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**AGENDA ITEM:** 1  
**MEETING DATE:** 6/12/2012  
**TO:** City Council/Planning Commission  
**FROM:** Bill Cahill, City Manager  
**PRESENTER:** Greg George, Director, Development Services

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**TITLE:**  
Panel discussion regarding oil and gas extraction and development

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**RECOMMENDED CITY COUNCIL/PLANNING COMMISSION ACTION:**  
Informational only

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**DESCRIPTION:**  
On May 15 2012, City Council approved an emergency ordinance (Attachment A) imposing a nine month moratorium on the acceptance, processing, and approval of any applications, permits, or other approvals for oil and gas uses. The ordinance is intended to allow the City time to investigate the extent of the City's authority to regulate such uses and develop and implement appropriate regulations, if necessary, to protect the public's health, safety and welfare.

Staff will seek direction from Council in the development of the appropriate regulations over the next few months.

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**SUMMARY:**  
The following six panelists have been invited to present information to City Council, Planning Commission, City staff and the public.

**1. DR. KENNETH H. CARLSON**

Ken Carlson is an Associate Professor in Civil and Environmental Engineering at Colorado State University with over 20 years of experience in water treatment, wastewater handling and environmental engineering. Dr. Carlson is the co-director of the Colorado Energy Water Consortium, a public-private partnership that is addressing water issues associated with oil and gas exploration and production in Colorado and the Rocky Mountain region. Through the consortium, Dr. Carlson is working with industry, the Colorado Oil and Gas Association and the National Renewable Energy Lab on water quantity characterization and frac flowback/produced water quality assessment. Current work includes studies related to fuel source water intensity, treatment of frac fluid flowback and produced water and optimization of water handling and management with GIS-based tools. Dr. Carlson has been instrumental in organizing the Colorado State University Natural Gas Symposium in 2011 and 2012 and the Fundamentals of the Natural Gas Industry class in 2012. Dr. Carlson has a BS in chemical engineering from

the University of Wisconsin, MS in Civil Engineering from Colorado State University and a PhD in Environmental Engineering from the University of Colorado – Boulder. Before coming to Colorado State University, Dr. Carlson worked for over 10 years in private industry including multiple positions in the environmental consulting field.

**2. TISHA CONOLY SCHULLER**

Ms. Tisha Conoly Schuller serves as President and Chief Executive Officer of the Colorado Oil & Gas Association. As President, Ms. Schuller is responsible for leading the industry in Colorado legislative, regulatory, and public relations matters. Previously, Ms. Schuller served as a Principal and Vice President with Tetra Tech, a national environmental consulting and engineering firm. In addition to running business operations, Ms. Schuller spent 15 years conducting environmental permitting for oil and natural gas projects across the country. She has a B.S. in Earth Systems with an emphasis in Geology from Stanford University. Tisha is an Advisory Board Member of the American Red Cross in Denver.

**3. SHANE DAVIS**

Shane Davis currently chairs the Poudre Canyon Group of the Rocky Mountain Chapter of the Sierra Club, and serves as the Group's Conservation Chair. He serves as an At-Large Member of the Chapter Executive Committee and as the Information and Research Manager - Oil & Gas Mining. Mr. Davis is a research biologist, and currently is a lead investigator into adverse environmental and human health impacts related to the Colorado oil and gas industry's use of hydraulic fracturing. He has also worked with the Colorado State Parks Department of Natural Resources, and is a former National Science Foundation grant recipient in molecular genetics. While overseas managing a pilot program in environmental safety and security for the Department of Defense, he was awarded a medal for his work by NATO.

**4. THOM KERR**

Thom Kerr is the Acting Director at the Colorado Oil and Gas Conservation Commission (COGCC). Prior to securing his COGCC position, Mr. Kerr spent fourteen years in the oil and gas industry with exploration and seismic firms. Since August 2007, Mr. Kerr has been heavily involved in COGCC's latest rule making initiative and has contributed to several other rulemaking proceedings since 1994.

**5. KENT KUSTER**

Kent Kuster has served as the Oil and Gas Liaison from the Colorado Department of Public Health and Environment for four years and prior to this Kent spent six years working for the Water Quality Control Division. In his role as CDPHE Oil and Gas Liaison, Kent is responsible for consultations with the Local Governmental Designee, COGCC and the Oil and Gas Operator as well as coordination between the COGCC and CDPHE. Before joining CDPHE in 2001, Kent was a Public Works Director with 20 years of experience in the public utility field.

**6. RANDY MIROWSKI**

Randy Mirowski is the Fire Chief for Loveland Fire Rescue Authority (LFRA). He is also the liaison to the City of Loveland's Management Team (M-Team), the Loveland Fire

Rescue Authority Board, the Loveland Rural Fire District Board, and the Fire Rescue Advisory Commission (FRAC). Chief Mirowski has accredited degrees from Aims Community College, (A.A.S. Fire Science Technology), Colorado State University (B.S. Technology, Education and Training), and an M.A. in Organizational Leadership from Gonzaga University in Spokane, WA (May 2011). Chief Mirowski's fire service career has spanned over 38 years. He holds numerous command certifications in the National Incident Management System (NIMS) and most recently completed his Blue Card certification in Hazard Zone Management.

Citizens have raised concerns regarding potential environmental impacts resulting from directional drilling and horizontal fracking. Attachments B, C and D provide information on potential impacts on air and water quality and Attachment E provides information on earthquakes.

A short video will be presented at the beginning of the meeting to illustrate the basic processes of directional drilling and horizontal fracking. The following is a link to that video:

[Natural Gas Shale Horizontal Drilling Video](#)

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**REVIEWED BY CITY MANAGER:**



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**LIST OF ATTACHMENTS:**

- A. Moratorium Ordinance
- B. Abstract - Human health risk assessment of air emission from development of unconventional natural gas resources: Lisa M. McKenzie, Roxana Z. Witter, Lee S. Newman, John L. Adgate (for a copy of the full study e-mail Dr. McKenzie at: [lisa.mckenzie@ucdenver.edu](mailto:lisa.mckenzie@ucdenver.edu))
- C. Investigation of Ground Water Contamination near Pavillion, Wyoming, (Draft): Dominic C. DiGiulio, Richard T. Wilkin and Carlyle Miller, U.S. Environmental Protection Agency and Gregory Oberley, U.S. Environmental Protection Agency, Region 8
- D. Abstract - Natural Gas Operations from a Public Health Perspective, Human and Ecological Risk Assessment: Theo Colborn, Carol Kwiatkowski, Kim Schultz, Mary Bachran\_(to link to this article: <http://cce.cornell.edu/EnergyClimateChange/NaturalGasDev/Documents/PDFs/fracking%20chemicals%20from%20a%20public%20health%20perspective.pdf>)
- E. Earthquakes Triggered by Humans in Colorado — a background paper by the Colorado Geological Survey: Submitted to the City of Loveland by Vince Matthews, Director and State Geologist
- F. Panelists' presentations/outlines

FIRST & ONLY READING: May 15, 2012

**ORDINANCE NO. 5685**

**AN EMERGENCY ORDINANCE OF THE COUNCIL OF THE CITY OF  
LOVELAND IMPOSING A NINE-MONTH MORATORIUM ON THE CITY'S  
ACCEPTANCE AND PROCESSING OF LAND USE APPLICATIONS, PERMITS  
AND OTHER APPROVALS CONCERNING THE CONDUCT OF OIL AND GAS  
EXTRACTION AND RELATED OPERATIONS WITHIN THE CITY**

**WHEREAS**, the Loveland City Council recognizes the importance of natural resources to the community, but believes it is important to minimize adverse impacts of any industry developing those resources on the City and the public's health, safety, and welfare through the exercise of the City's general police power and its zoning and land use regulations; and

**WHEREAS**, there has been considerable interest in oil and gas resources underlying portions of Loveland, including property owned by the City; and

**WHEREAS**, the exploration for and extraction of liquid and gaseous hydrocarbon resources and related activities present unique public health, safety, and welfare issues which may be inadequately addressed in the City's current zoning and land use regulations; and

**WHEREAS**, the present City regulations related to oil and gas exploration, extraction, production, transportation and related operations and activities, including, without limitation, all those oil and gas activities regulated by the Colorado Oil and Gas Conservation Commission (collectively "Oil and Gas Uses") in the City require updating with respect to current regulatory best management practices consistent with the Colorado Oil and Gas Conservation Commission ("Commission") Rules and industry technologies in order to preserve and protect the health, safety, and welfare of Loveland's citizens and the resources of the City; and

**WHEREAS**, Oil and Gas Uses may negatively impact Loveland citizens and the use and integrity of local water supplies and water infrastructure, air quality, roads and transportation infrastructure, wastewater infrastructure, land resources, wildlife and aesthetic values; and

**WHEREAS**, Title 18 of the Loveland Municipal Code provides that the City's zoning and land use regulations are designed to lessen congestion in the streets; to secure safety from fire, panic and other dangers; to promote health and general welfare; to provide adequate light and air; to prevent overcrowding of land; to avoid undue

concentration of population; and to facilitate the adequate provision of transportation, water, sewage, schools, parks and other public requirements; and

**WHEREAS**, a comprehensive study of the impacts of Oil and Gas Uses is needed to determine whether the City's existing zoning and land use regulations are sufficient to protect the public's health, safety, and welfare or whether additional regulations are necessary to address the impact of Oil and Gas Uses; and

**WHEREAS**, if land use applications, permit applications or any other applications are submitted to the City requesting approval of an Oil and Gas Use prior to the City's examination of the impact of any such Use and before a determination can be made by the Council as to whether any additional local regulations are necessary to protect the public's health, safety, and welfare, irreparable harm may be done to the public's health, safety and welfare and to the City's interests; and

**WHEREAS**, municipalities throughout Colorado are struggling to address the potential adverse impacts of proliferating Oil and Gas Uses in urban and suburban environments on their citizens' health, safety, and welfare and several municipalities have enacted moratoria permitting a period of time to evaluate those impacts of Oil and Gas Uses in order to assess and determine the appropriate local regulation of such; and

**WHEREAS**, it is Council's belief that Oil and Gas Uses are likely to commence on property in the City within the next nine (9) months; and

**WHEREAS**, a significant period of time will be required in order for the City Manager and City Attorney, and their respective staffs, to clarify the extent of the City's legal authority with regard to local regulation of such expected future Oil and Gas Uses and to formulate any recommended amendments to the City Code to deal specifically with those Uses in an adequate manner; and

**WHEREAS**, the imposition of a nine-month moratorium on the submission, acceptance, consideration, and approval of any and all applications for City licenses, permits and other approvals related in any way to Oil and Gas Uses within the City, will allow City staff and the Council the time needed to investigate the extent of City's authority to regulate such Uses and develop and implement appropriate regulations; and

**WHEREAS**, nine (9) months is a reasonable period of time and is no longer than necessary for the City to determine the extent to which Oil and Gas Uses may be locally regulated and to properly investigate, develop, and, if appropriate, adopt and implement any local regulations related to Oil and Gas Uses in Loveland in order to protect and preserve the public's health, safety and welfare; and

**WHEREAS**, existing Oil and Gas Uses in Loveland will not be unduly prejudiced by the imposition of such a moratorium, since such Uses currently permitted and existing in the City will not be prohibited or terminated by this moratorium; and

**WHEREAS**, Loveland Charter Section 4-10 authorizes the City Council to adopt at one reading an emergency ordinance that goes into effect immediately upon an affirmative vote of at least six (6) members of the Council with a specific statement of the nature of the emergency set forth in the ordinance.

