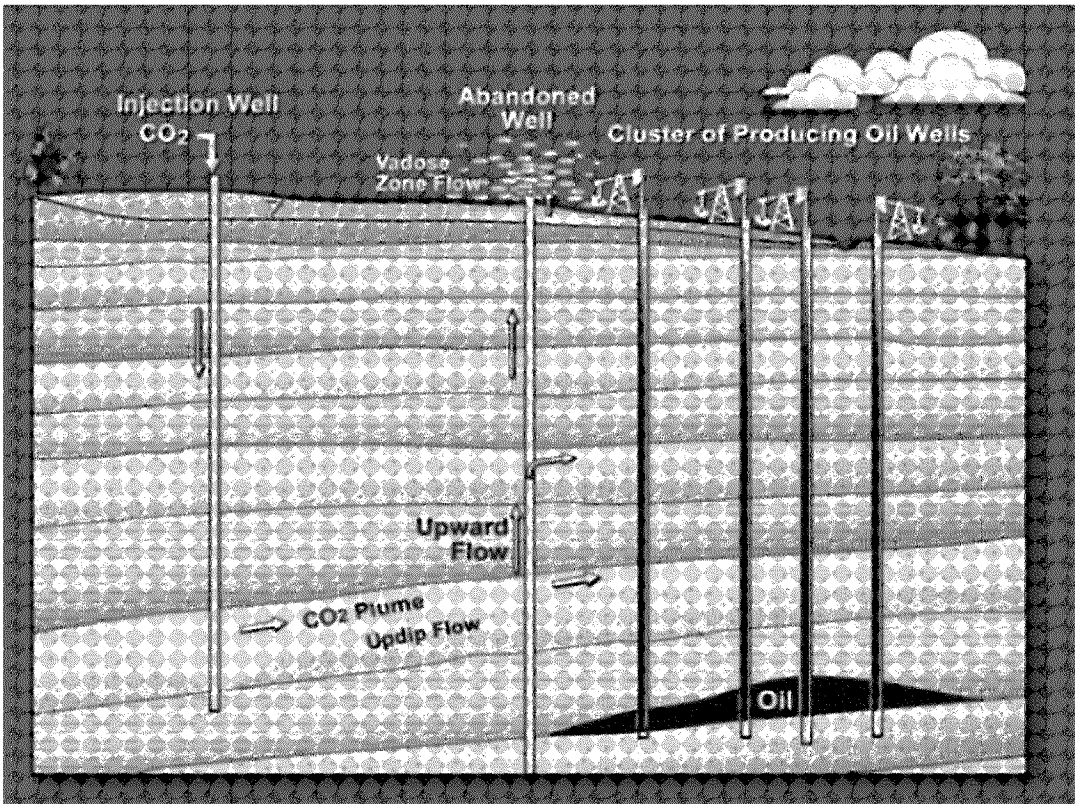


Figure 1. Conceptual model of gas migration from a storage unit. Figure from Celia et al. 2006.