**NOW, THEREFORE, BE IT ORDAINED BY THE COUNCIL OF THE CITY OF LOVELAND:**

**Section 1.** That the preceding recitals contained in this Ordinance are hereby adopted and incorporated by reference as findings of fact of the City Council.

**Section 2.** That it is necessary for the immediate preservation of the public's health, safety and welfare to delay the processing of applications for any and all City licenses, permits and any other approvals related to or in any way needed for any and all Oil and Gas Uses within the City until the City has had a reasonable opportunity to investigate the extent of the City's legal authority to regulate such Uses and, if appropriate, adopt and implement any local regulations related to Oil and Gas Uses in Loveland in order to protect and preserve the public's health, safety and welfare.

**Section 3.** That a nine-month moratorium is hereby imposed upon the acceptance, processing, and approval by the City of any and all applications for City licenses, permits and any other approvals related to or in any way needed for any and all Oil and Gas Uses in the City. No such applications requesting approval to use property within the City for Oil and Gas Uses shall be accepted, processed, or approved commencing May 16, 2012 and for the duration of the nine-month moratorium thereafter. Therefore, this moratorium shall begin on May 16, 2012, and end on February 16, 2013, or such earlier date as may be determined by the City Council by ordinance.

**Section 4.** That if any section, paragraph, sentence, clause or phrase of this Ordinance is held to be unconstitutional or invalid for any reason, such decision shall not affect the validity or constitutionality of and shall be severable from the remaining portions of this Ordinance. The City Council hereby declares that it would have adopted this Ordinance and each part or parts hereof irrespective of the fact that any one part or parts may be declared unconstitutional or invalid.

**Section 5.** That all other ordinances or portions thereof, and all City Code provisions inconsistent or conflicting with this Ordinance or any portion hereof, are hereby superseded by this Ordinance and their legal effect held in abeyance but only to the extent of such inconsistency or conflict and only for the duration of the moratorium herein imposed.

**Section 6.** That because of the likely and imminent filing of applications for the approval of Oil and Gas Uses on property within the City prior to the City's examination of the impact of such Uses and, if appropriate, its adoption and implementation of specific or adequate zoning, land use and other police power

regulations to govern such Uses, an emergency for the adoption of this Ordinance exists in order to avoid the following adverse consequences:

- a. Adverse changes in the character of the City and its neighborhoods; and
- b. Adverse impacts to the health, safety and welfare of the City's residents as a result of unmitigated or inadequately regulated impacts on water quality, air quality, road and transportation impacts, noise and erosion and stormwater.

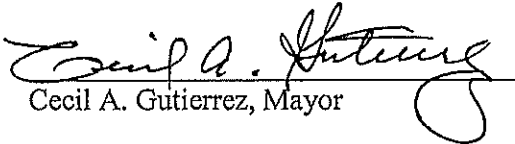
Accordingly, the City Council hereby finds and determines that an emergency exists requiring the immediate passage of this Ordinance for the preservation of the health, safety, morals and welfare of the citizens of the City of Loveland.

**Section 7.** That pursuant to City Charter Section 4-10(b), this Ordinance shall become effective immediately upon its adoption by the City Council.


Signed this 15th day of May, 2012.

CITY OF LOVELAND, COLORADO

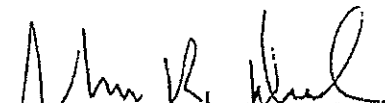


  
Cecil A. Gutierrez, Mayor

ATTEST:

  
Susan L. Andrews  
City Clerk

APPROVED AS TO FORM:

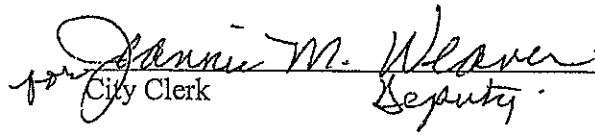
  
City Attorney



Ordinance # 5685

I, Teresa G. Andrews, City Clerk of the City of Loveland, Colorado, hereby certify that the above and foregoing Ordinance was introduced at a regular (or special) meeting of the City Council, held on May 15, 2012 and was initially published in the Loveland Daily Reporter-Herald, a newspaper published within the city limits in full on May 19, 2012 and by title except for parts thereof which were amended after such initial publication which parts were published in full in said newspaper on (NA).

Effective Date: May 15, 2012

  
for City Clerk Deputy

# Human health risk assessment of air emissions from development of unconventional natural gas resources.

McKenzie LM, Witter RZ, Newman LS, Adgate JL.

## Source

Colorado School of Public Health, University of Colorado, Anschutz Medical Campus, Aurora, Colorado 80045, USA.

(For copy of complete study, please email Dr. Lisa McKenzie: [lisa.mckenzie@ucdenver.edu](mailto:lisa.mckenzie@ucdenver.edu))

## Abstract

### BACKGROUND:

Technological advances (e.g. directional drilling, hydraulic fracturing), have led to increases in unconventional natural gas development (NGD), raising questions about health impacts.

### OBJECTIVES:

We estimated health risks for exposures to air emissions from a NGD project in Garfield County, Colorado with the objective of supporting risk prevention recommendations in a health impact assessment (HIA).

### METHODS:

We used EPA guidance to estimate chronic and subchronic non-cancer hazard indices and cancer risks from exposure to hydrocarbons for two populations: (1) residents living  $> \frac{1}{2}$  mile from wells and (2) residents living  $\leq \frac{1}{2}$  mile from wells.

### RESULTS:

Residents living  $\leq \frac{1}{2}$  mile from wells are at greater risk for health effects from NGD than are residents living  $> \frac{1}{2}$  mile from wells. Subchronic exposures to air pollutants during well completion activities present the greatest potential for health effects. The subchronic non-cancer hazard index (HI) of 5 for residents  $\leq \frac{1}{2}$  mile from wells was driven primarily by exposure to trimethylbenzenes, xylenes, and aliphatic hydrocarbons. Chronic HIs were 1 and 0.4. for residents  $\leq \frac{1}{2}$  mile from wells and  $> \frac{1}{2}$  mile from wells, respectively. Cumulative cancer risks were 10 in a million and 6 in a million for residents living  $\leq \frac{1}{2}$  mile and  $> \frac{1}{2}$  mile from wells, respectively, with benzene as the major contributor to the risk.

### CONCLUSIONS:

Risk assessment can be used in HIAs to direct health risk prevention strategies. Risk management approaches should focus on reducing exposures to emissions during well completions. These preliminary results indicate that health effects resulting from air emissions during unconventional NGD warrant further study. Prospective studies should focus on health effects associated with air pollution.

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# DRAFT

## Investigation of Ground Water Contamination near Pavillion, Wyoming



**DRAFT**

DRAFT

# Investigation of Ground Water Contamination near Pavillion, Wyoming

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**DRAFT**

# **Notice**

This report has been reviewed and approved by the U.S. Environmental Protection Agency's Office of Research and Development. Approval does not signify that the contents necessarily reflect the views and policies of the Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

**DRAFT**

# **Foreword**

The U.S. Environmental Protection Agency (EPA) is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. The scientific arm of EPA, the Office of Research and Development (ORD), conducts leading-edge research that helps provide the solid underpinning of science and technology for the Agency. The work at ORD laboratories, research centers, and offices across the country helps improve the quality of air, water, soil, and the way we use resources. The research described in this report was designed and conducted by ORD's National Risk Management Research Laboratory in Ada, Oklahoma, working in close collaboration with scientists from EPA Region 8 in Denver, Colorado.

# Acknowledgements

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# Extended Abstract

In response to complaints by domestic well owners regarding objectionable taste and odor problems in well water, the U.S. Environmental Protection Agency initiated a ground water investigation near the town of Pavillion, Wyoming under authority of the Comprehensive Environmental Response, Compensation, and Liability Act. The Wind River Formation is the principal source of domestic, municipal, and stock (ranch, agricultural) water in the area of Pavillion and meets the Agency's definition of an Underground Source of Drinking Water. Domestic wells in the area of investigation overlie the Pavillion gas field which consists of 169 production wells which extract gas from the lower Wind River Formation and underlying Fort Union Formation. Hydraulic fracturing in gas production wells occurred as shallow as 372 meters below ground surface with associated surface casing as shallow as 110 meters below ground surface. Domestic and stock wells in the area are screened as deep as 244 meters below ground surface. With the exception of two production wells, surface casing of gas production wells do not extend below the maximum depth of domestic wells in the area of investigation. At least 33 surface pits previously used for the storage/disposal of drilling wastes and produced and flowback waters are present in the area. The objective of the Agency's investigation was to determine the presence, not extent, of ground water contamination in the formation and if possible to differentiate shallow source terms (pits, septic systems, agricultural and domestic practices) from deeper source terms (gas production wells).

The Agency conducted four sampling events (Phase I - IV) beginning in March 2009 and ending in April, 2011. Ground water samples were collected from domestic wells and two municipal wells in the town of Pavillion in Phase I. 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 additional ground water samples from domestic and stock wells and 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 prompted the Agency to install 2 deep monitoring wells screened at 233 - 239 meters (MW01) and 293 - 299 meters (MW02) below ground surface, respectively, in June 2010 to better evaluate to deeper sources of contamination. The expense of drilling deep wells while utilizing blowout prevention was the primary limiting factor in the number of monitoring wells installed. 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 number of domestic wells. In April 2011 (Phase IV), EPA resampled the 2 deep monitoring wells to compare previous findings and to expand the analyte list to include glycols, alcohols, and low molecular weight acids.

Detection of high concentrations of benzene, xylenes, gasoline range organics, diesel range organics, and total purgeable hydrocarbons in ground water samples from shallow monitoring wells near pits indicates that pits are a source of shallow ground water contamination in the area of investigation. When considered separately, pits represent potential source terms for localized ground water plumes of unknown extent. When considered as whole they represent potential broader contamination of shallow ground water. A number of stock and domestic wells in the area of investigation are fairly shallow (e.g., < 30 meters below ground surface) representing potential receptor pathways.

Determination of the sources of inorganic and organic geochemical anomalies in deeper ground water was considerably more complex than determination of sources in shallow media necessitating the use of multiple

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lines of reasoning approach common to complex scientific investigations. pH values in MW01 and MW01 are highly alkaline (11.2-12.0) with up to 94% of the total alkalinity contributed by hydroxide suggesting addition of a strong base as the causative factor. Reaction path modeling indicates that sodium-sulfate composition of ground water typical of deeper portions of the Wind River Formation provides little resistance to elevation of pH with small addition of potassium hydroxide. Potassium hydroxide was used in a crosslinker and in a solvent at this site.

The inorganic geochemistry of ground water from the deep monitoring wells is distinctive from that in the domestic wells and expected composition in the Wind River formation. Potassium concentration in MW02 (43.6 milligrams per liter) and MW01 (54.9 milligrams per liter) is between 14.5 and 18.3 times values in domestic wells and expected values in the formation. Chloride concentration in monitoring well MW02 (466 milligrams per liter) is 18 times the mean chloride concentration (25.6 milligrams per liter) observed in ground water from domestic wells and expected in the formation. Chloride enrichment in this well is significant because regional anion trends show decreasing chloride concentration with depth. In addition, the monitoring wells show low calcium, sodium, and sulfate concentrations compared to the general trend observed in domestic well waters. The formulation of fracture fluid provided for carbon dioxide foam hydraulic fracturing jobs typically consisted of 6% potassium chloride. Potassium metaborate was used in crosslinkers. Potassium hydroxide was used in a crosslinker and in a solvent. Ammonium chloride was used in crosslinker.

A number of synthetic organic compounds were detected in MW01 and MW02. Isopropanol was detected in MW01 and MW02 at 212 and 581 micrograms per liter, respectively. Diethylene glycol was detected in MW01 and MW02 at 226 and 1570 micrograms per liter, respectively. Triethylene glycol was detected in MW01 and MW02 at 46 and 310 micrograms per liter, respectively. Another synthetic compound, *tert*-butyl alcohol, was detected in MW02 at a concentration of 4470 micrograms per liter. Isopropanol was used in a biocide, in a surfactant, in breakers, and in foaming agents. Diethylene glycol was used in a foaming agent and in a solvent. Triethylene glycol was used in a solvent. *Tert*-butyl alcohol is a known breakdown product of methyl *tert*-butyl ether (a fuel additive) and *tert*-butyl hydroperoxide (a gel breaker used in hydraulic fracturing). Material Safety Data Sheets do not indicate that fuel or *tert*-butyl hydroperoxide were used in the Pavillion gas field. However, Material Safety Data Sheets do not contain proprietary information and the chemical ingredients of many additives. The source of *tert*-butyl alcohol remains unresolved. However, *tert*-butyl alcohol is not expected to occur naturally in ground water.

Benzene, toluene, ethylbenzene, and xylenes (BTEX) were detected in MW02 at concentrations of 246, 617, 67, and 750 micrograms per liter, respectively. Trimethylbenzenes were detected in MW02 at 105 micrograms per liter. Gasoline range organics were detected in MW01 and MW02 at 592 and 3710 micrograms per liter. Diesel range organics were detected in MW01 and MW02 at 924 and 4050 micrograms per liter, respectively. Aromatic solvent (typically BTEX mixture) was used in a breaker. Diesel oil (mixture of saturated and aromatic hydrocarbons including naphthalenes and alkylbenzenes) was used in a guar polymer slurry/liquid gel concentrate and in a solvent. Petroleum raffinates (mixture of paraffinic, cycloparaffinic, olefinic, and aromatic hydrocarbons) were used in a breaker. Heavy aromatic petroleum naphtha (mixture of paraffinic, cycloparaffinic and aromatic hydrocarbons) was used in surfactants and in a solvent. Toluene and xylene were used in flow enhancers and a breaker.

Detections of organic chemicals were more numerous and exhibited higher concentrations in the deeper of the two monitoring wells. Natural breakdown products of organic contaminants like BTEX and glycols include



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acetate and benzoic acid. These breakdown products are more enriched in the shallower of the two monitoring wells, suggesting upward/lateral migration with natural degradation and accumulation of daughter products. Hydraulic gradients are currently undefined in the area of investigation. However, there are flowing conditions in a number of deep stock wells suggesting that upward gradients exist in the area of investigation.

Alternative explanations were carefully considered to explain individual sets of data. However, when considered together with other lines of evidence, the data indicates likely impact to ground water that can be explained by hydraulic fracturing. A review of well completion reports and cement bond/variable density logs in the area around MW01 and MW02 indicates instances of sporadic bonding outside production casing directly above intervals of hydraulic fracturing. Also, there is little lateral and vertical continuity of hydraulically fractured tight sandstones and no lithologic barrier (laterally continuous shale units) to stop upward vertical migration of aqueous constituents of hydraulic fracturing in the event of excursion from fractures. In the event of excursion from sandstone units, vertical migration of fluids could also occur via nearby wellbores. For instance, at one production well, the cement bond/variable density log indicates no cement until 671 m below ground surface. Hydraulic fracturing occurred above this depth at nearby production wells.

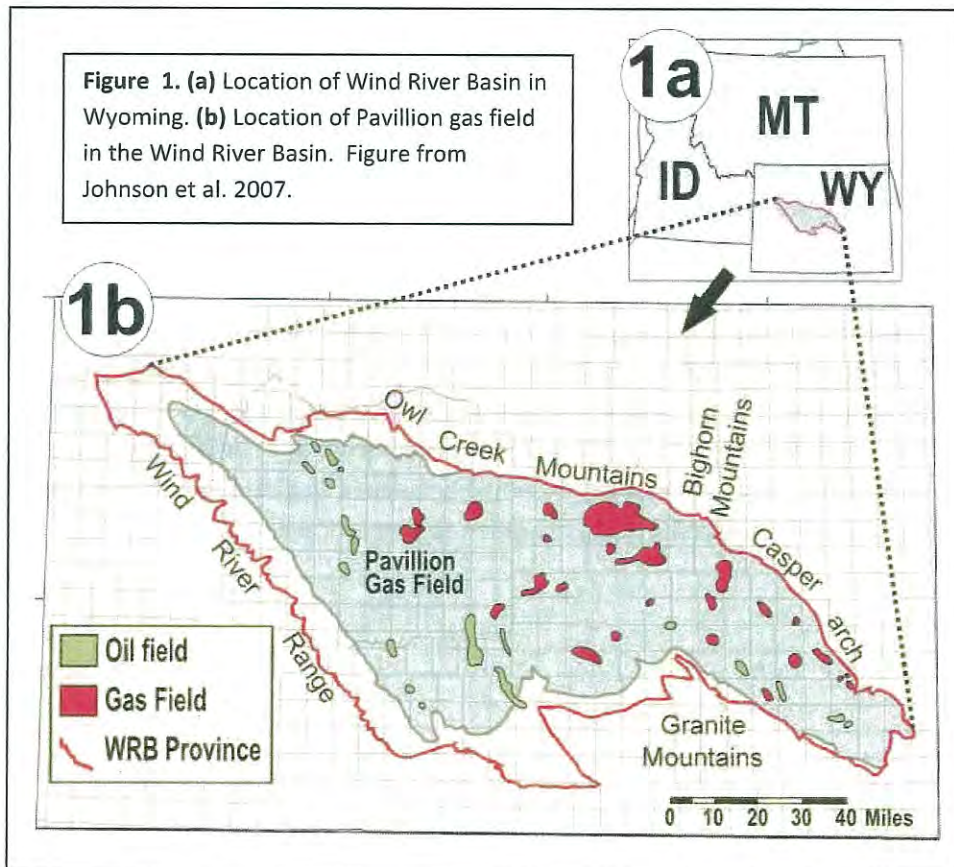
A similar lines of reasoning approach was utilized to evaluate the presence of gas in monitoring and domestic wells. A comparison of gas composition and stable carbon isotope values indicate that gas in production and monitoring wells is of similar thermogenic origin and has undergone little or no degradation. A similar evaluation in domestic wells suggests the presence of gas of thermogenic origin undergoing biodegradation. This observation is consistent with a pattern of dispersion and degradation with upward migration observed for organic compounds.

Elevated levels of dissolved methane in domestic wells generally increase in those wells in proximity to gas production wells. Near surface concentrations of methane appear highest in the area encompassing MW01. Ground water is saturated with methane at MW01 which is screened at a depth (239 meters below ground surface) typical of deeper domestic wells in the area. A blowout occurred during drilling of a domestic well at a depth of only 159 meters below ground surface close to MW01. A mud-gas log conducted in 1980 (prior to intensive gas production well installation) located only 300 m from the location of the blowout does not indicate a gas show (distinctive peaks on a gas chromatograph) within 300 meters of the surface. Again, with the exception of two production wells, surface casing of gas production wells do not extend below the maximum depth of domestic wells in the area of investigation. A number of production wells in the vicinity of MW01 have sporadic bonding or no cement over large vertical instances. Again, alternate explanations of data have been considered. Although some natural migration of gas would be expected above a gas field such as Pavillion, data suggest that enhanced migration of gas has occurred within ground water at depths used for domestic water supply and to domestic wells. Further investigation would be needed to determine the extent of gas migration and the fate and transport processes influencing migration to domestic wells.

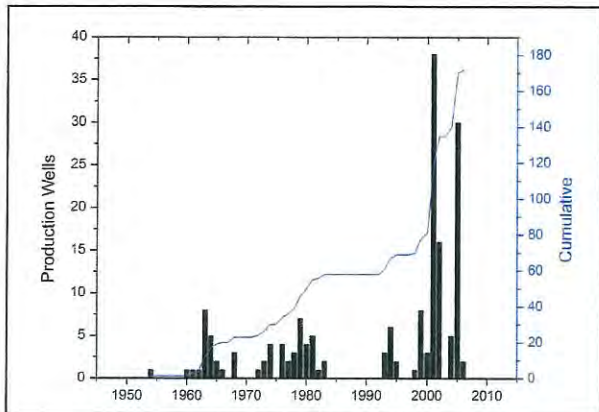
# 1.0 Site Background

In early 2008, the U.S. Environmental Protection Agency (EPA) received complaints from several domestic well owners near the town of Pavillion, Wyoming regarding sustained objectionable taste and odor problems in well water following hydraulic fracturing at nearby gas production wells. In response to these complaints, EPA initiated a comprehensive ground water investigation in September 2008 under authority of the Comprehensive Environmental Response, Compensation, and Liability Act. The area of investigation is a sparsely populated rural area in west-central Wyoming directly east of the town of Pavillion. Land use by residents consists primarily of ranching (horse and cattle) and alfalfa hay production for use by ranchers and commercial sale. Fields are periodically flooded using water obtained from canals and laterals.

Domestic wells in the area of investigation overlie the Pavillion gas field which is one of several gas fields within the Wind River Basin - a large, complex, structural, asymmetric, deep sedimentary basin covering much of central Wyoming (**Figure 1**). Oil and gas exploration wells were drilled in the 1950s. Commercial natural gas extraction in the field commenced in 1960 (Single 1969) with gas production well installation activity intensifying in the late 1990s through 2006 (**Figure 2**). The field currently consists of approximately 169 vertical production wells. Ninety-seven production wells are designated as "Tribal Pavillion" and are regulated by the U.S. Bureau of Land Management (BLM). The remaining wells are designated as "Pavillion Fee" and are regulated by Wyoming Oil and Gas Conservation Commission (WOGCC).