EPAPAV0025564

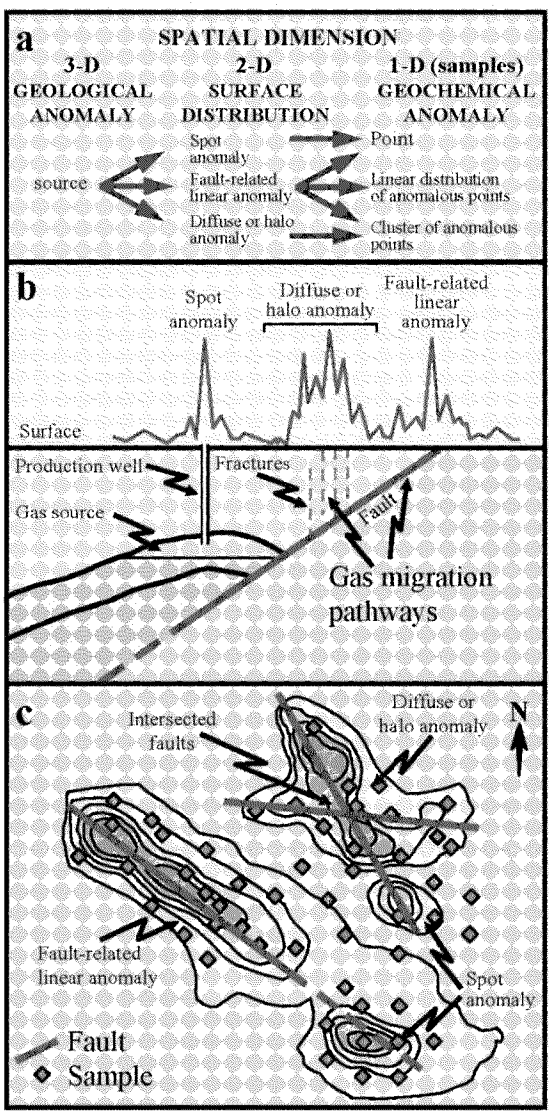


Figure 2. Different types of geochemical anomalies in relation to their spatial dimension (a). Frames (b) and (c) show section and plan view, respectively, of the possible types of geochemical anomalies occurring in faulted areas. Frame (b) shows the case of a gas reservoir confined in a structural tap by low-angle faults, which constitute enhanced permeability pathways for gas migration toward the surface. At the surface, this causes anomalies with different geometry (being the surface expression of fractures and faults), as well as their shifting some distance away from the gas source. In some cases, the anomaly could be the direct result of production activity (i.e., spot anomaly) (From Ciotoli et al., 2004).

EPAPAV0025565

Figure 3. Outline of study area and location of Type A and B monitoring wells

EPAPAV0025566

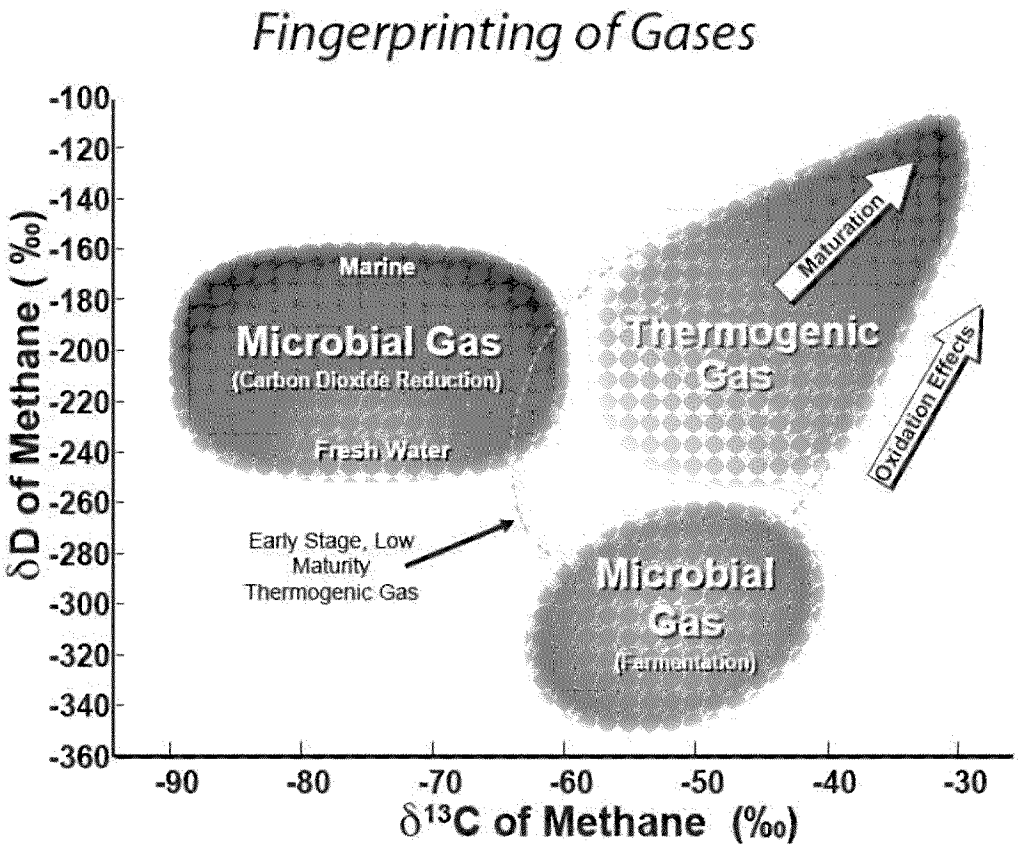


Figure 4. Plot of $\delta^{13}C$ versus δD for methane to discern the origin of methane. Figure from Isotech Laboratories.

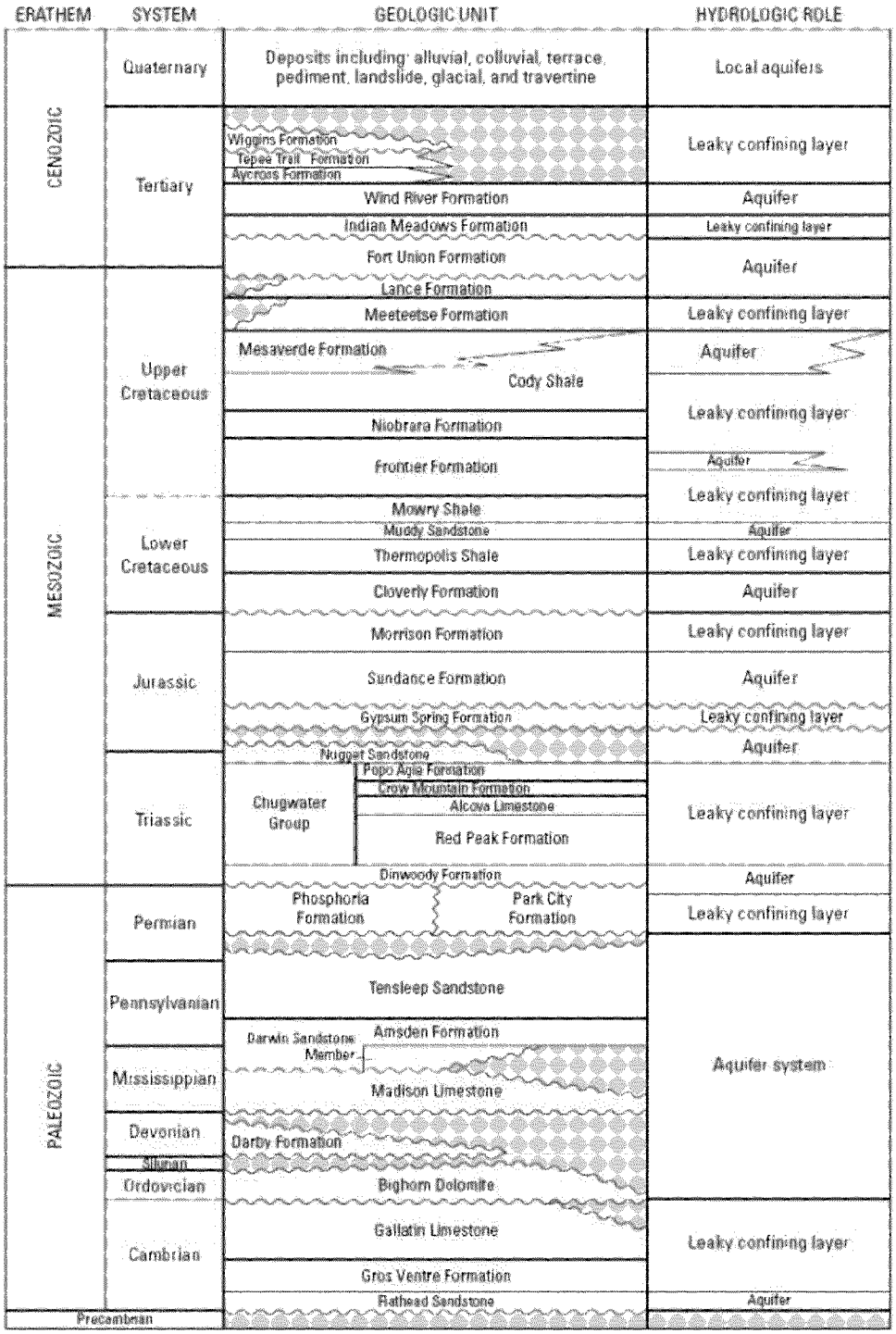


Figure 5. Stratigraphic section and hydrologic roles of rocks on the Wind River Indian Reservation, Wyoming. From USGS (2005).