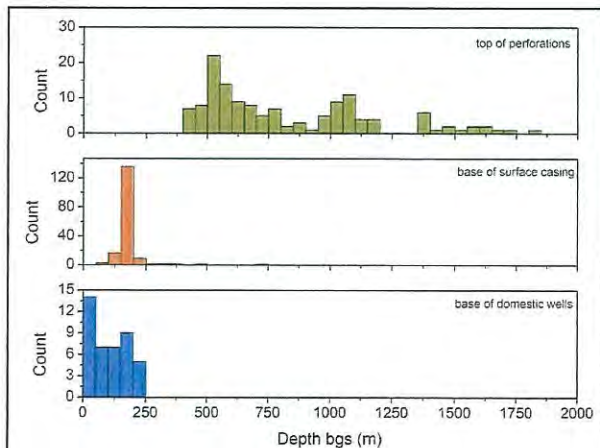


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**Figure 2.** Chronology of production well completion at the Pavillion gas field.

A review of production well records obtained on line from WOGCC indicates that hydraulic fracturing in gas production wells occurred as shallow as 372 m (1220 ft) below ground surface (bgs) with associated surface casing in production wells as shallow as 110 m (361 ft) bgs. Information obtained from the Wyoming State Engineer's Office and homeowners indicates that domestic wells (including stock wells) in the area of investigation are screened as deep as 244 m (800 ft) bgs. With the exception of two production wells, surface casings of gas production wells do not extend below the maximum depth of domestic wells in the area of investigation (**Figure 3**).



**Figure 3.** Histograms summarizing depths of top of perforation interval of production wells, base of surface casing of production wells, and base of screened interval of domestic wells.

Gas extraction occurs from both the lower Eocene Wind River Formation and underlying Paleocene Fort Union Formation (**Figure 4**). The Wind River Formation consists of interbedded layers of sandstones and shale with coarse-grained meandering stream channel deposits (Osiensky et al. 1984) and extends from the surface to approximately 1036 m (3400 ft) bgs. The Fort Union Formation ranges in thickness from 762 to 914 m (2500 to 3000 ft) in the area (Flores and Keighin 1993). The Waltman Shale Member in the Fort Union Formation is absent below the Pavillion Gas Field. The most productive zone of gas extraction in the Wind River Formation occurs at its base and is often targeted for gas extraction (Single 1969). Gas trapping in the lower Wind River and Fort Union Formations occurs in localized stratigraphic sandstone pinchouts on the crest and along flanks of a broad dome (Mueller 1989, Keefer and Johnson 1993).

There is substantial vertical and lateral stratigraphic variation over short distances in both formations (Single 1969, Flores and Keighin 1993). Individual productive sandstones in the two formations generally vary in thickness from 1 to 21 m with permeability varying from 0.1 to 300 millidarcies and porosity ranging from 4 to 28 percent (Single 1969). Gas from the Fort Union and lower Wind River Formations varies little in  $\delta^{13}\text{C}$  for methane, ethane, and propane with depth from the lower Eocene Wind River Formation to deeper mature and post-mature Upper Cretaceous source rocks (**Figure 4**) suggesting upward gas migration (Johnson and Rice 1993, Johnson and Keighin 1998) from deep source rocks.  $\delta^{13}\text{C}$  is defined as

$$\delta^{13}\text{C}(\text{‰}) = \left[ \frac{(^{13}\text{C}/^{12}\text{C})_{\text{sample}}}{(^{13}\text{C}/^{12}\text{C})_{\text{standard}}} - 1 \right] \times 1000$$

where the standard is the Pee Dee Belemnite (PDB) reference standard. Stable isotope ratios 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

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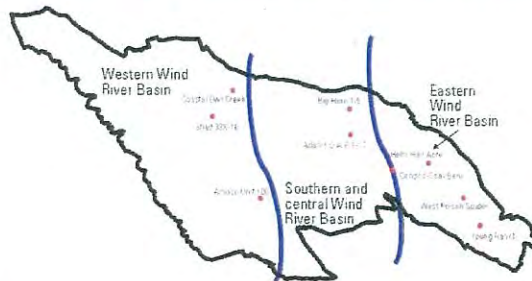
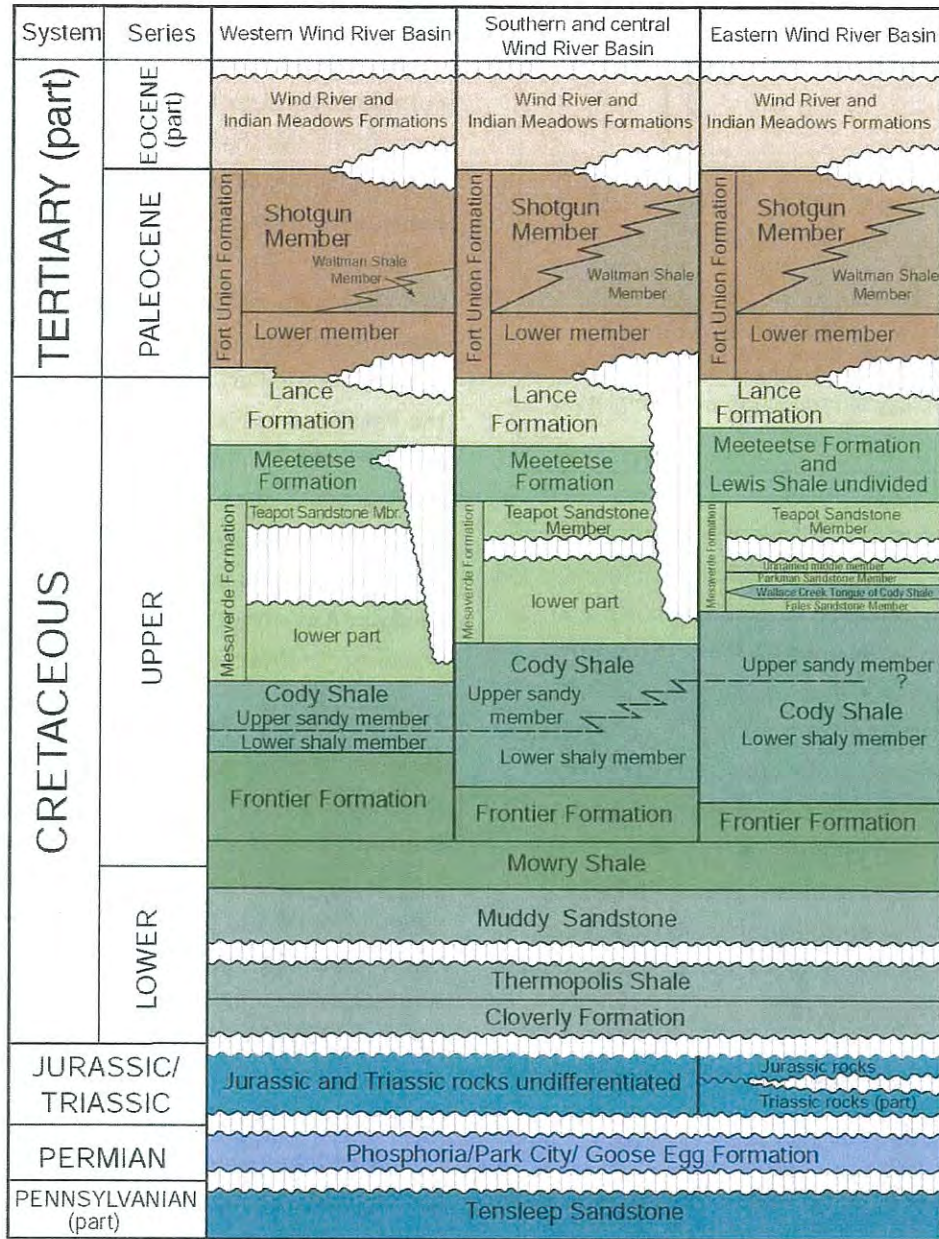


Figure 4. Generalized stratigraphic columns and correlations of Mississippian through Eocene strata in the Wind River Basin, Wyoming. The Pavillion Gas Field is located in the Western Wind River Basin. Figure from Johnson et al. 2007.

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reference standard. Ratios are expressed in parts per thousand or permil (‰). A substantial amount of additional compositional and isotopic data is available on the Wind River and Fort Union Formations but is classified as Confidential Business Information by the gas field operator.

Ground water from the upper Wind River Formation is the principal source of domestic, municipal, and stock (ranching, agriculture) water in the Pavillion area (WY State Water Plan 2003). The Wind River Formation meets the definition of an Underground Source of Drinking Water (USDW) under the United States Code of Federal Regulations, Title 40, Section 144.3. Water yields from wells in the upper Wind River Formation range up to 11,300 L/min with total dissolved-solids (TDS) concentrations ranging from 100 to 5,110 mg/L (WY State Water Plan 2003, Daddow 1996). The town of Pavillion has five municipal wells screened at depths ranging from 122 to 158 m bgs with average daily use estimated at 60,000 L/day (WY State Water Plan 2003). Fluids used for hydraulic fracturing were injected directly into the Wind River Formation.

## 2.0 Methods

### Sampling Chronology

Four sampling events (Phase I - IV) were conducted commencing in March 2009 and ending in April 2011. In March 2009 (Phase I), EPA collected aqueous samples from 35 domestic wells (including two samples from post reverse osmosis systems) 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.