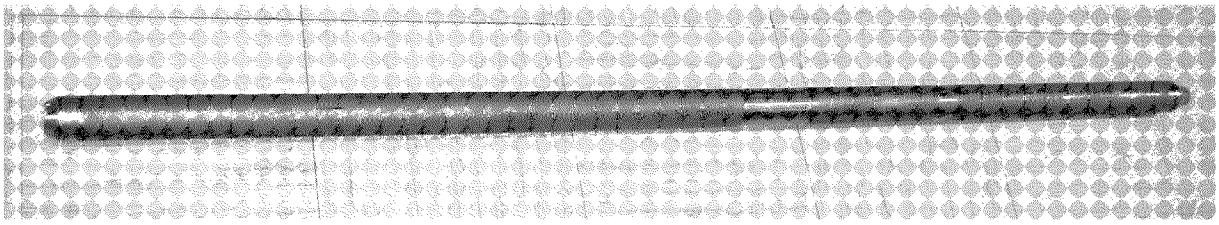


Figure 6. Photograph of bomb sampler to be used to sample water from Type A and Type B monitoring wells.

EPAPAV0025569

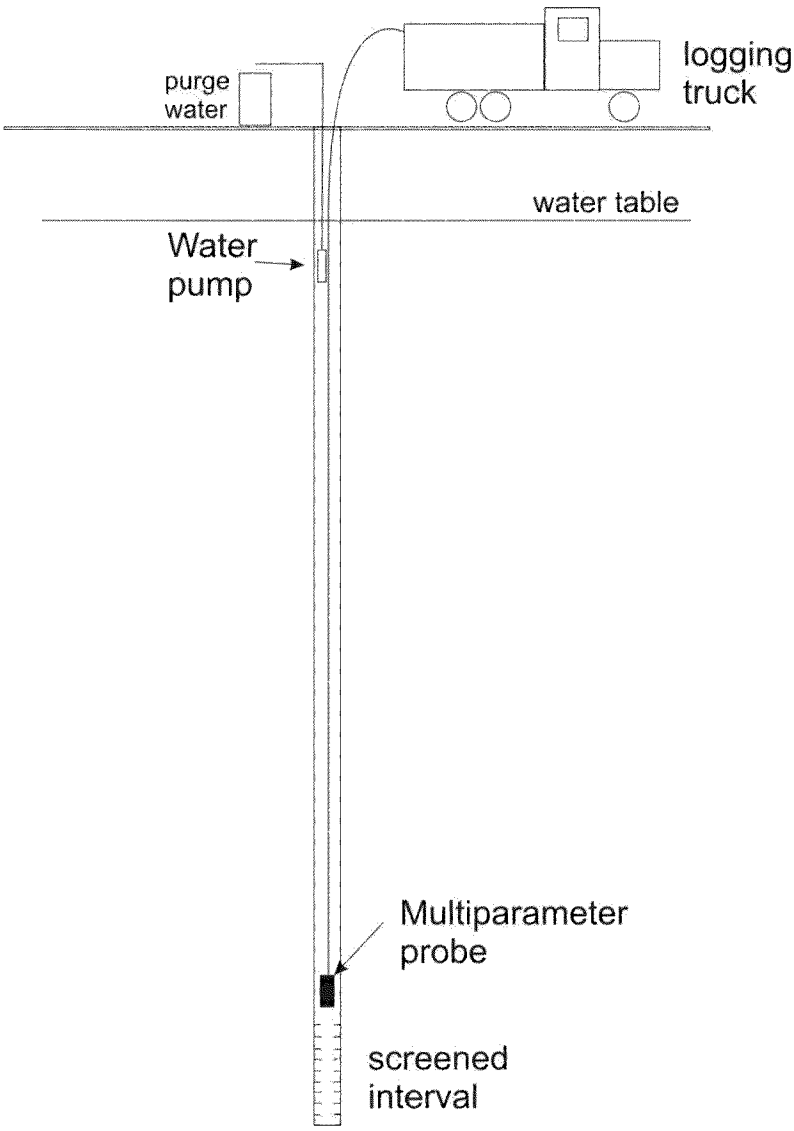


Figure 7. Sample train for ground-water sampling.