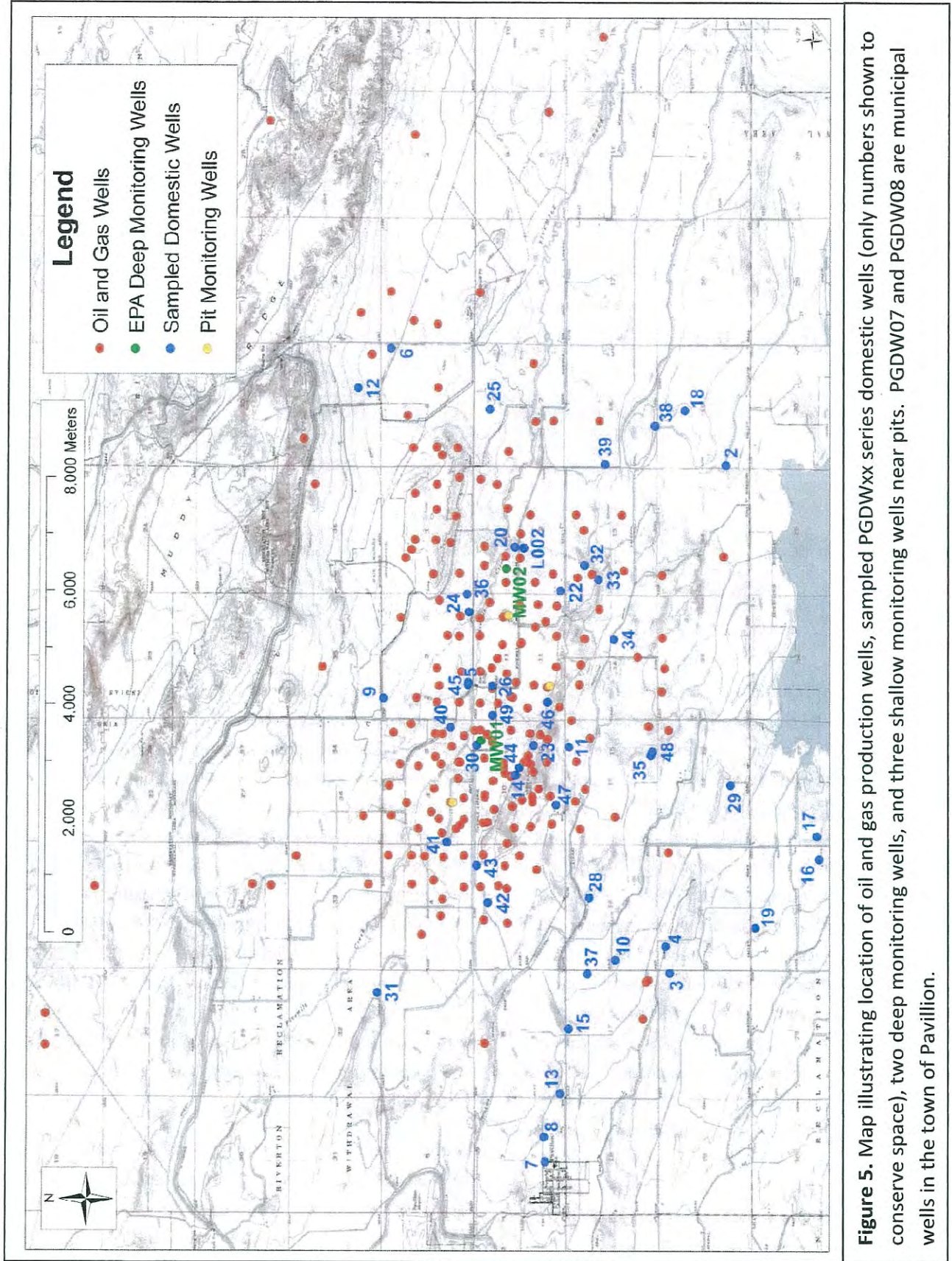
Detection of elevated levels of methane and diesel range organics (DRO) in deep domestic wells prompted EPA to install 2 deep monitoring wells in June 2010 to differentiate potential deep (e.g., gas production related) versus shallow (e.g., pits) sources of ground water contamination. Monitoring wells MW01 and MW02 were screened at 233 - 239 m (765 - 785 ft) and 293 - 299 m (960 - 980 ft) bgs, respectively. The expense of drilling deep wells while utilizing blowout prevention was the primary limiting factor in the number of monitoring wells installed. 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. 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. Sampling chronology and analytical methods for all sampling events are summarized in **Table A1**. The location of production wells, monitoring wells, and sampled domestic wells is illustrated in **Figure 5**.

### Deep Monitoring Well Installation

EPA installed two deep monitoring wells (designated as MW01 and MW02) using air (0 - 6 m bgs) and mud rotary (6 m bgs to target depth). Mud rotary was selected for installation of deep monitoring wells because it allowed the use of blowout prevention (BOP). Use of mud rotary with BOP was necessary given that a blowout occurred during installation of a domestic well at only 159 m (522 ft) bgs in December 2005 in the vicinity of MW01. Both deep monitoring wells were located away from gas production wells, known locations of pits, and areas of domestic waste disposal (abandoned machinery). There were no incidents of fuel spillage used to power pumps and generators.

Mud rotary required the use of drilling mud to remove cuttings and additives to avoid heaving of shale during drilling and well placement. Jet Lube Well Guard hydrocarbon free lubricant was used for outside threads for drillstem and submersible pipe connections. Mud composition consisted of formation water, municipal drinking water from Riverton, WY (transported on site by water truck), Quik-Gel high yield bentonite and additives listed on **Table 1**. Municipal water was mixed with bentonite to create drilling mud. The pH of mud during drilling varied between pH 8 - 9. Aqua-Clear (Halliburton) was used during well development to facilitate removal of mud. Drilling additives were extracted in water (1:20 to 1:100 dilution) and analyzed for pH, inorganics, organics, glycols, and alcohols. Despite the highly concentrated nature of these solutions (not



**Figure 5.** Map illustrating location of oil and gas production wells, sampled PGDWxx series domestic wells (only numbers shown to conserve space), two deep monitoring wells, and three shallow monitoring wells near pits. PGDW07 and PGDW08 are municipal wells in the town of Pavillion.

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<b>Table 1. Drilling additives, properties and product use recommendations</b>							
<b>Ingredient</b>	<b>Manufacturer</b>	<b>Purpose</b>	<b>Composition from MSDS</b>	<b>Specific gravity</b>	<b>Recommended mixture with water (wt/wt)</b>	<b>pH</b>	<b>Properties</b>
<b>Aqua-Clear PFD</b>	Halliburton	Dispersant/mud removal	anionic polyacrylamide (30-60%)	1.2-1.4	1:2500	neat 6.5 to 7.5	liquid
<b>Penetrol</b>	Halliburton	Non-ionic wetting agent	diethanolamine (1-5%) and coco diethanolamide (10-30%)	0.98	1:400 to 1:100	1% solution 9.5	liquid
<b>EZ-Mud Gold</b>	Halliburton	Clay/shale stabilizer	"no hazardous substances"	0.8-1	1:1400 to 1:350	1% solution 7.75	solid
<b>Dense Soda Ash</b>	OCI Chemical Corp	Improve bentonite	Sodium carbonate (100%)	2.5	1:100 to 1:50	5% solution 11.5	solid
<b>Quik-Gel</b>	Halliburton	Viscosifier/bentonite	bentonite (60%), crystalline silica quartz (1-5%), crystalline silica cristobalite (0-1%), crystalline silica tridymite (0-1%).	2.6	1:60 to 1:30	3% solution 8.9	solid
<b>Quik-Trol Gold</b>	Halliburton	Ease of mixing and improved filtration	cellulose derivative (polysaccharide) (60-100%)	0.6 - 0.9	1:3500 to 1:200	1% solution 6 -8 (listed)	solid

representative of significantly lower levels in drilling mud, see recommended product use mixture listed in **Table 1**), the pH of samples varied between 6.6 to 11.2, potassium varied between 0.1 to 1.2 mg/L, chloride varied between not detected to 214 mg/L, ethanol and isopropanol detections were less than 90 µg/L, and acetone, *tert*-butyl alcohol (TBA), benzene, toluene, ethylbenzene, xylenes (BTEX), trimethylbenzenes, and glycols were not detected (**Table 2**). Organics were not analyzed in the dense soda ash and Quik-Gel because dissolved organic carbon concentrations were low and because of difficulties in analyzing the viscous gel (Quik-Gel). Since inorganic and organic concentration patterns measured in the drilling additives do not match patterns observed in the deep monitoring wells and because large volumes of ground water were extracted from the wells during development and prior to sampling, it is unlikely that ground water chemistry was impacted by drilling additives.

Composite samples of cuttings were collected and sent to TestAmerica Laboratories in Denver, Colorado for Toxic Characteristic Leaching Procedure (TCLP). Samples were analyzed for TCLP volatile organic compounds using gas chromatography-mass spectrometry (GC-MS) in accordance with EPA SW-846 Methods 1311/8260B, and for TCLP semivolatile organic compounds (GC-MS) in accordance with EPA SW-846 Methods 1311/8270C, for TCLP metals in accordance with EPA SW-846 Methods 1311/6010B, for TCLP mercury in accordance with EPA SW-846 Methods 1311/7470A. Acetone, toluene, and m & p-xylene were detected in one sample at 6.9, 0.63, and 1.0 µg/L, respectively. Cuttings were disposed offsite in a landfill.

A photographic log of drilling, mud circulation, examination of cuttings, screen placement, and well development is provided in **Appendix C**. Well construction schematics are provided for MW01 and



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Table 2. Analytical results of additives (compounds listed are those detected in ground water)						
	Aqua-Clear PFD	Penetrol	EZ-Mud Gold	Dense Soda Ash	Quik-Gel	Blank
Extraction ratio (wt/wt)	1:20	1:20	1:100	1:100	1:100	----
pH measured	7.96	8.51	6.64	11.2	8.35	----
Specific Conductance (mS/cm)	13.3	0.47	0.24	15.5	0.20	----
Dissolved Organic Carbon (ppm)	1640 (1650) †	1500	388	0.58	2.11	0.28
Cl (ppm)	214 (230) †	85	2.22	7.03	nd	nd
SO4 (ppm)	121 (117) †	597	nd	nd	3.53	nd
K (ppm)	0.40 (0.40) †	0.63	1.16	0.12	0.09	0.07*
Acetone (µg/L)	nd	nd	nd	----	----	nd
Tert-butyl alcohol (µg/L)	nd	nd	nd	----	----	nd
Isopropanol (µg/L)	85 (87)†*	43*	27*	----	----	nd
Ethanol (µg/L)	59 (62) †*	58*	nd	----	----	nd
Benzene (µg/L)	nd	nd	nd	----	----	nd
Toluene (µg/L)	nd	nd	nd	----	----	nd
Ethylbenzene (µg/L)	nd	nd	nd	----	----	nd
Xylene (µg/L)	nd	nd	nd	----	----	nd
Trimethylbenzenes (µg/L)	nd	nd	nd	----	----	nd
Naphthalene	nd	2.00	nd	----	----	nd
Ethylene glycol (µg/L)	nd	nd	nd	----	----	nd
Diethylene glycol (µg/L)	nd	nd	nd	----	----	nd

nd – not detected. ---- not measured. Drilling additives were extracted at the specified weight ratio into deionized water.  
 † - Duplicate analysis. Blank sample is analysis of water used for the extraction of drilling additives. \* Concentration above minimum detection limit, but below the level of quantification.

MW02 in **Figures 6a** and **6b**, respectively. During installation of MW02, cuttings were allowed to settle at the cessation of drilling and form a 5 m (17 ft) base for placement of the screen. Cuttings were never added to the borehole. Since a significant vertical distance existed between the depth of drilling and screen placement at MW01, cement grout was utilized to form the base for screen placement. No lubricants were used to attach sections of casing or casing to screens. Well screens, sections of casing and tremie pipe were mounted above ground (never touched soil)

and power washed (no detergents used) prior to deployment. Locations of both MW01 and MW02 were in fields used for alfalfa hay production away from production wells, pads, and pits.