EPAPAV0025570

USEPA, ORD, NRMRL

Sample Analysis Request
and
Chain of Custody (COC) Record

Page ____ of ____

Project: Location: Project Manager/Phone:	Lab Name: Address: Contact Name/Phone:
Shipping Method: Shipping Tracking Number:	Shipping Date: Total Number of Shipping Containers:

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

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

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

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

EPA-442 (CIN) (09/08)

Figure 8. Chain of Custody form for submittal of water samples to R.S. Kerr Environmental Research Center.

EPAPAV0025571

Figure 9. Phototgraph of soil-gas sampling train.

Location Identification:				Latitude:			Longitude:					PRT/Probe	
Length of Tubing (ft)													
Flow (sccm)			Headloss ("H2O)										
Flow (sccm)			Headloss ("H2O)										
Flow (sccm)			Headloss ("H2O)										
Flowmeter (Cole-Parmer or Gilmont)				Ball (Stainless-steel or glass)									
Date				Sample Train								Chamber	
Time	Ball Reading	SG Flow (sccm)	Vacuum (in H20)	O2 (%)	CO2 (%)	CH4 (%)	CO/R-123 (ppmv)	H2S (ppmv)	H2 (ppmv)	FID (ppmv)	PID (ppmv)	O2 (%)	CO/R-123 (ppmv)

Figure 10. Spreadsheet for manually recording readings from the LANDTEC-CES GEM2000 Plus Gas Analyzer.

ISOTECH

Send Data and Invoice to

Name _____ Project: _____

Company _____ Purchase Order # _____

Address _____ Location _____

_____ Sampled By: _____

Phone _____ Circle one: Standard

Fax _____ Priority

Email _____ Rush

Sample Description

Container Number	Sample Identification	Date Sampled	Time				Comments

Chain-of-Custody Record

Signature	Company	Date	Time
Relinquished by			
Received by			
Relinquished by			
Received by			
Relinquished by			
Received by			

Figure 11. Chain of Custody form for submittal of soil-gas samples to Isotech Laboratories.

ISOTECH
ISOTECH LABORATORIES INC
1308 Parkland Court Champaign, IL 61821 • (877) 362-4100 • www.isotechlabs.com

Material Safety Data Sheet (MSDS)

SECTION I
TRADE NAME Gas Samples, non-pressurized, flammable (UN3167)
CHEMICAL NAME AND SYNONYMS Methane Gas, Hydrocarbon Gas Mixture, Natural Gas

SECTION II -
HAZARDOUS INGREDIENTS

Methane (CAS 74-82-8)	5 - 99%
Carbon dioxide (CAS 124-38-9)	0 - 50%
Nitrogen (CAS 124-38-9)	0 - 95%
Ethane (CAS 74-84-0)	0 - 10%
Propane (CAS 74-98-6)	0 - 5%
Butane (CAS 106-97-8)	0 - 2%
CxH2x+2 (x=5 and above)	0 - 1%

Gas samples may also contain trace quantities (<0.1%) of various organic gases not listed above.

SECTION III - PHYSICAL DATA
Solubility: appreciable
Appearance (Color, Odor, etc.): colorless, tasteless and normally odorless gas, however may have a characteristically organic odor.
Boiling Point: less than -258°F
Specific Gravity: see Gas Density
Vapor Pressure: not established
Percent Volatile (Volume %): 100
Evaporation: n/a
Gas Density: 0.6 to 1.2 (air = 1.0)

SECTION IV -
FIRE AND EXPLOSION HAZARD DATA
Gas Samples can present a fire hazard. Being a mixture, the gas can explode violently on contact with any source of ignition.
Flash Point: less than -305°F (est.)
Autoignition Temp.: approx. 930°F
Flammability Limits: LEL 5% to UEL 15%
Extinguishing Media: Carbon dioxide or dry chemical.
Special Fire Fighting Procedures: For fires involving this material, do not enter any enclosed or confined fire space without proper protective equipment. Read the entire MSDS.

SECTION V
HEALTH HAZARD INFORMATION
Eye Contact: Not expected to cause eye irritation.
Skin Contact: Not expected to be irritating to the skin.
Inhalation: Breathing high concentrations of gas samples is not expected.
Chronic Effects: Not expected.
EMERGENCY FIRST AID PROCEDURES
Eye Contact: If irritation occurs, flush eyes immediately with fresh water for at least 15 minutes while holding the eyelids open. If irritation continues, seek medical attention.
Skin Contact: Not applicable
Inhalation: Not applicable
Ingestion: Not applicable

SECTION VI - REACTIVITY DATA
Stability (Thermal, Light, etc.): Stable, avoid heat, sparks and open flame.
Incompatibility (Materials to Avoid): Oxidizers
Hazardous Decomposition Products: Combustion may produce carbon monoxide, carbon dioxide, ethylene, and acetylene.
Hazardous Polymerization: Will not occur.

ISOTECH

SECTION VII -
SPILL OR LEAK PROCEDURES
Eliminate all sources of ignition in vicinity of released gas. Stop gas flow if it can be done without risk. Ventilation is required to keep concentrations below the explosive range.
Waste Disposal Methods: Burn through a flare stack in accordance with federal, state and local regulations.

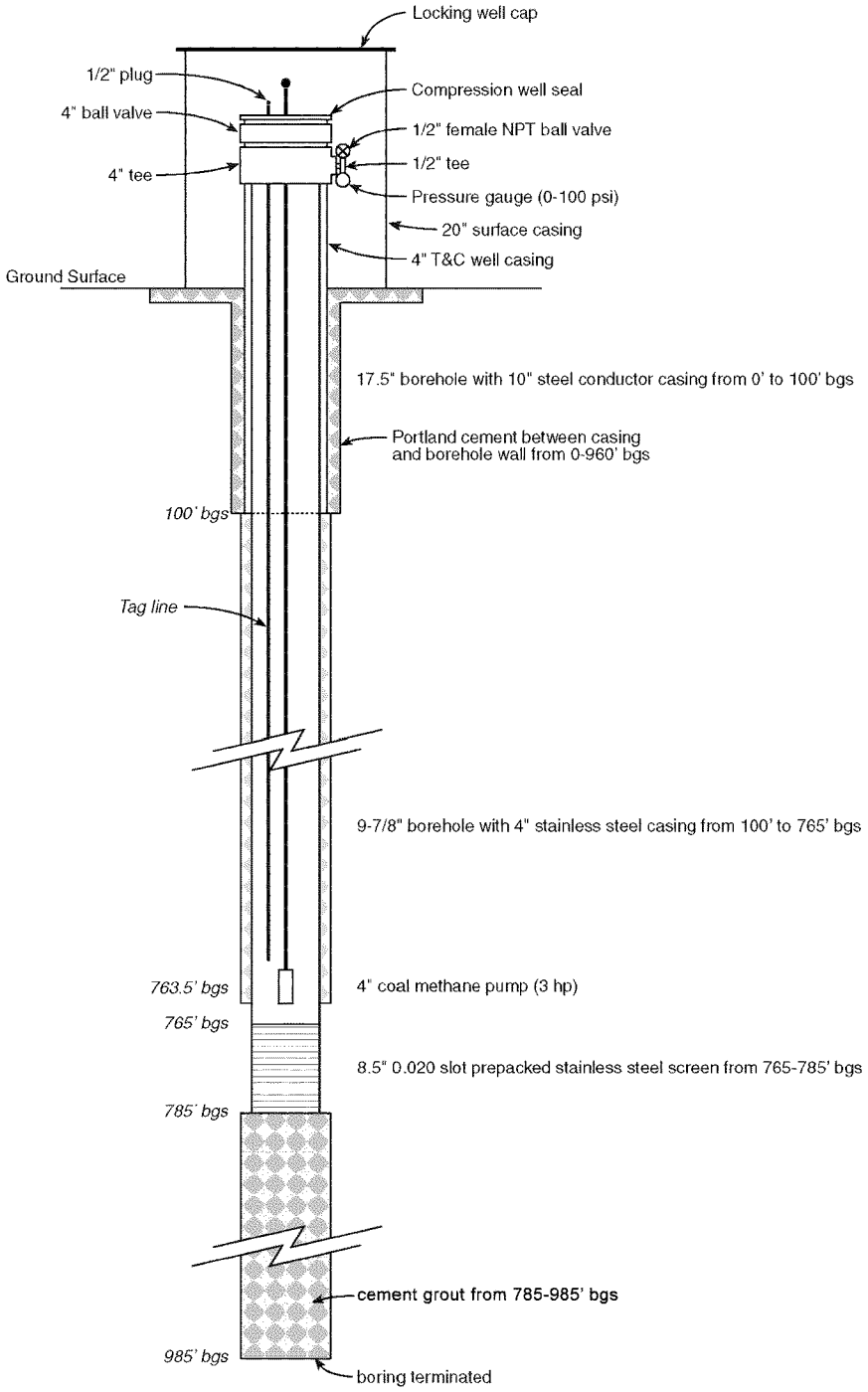
SECTION VIII -
SPECIAL PROTECTIVE INFORMATION
Eye Protection: No special eye protection is required.
Skin Protection: No special skin protection is required.
Respiratory Protection: No special respiratory protection is normally required.