Cuttings were continuously examined during drilling by manually washing drilling mud from rock fragments with observations recorded as a function of depth in borehole logs. At the cessation of drilling, open-hole geophysical logging (caliper, density, resistivity, spontaneous potential, natural gamma) was conducted by Colog Inc., prior to placement of well

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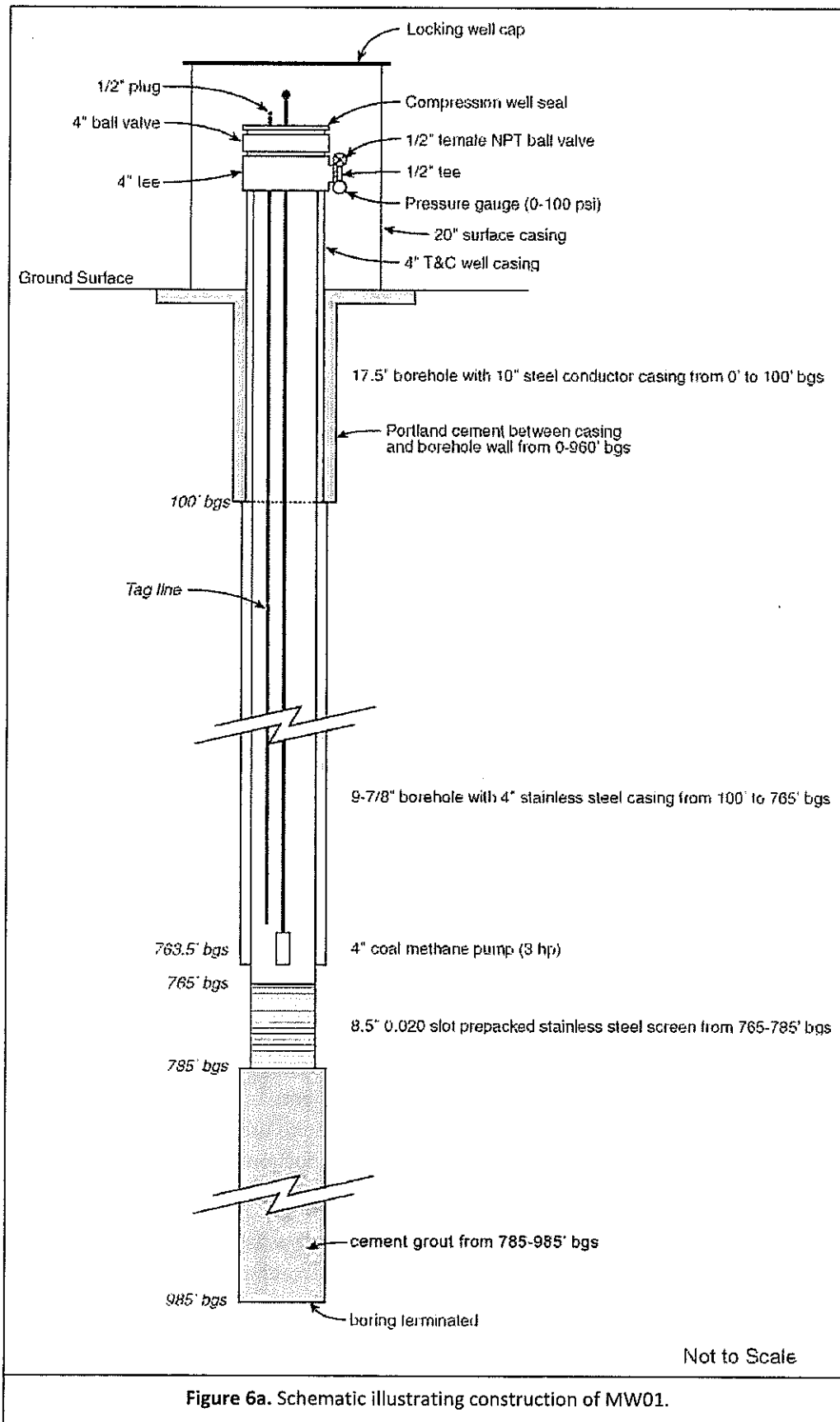


Figure 6a. Schematic illustrating construction of MW01.

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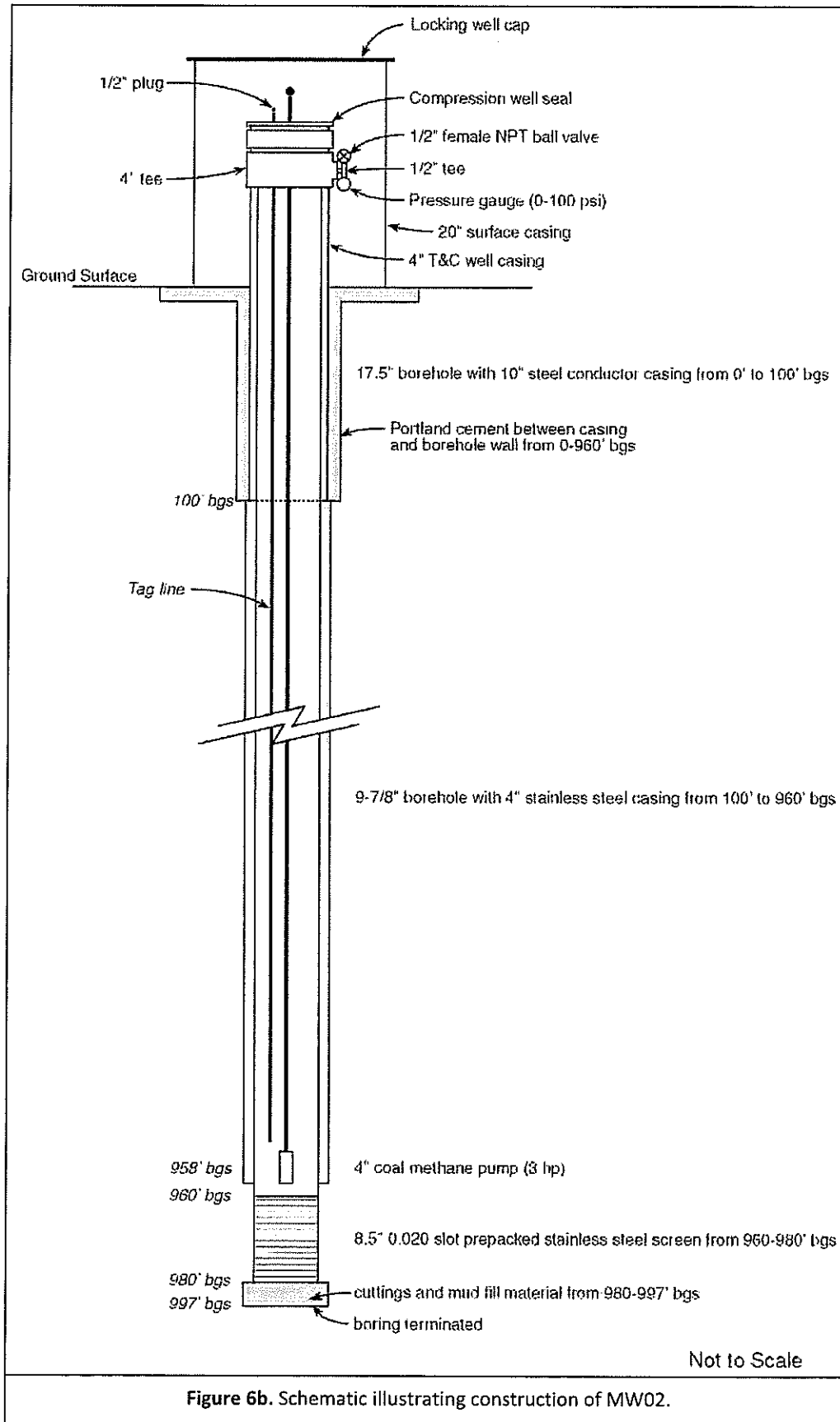


Figure 6b. Schematic illustrating construction of MW02.

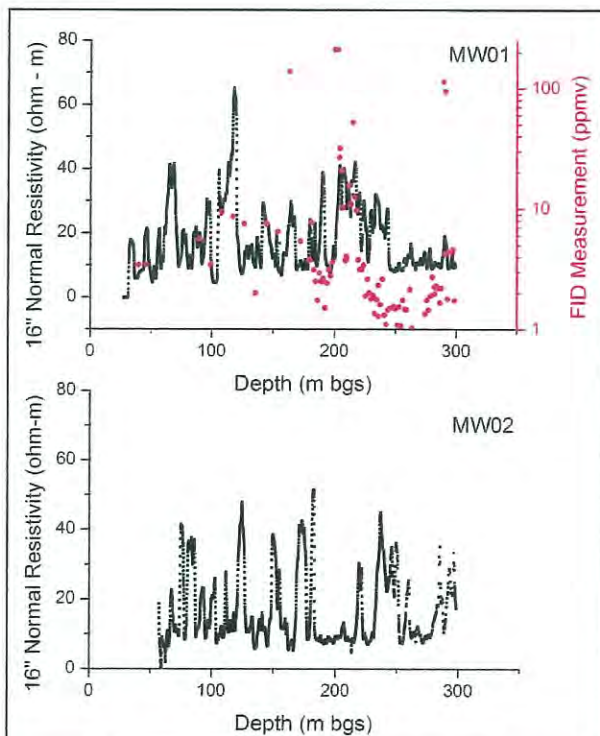
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### Ground Water Sampling of Deep Monitoring Wells in Phase III and IV

construction materials. Examination of resistivity and cuttings indicated elevated resistivity at depths where white coarse-grained sandstone was observed. This relationship was utilized to place screens at both deep monitoring wells at the deepest observed interval of white coarse-grained sand (Figure 7). White coarse-grained sandstones in the area of investigation contain little or no shale and are targeted by local well drillers for domestic well installation. During drilling, mud and cuttings were monitored in an open atmosphere with a TVA-1000B Thermo-Scientific portable flame- and photo-ionization detector (FID/PID) for health and safety monitoring. Comparison of FID and PID readings (PID readings remained at background and are not sensitive to methane) indicates the presence of methane at various intervals from ground surface in MW01 (Figure 7).

Ground water in deep monitoring wells was sampled using dedicated explosion proof submersible pumps (10-cm Franklin Electric 3HP). Wells were purged at a flow rate of approximately 5 to 30 L/min. The rate of pumping was measured using a Model TM0050 in-line turbine flow meter with associated Model FM0208 flow monitor manufactured by Turbines, Inc. Drawdown during pumping was measured with a sonic water level sensor obtained from Eno Scientific, Inc. (Model WS2010 PRO). The flow was split, with one portion going to waste and the other portion going to a flow-cell equipped with a YSI 5600 multiparameter probe to track stabilization of pH (<0.02 standard units per minute), oxidation-reduction potential (<2 mV per minute), specific conductance (<1% per minute), dissolved oxygen (DO), and temperature. Purge volumes prior to sampling ranged from about 200 to 450 L (Phase III) and 1100 to 1250 L (Phase IV). Lower purge volumes in Phase III sampling were due to initial gas invasion into the screened intervals that caused cavitation and concern about prolonged pump operation. By the time of Phase IV sampling, disruptive gas invasion was no longer observed and extended purging was possible. Turbidity ranged from 1.7 to 29.7 Nephelometric Turbidity Units (NTUs) in domestic wells (Phase III and IV). Turbidity in MW01 was 7.5 NTUs in Phase III and 7.9 NTUs in Phase IV. Turbidity in MW02 was 28.8 NTUs in Phase III and 24.0 NTUs in Phase IV. Turbidity measurements in MW01 and MW02 could be impacted by gas exsolution. A photographic log of deep monitoring and domestic well sampling is provided in Appendix D.

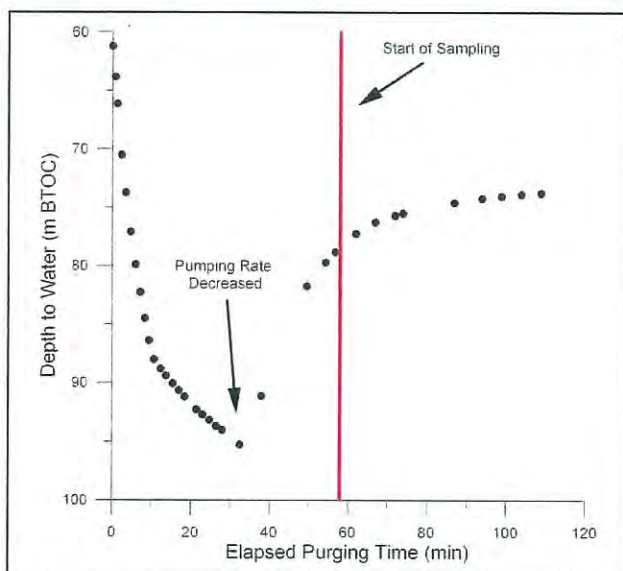
In April 2011, the static water level in MW01 prior to purging was 61.2 m (200.8 ft) below the top of the casing (BTOC) measured using the Well Sounder 2010. The initial pumping rate was approximately 27.6 L/min. The pumping rate declined during purging to approximately 24.2 L/min as a result of the increasing depth to water. At approximately 30 min after the



**Figure 7.** Resistivity as a function of depth in MW01 and MW02. MW01 and MW02 were screened at 233 - 239 m and 293 - 299 m bgs, respectively, corresponding to elevated resistivity and presence of coarse-grained sandstone. FID readings in MW01 denote detections of methane during open air logging of mud. FID monitoring at MW02 was sporadic and is not illustrated here.

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start of purging, the pumping rate was reduced using an in-line valve to 7.6 L/min. This resulted in approximately 18.2 m (60 ft) of rebound in the water level within the well at the start of sampling (Figure 8). Given that the screen length is only 6.1 m (20 ft) and that the pump was set approximately 0.6 m (2 ft) above the screen, this indicates that ground water obtained during sampling was derived from the formation with no component of casing storage. The total volume of water purged at the start of sampling was approximately 1117 L. The static water level in MW02 prior to purging was 80.5 m (264.2 ft) BTOC measured using the Well Sounder 2010 (April 2011). The initial pumping rate was approximately 18.9 L/min. The Eno Scientific well sounder was unable to measure the depth to water during most of the purging cycle perhaps due to a more rapid rate of decline in the water level in the casing. Sampling was initiated after approximately 1249 L of water were removed. The pump cavitated after approximately 1287 L were purged. The pump was subsequently stopped, allowed to cool, and restarted approximately 10 min later to complete the sampling.



**Figure 8.** Variation of water level as a function of time in MW01 during Phase IV well purging. The initial pumping rate was 24.2 L/min. After approximately 30 minutes of purging, the flow rate was decreased to 7.6 L/min. This reduced flow rate caused partial recovery of the water level and confirmation that formation water was being accessed.

An example of flow-cell readings through the purging of well MW02 is shown in Figure 9. The electrode readings show fairly rapid equilibration of pH and dissolved oxygen. Oxidation-reduction potential steadily decreased with the rate of change falling into the desired range (<2 mV per minute) by the end of purging. Specific conductance readings were typically variable, likely due to continuous off-gassing and bubble formation within the conductivity sensor. After field measurements stabilized, ground water was collected into sample bottles as summarized in Table B1. Samples were collected for a wide range of inorganic, organic, and stable isotope analyses. A 500 mL sample was collected for field determinations of alkalinity, turbidity, ferrous iron, and dissolved sulfide. Alkalinity was determined onsite by incremental titration of ground water with sulfuric acid. Turbidity measurements were made with a portable meter (Hach 2100Q). Measurements were made for dissolved sulfide and ferrous iron using the methylene blue and 1,10-phenanthroline colorimetric methods, respectively (APHA 1998a,b). Samples collected for dissolved gases, volatile organic compounds, semi-volatile organic compounds, diesel-range organics, gasoline-range organics, glycols, low molecular weight acids, and  $\delta^{13}\text{C}/\delta\text{D}$  of methane were not filtered.  $\delta\text{D}$  is defined as

$$\delta\text{D}(\text{‰}) = \left[ \frac{(^2\text{H}/^1\text{H})_{\text{sample}}}{(^2\text{H}/^1\text{H})_{\text{standard}}} - 1 \right] \times 1000$$

where the standard is the Vienna Standard Mean Ocean Water Standard (VSMOW). Samples collected for metals, anions, nutrients, dissolved organic carbon, dissolved inorganic carbon (DIC),  $\delta^{13}\text{C}$  of dissolved inorganic carbon, and  $\delta^{18}\text{O}/\delta\text{D}$  of water were filtered onsite using 0.45-micron pore-size, disposable-capsule filters.  $\delta^{18}\text{O}$  is defined as

$$\delta^{18}\text{O}(\text{‰}) = \left[ \frac{(^{18}\text{O}/^{16}\text{O})_{\text{sample}}}{(^{18}\text{O}/^{16}\text{O})_{\text{standard}}} - 1 \right] \times 1000$$

where the standard is the VSMOW.

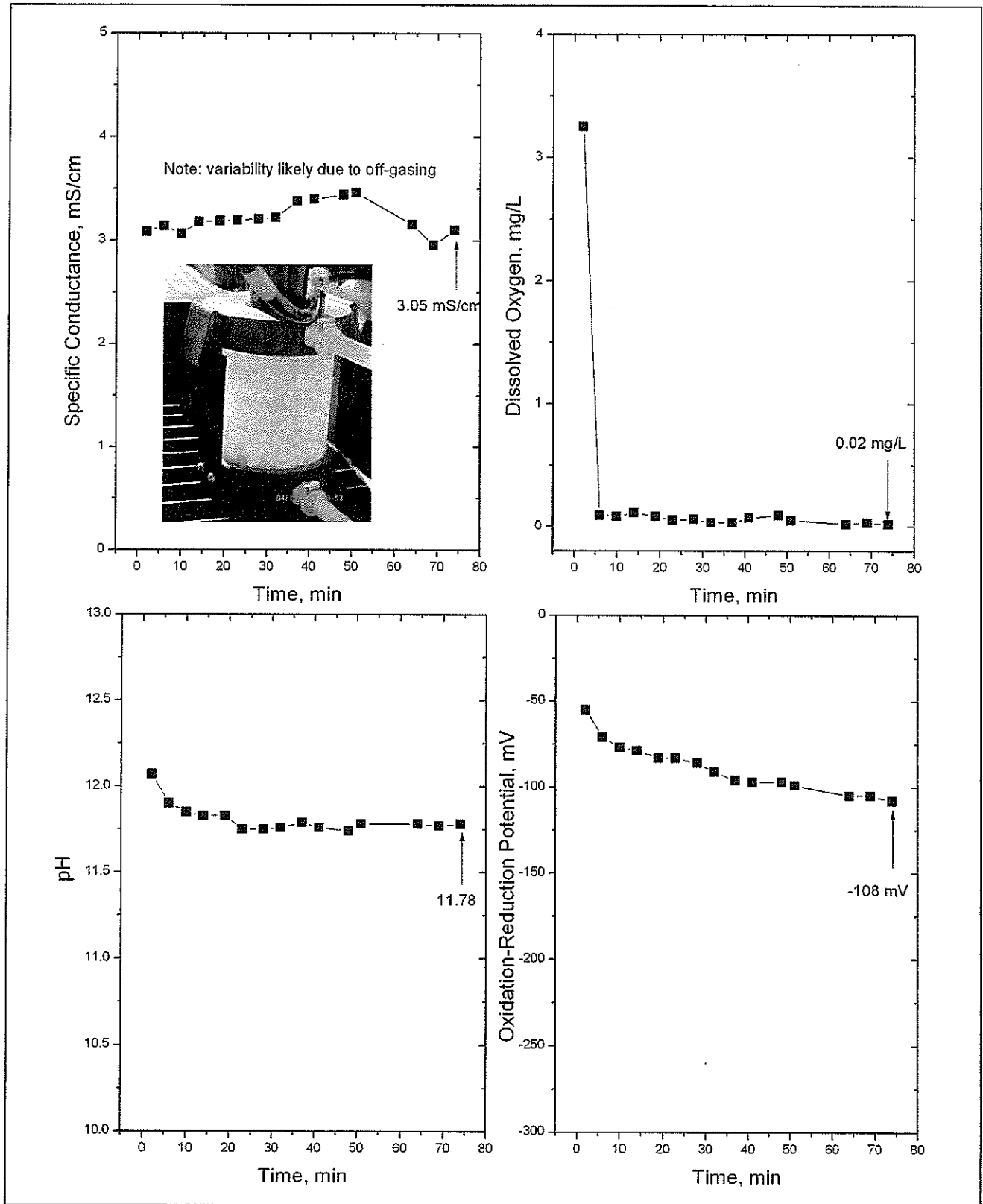


Figure 9. Flow-cell readings as a function of time for specific conductance, dissolved oxygen, pH, and oxidation-reduction potential (well MW02, Phase IV sampling).