SECTION IX - SPECIAL PRECAUTIONS
Flammable gas. Ground all lines and equipment used with gas to prevent static sparks. Do not smoke where gas is used or stored.
A 19.5% oxygen concentration in air is the minimum recommended for working without special breathing equipment.

n/a = Not Applicable

The information contained herein has been developed based upon current available scientific data. New information may be developed from time to time which may render the conclusions of this report obsolete. Therefore, no warranty is extended as to the applicability of this information to the user's intended purpose or for the consequences of its use or misuse.

Figure 12 MSDS to accompany soil-gas samples exceeding 5% methane.



Not to Scale

Figure 13a. Schematic of deep monitoring well MW-01.

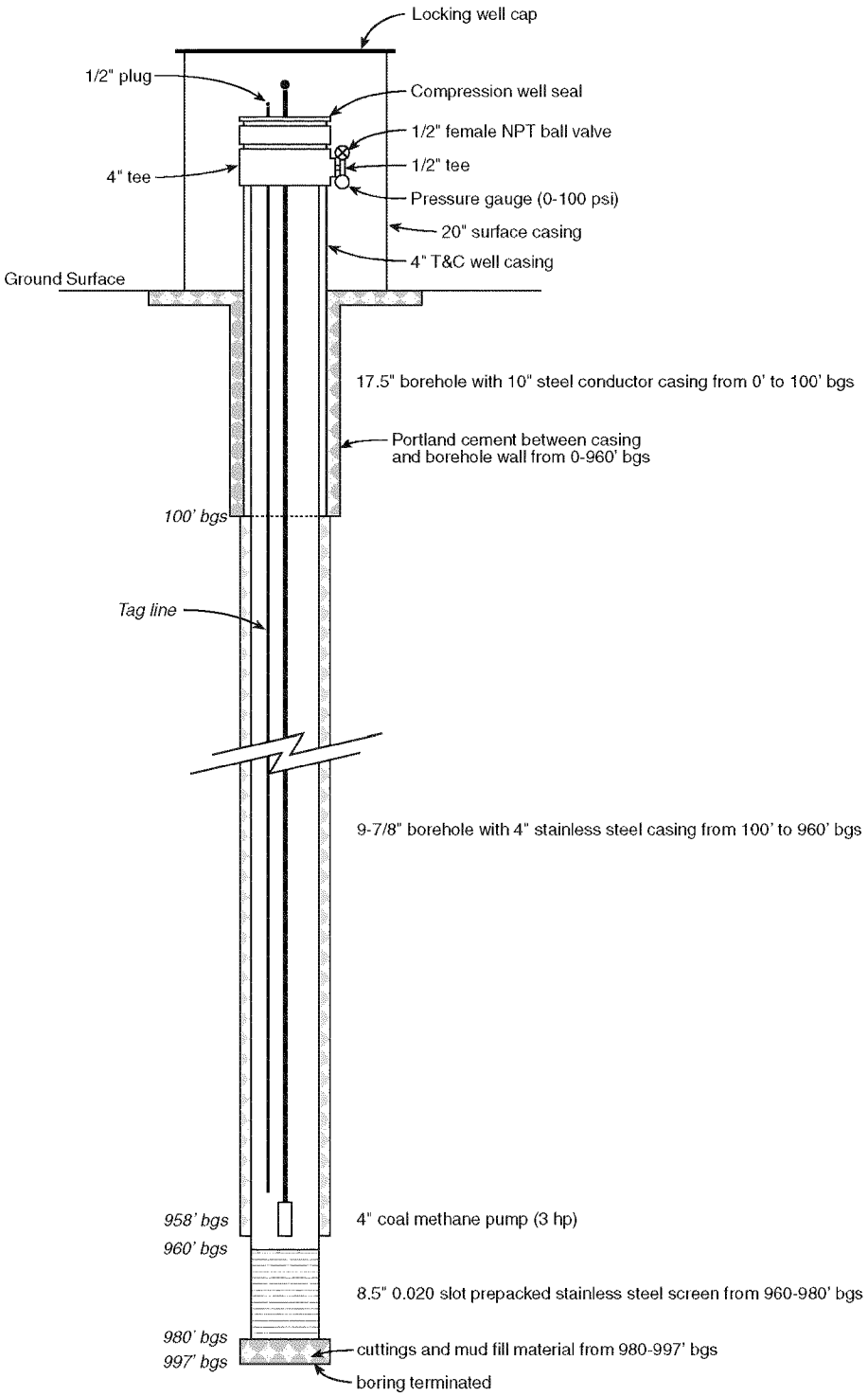


Figure 13b. Schematics of deep monitoring well MW-02.

APPENDIX A

See accompanying pdf file "Appendix A Isotech QAP"

EPAPAV0025579

REVISION HISTORY:

Revision Number	Date Approved	Revision
0	6/8/10	New document
1	9/13/10	Revised ground water and soil gas sampling information
2	9/15/10	Modifications made to sampling strategy for LD01 using a sampling "bomb."
3	3/31/11	Diethylene, triethylene, tetraethylene glycols, and 2-butoxyethanol analysis by HPLC-MS-MS were added to the analyte list. Propylene, ethylene, diethylene, triethylene, tetraethylene glycols and 2-butoxyethanol analysis by GC-FID analysis were added to the analyte list. Real time monitoring of headspace off purge water from domestic wells was added. On-site GC-TCD analysis of water from domestic wells for methane was added. Gas sampling from the casing of domestic wells was added.
4	4/13/11	Minor changes in text added.
5	6/19/11	Language specifying review and release of data updated to incorporate release of data subsequent to audits of data quality as required in a Category I QAPP.
6	2/17/12	1.2: Text added to describe activities in Phases I-IV and upcoming Phase V. Objectives clarified 2.1: additional project personnel added. 3.1: description of Type D wells added as well as info for Phase V. 3.4 & 4.3: added analysis of drilling additives. 4.1.c, 4.1.f, 5.1, 6.3, Tables 2 and 3: Tritium, methylene blue active substances, methanol, alkylphenols, ethoxylated alcohols, ethoxylated phenols, acrylamide, H and O stable isotopes of water, propylene and ethylene glycols, and methanol were added to the analyte list. 4.1.c: The sampling strategy at MW02 was modified to collect samples after a period of recharge subsequent to purging as opposed to sampling immediately after purging. Real time monitoring of headspace off purge water from MW01 and MW02 using portable infrared gas analyzers and flame- and photoionization detectors was added. 4.1.c: sampling of Type D wells 4.1.d: added info on calibration and checks for field measurements of ferrous iron, sulfide, alkalinity, and turbidity. 5.3 and 5.4: added sections on cement bond logs and borehole geophysical logs. 6.3: added criteria for evaluating field duplicates and blanks; updated

EPAPAV0025580

		SOW for Isotech and added QA/QC for MBAS by TestAmerica, methanol and glycols by ALS, and alkylphenols and ethoxylated alcohols and alkylphenols by ORD/NERL lab. 7: added text to clarify data verification/validation process. 8.1: added text on QA requirements if another agency takes the lead on sampling. References: additional references added. Table 2: added EPA method numbers, correct refrigeration temperature; correct holding time for VOC analysis by Shaw. Table 3: added text to clarify requirements Added Tables 9, 10, 11, and 12. Replaced MW schematics.

EPAPAV0025581