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Sample preservation and holding time criteria are listed in **Table B1**. Field quality control (QC) samples are summarized in **Table B2**. These included several types of blanks, duplicate samples, and field matrix-spike samples. All of these QC sample types were collected, preserved, and analyzed using identical methodologies as used for the water samples collected in the field (**Table B1**). Quality assurance/quality control (QA/QC) requirements for analysis of metals and major ions are summarized in **Table B3**. QA/QC requirements for analysis of dissolved gases, DIC/DOC, VOCs, low molecular weight acids and stable isotopes of water are summarized in **Table B4**. QA/QC requirements for analysis of semivolatile organic compounds (SVOCs), GRO, and DRO are summarized in **Table B5**. QA/QC requirements for analysis of glycols are summarized in **Table B6**. Results of Phase III and Phase IV blank samples are provided in **Tables B7 to B12**. Detections observed in the blank samples were generally very low-level and generally much lower than concentrations measured in the deep monitoring wells. Some blank samples showed detections of acetone (1 µg/L), m,p-xylene (up to 0.7 µg/L), toluene (up to 0.5 µg/L), benzoic acid (3 µg/L), and tetraethylene glycol (3 µg/L). Concentrations of these analytes in MW01 and MW02 in Phase III and Phase IV sampling ranged from: 80 to 641 µg/L (acetone), non-detect to 750 µg/L (total xylenes), 0.6 to 617 µg/L (toluene), 209 to 457 µg/L (benzoic acid), and 7 to 27 µg/L (tetraethylene glycol). Detected concentrations of toluene (Phase III), xylene (Phase IV), and tetraethylene glycol (Phase IV) in MW01 are within about 2 times the detected levels of these chemicals in some of the applicable blank samples. Consequently, reported detections and concentrations of these chemicals in MW01 were used cautiously in this study. In one of the six blank samples collected for DRO, an elevated concentration of 135 µg/L or 6 times the reporting limit was observed (**Table B12**); all other DRO blank samples were non-detects (<20 µg/L). Concentrations of DRO in the deep monitoring wells ranged from 634 to 4050 µg/L.

Duplicate samples were collected in three locations during Phase III and Phase IV sampling activities. Results for the duplicate analyses are presented **Tables B13 and B14**. Relative percent differences (RPDs) were generally less than 10% for most inorganic constituents indicating very good precision. RPD is defined as

$$RPD = \left[ \frac{x1 - x2}{(x1 + x2) / 2} \right] \times 1000$$

where x1 = sample and x2 = sample duplicate. RPDs for methane, volatile organic compounds, and semi-volatile organic compounds were generally less than 25% (**Table B14**). The lower reproducibility for these compounds detected in MW02 is likely due to difficulties in sampling and preserving water that is oversaturated in gas.

Major ions were quality checked by calculating ion balances. The AqQA (v.1.1.1) software package was used to evaluate cation/anion balance, which ranged from <0.1 to 17.2% with 90% of the calculated balances better than 5%.

Geochemical equilibria in ground water were evaluated with the Geochemist's Workbench package (version 8; Bethke 1996). Speciation and mineral equilibria calculations were made by entering the concentrations of major cations (Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>), anions (Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup>), pH, and temperature. For domestic well samples, bicarbonate concentrations were determined from alkalinity measurements. For the deep monitoring wells, because alkalinity included a significant contribution from hydroxide, concentrations of dissolved inorganic carbon were used for bicarbonate/carbonate input. Activity corrections were made using the Debye-Hückel equation. The LLNL (EQ3/6) thermodynamic database was selected for use in the calculations (Delany and Lundeen 1990). Model simulations were also conducted by tracing alkaline-addition titration paths. In order to do this, an additional entry was made to

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the thermodynamic database describing the solubility of KOH ( $\log K = 24.9$ ;  $\text{KOH}_{(s)} + \text{H}^+ = \text{K}^+_{(aq)} + \text{H}_2\text{O}_{(l)}$ ).

Audits of Data Quality (ADQs) were conducted by a contractor (independent of this investigation) or an EPA QA Manager for all analyses conducted outside EPA's Contract Laboratory Program (CLP) with the exception of data collected during Phase I, which is still in progress. This included data from EPA's Region VIII laboratory in Golden, Colorado, EPA's Region III laboratory in Fort Mead, MD, EPA's Office of Research and Development Laboratory in Ada, Oklahoma, and Isotech Laboratories in Champaign, Illinois. A technical systems audit of Isotech Laboratories included an on-site visit by the independent contractor and EPA QA Manager. Two on-site field technical system audits were also conducted by the independent contractor and the EPA QA Manager to ensure compliance with the Category I (highest of four levels in EPA) Quality Assurance Project Plan established for this site for ground water and gas sample collection.

### Gas Sampling from Casing of Deep Monitoring Wells in Phase III and IV

Gas samples were collected from casing of deep monitoring wells by connecting a 12.7 mm NPT stainless-steel Swagelok quick-connect body and a Swagelok single-end shutoff stem to a 12.7 mm brass ball valve. The stem was connected to 6.35 mm internal diameter Tygon Masterflex tubing and a 0.5 liter Cali-5 Bond gas sampling bag equipped with a Leur-Fit Valve™ and a Leur-taper Quick-Mate™ connector. A Masterflex E/S portable peristaltic pump was used to extract gas at 1 L/min. Samples were collected after stabilization ( $\pm 1\%$ ) of  $\text{O}_2$ ,  $\text{CO}_2$ , and  $\text{CH}_4$  readings on a GEM-2000 Plus CES-LANDTEC portable gas analyzer.

### Domestic Well Sampling for Methane Using a Closed System in Phase IV

During the Phase IV sample event, water from domestic wells was screened using a Thermo-Scientific

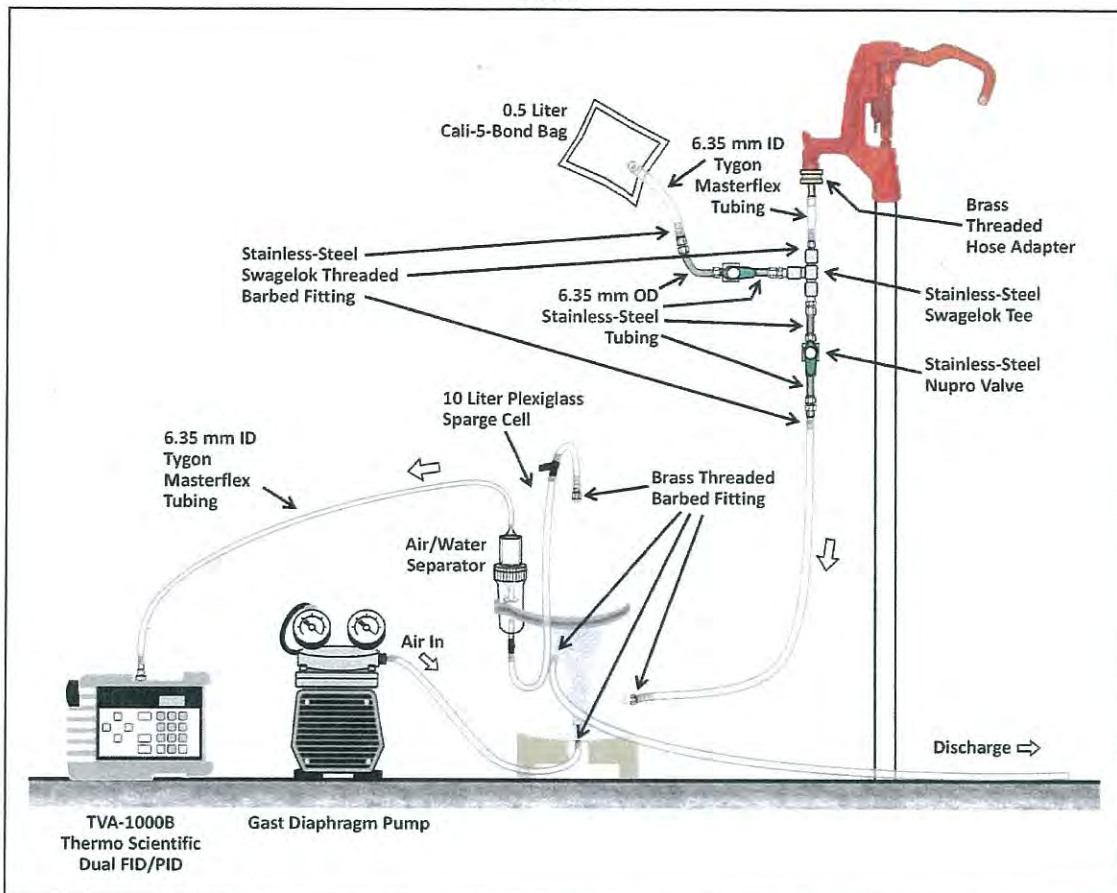
TVA-1000B portable FID/PID and a 10 L Plexiglas sparge cell (**Figure 10**). Samples from domestic wells were routed through a closed (no contact with the atmosphere to avoid offgassing) sample train and collected in 0.5 L Cali-5 Bond gas sample bags. Ultrapure  $\text{N}_2$  gas was introduced into the bags and placed on a rotary shaker for one hour prior to headspace analysis on site using a portable GC equipped with a thermal conductivity detector. Portable FID readings provided an immediate indication of methane in well water prior to GC analysis. Samples were also submitted to EPA's Office of Research and Development (ORD) laboratory in Ada, Oklahoma for analysis of dissolved gases.

### Review of Borehole Geophysical Logs

Borehole geophysical logs available on line from WOGCC were utilized to map lithology in the area of investigation. Depending upon the specific well, various combinations of natural gamma, resistivity, self-potential, density, and neutron porosity logs were utilized. Log resolution was sufficient to discern distinct layers of shale 1 m or greater in thickness but not sufficient to differentiate coarse-, medium-, and fine-grained sandstones nor sandstones containing various proportions of shale. Descriptions of cuttings logged during installation of deep monitoring wells and domestic wells obtained from a local driller were used for near surface description. Neither grain size nor proportions of shale in sandstone were differentiated in near surface sandstones to maintain consistency with descriptions from geophysical logs. Lithology in the area of investigation is highly variable and 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 (Osienky 1984). Sandstone and shale layers appeared thin and of limited lateral extent, again consistent with previous observations of lithology in the Wind River Formation (Single 1969, Flores and Keighin 1993).



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**Figure 10.** Schematic of closed (no contact to atmosphere) sampling train for domestic wells. Water flow from domestic well and into sparge cell was approximately 5 and 1 L/min respectively. Excess water bled through valve used for sampling prior to sample collection. Gas flow into sparge cell and portable FID/PID sparge cell was approximately 20 and 1 L/min. Excess air was bled through splitter above sparge cell.

## Review of Cement Bond/Variable Density Logs

Cement bond/variable density (CBL/VDL) logs, available for less than half of production wells, were obtained online from WOGCC to evaluate well integrity. Sporadic bonding is defined as an interval having an amplitude (mV) greater than  $A_{80}$  (EPA 1994) where

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

and  $A_{80}$ ,  $A_0$ , and  $A_{100}$  = amplitude at 80%, 0%, and 100% bond respectively.  $A_0$  typically corresponds to amplitude in free pipe whereas  $A_{100}$  corresponds to the best-bonded interval on the CBL. Examples of "no cement", "sporadic bonding", and "good bonding" are provided in **Appendix E**.

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 condition 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.

## 3.0 Results and Discussion

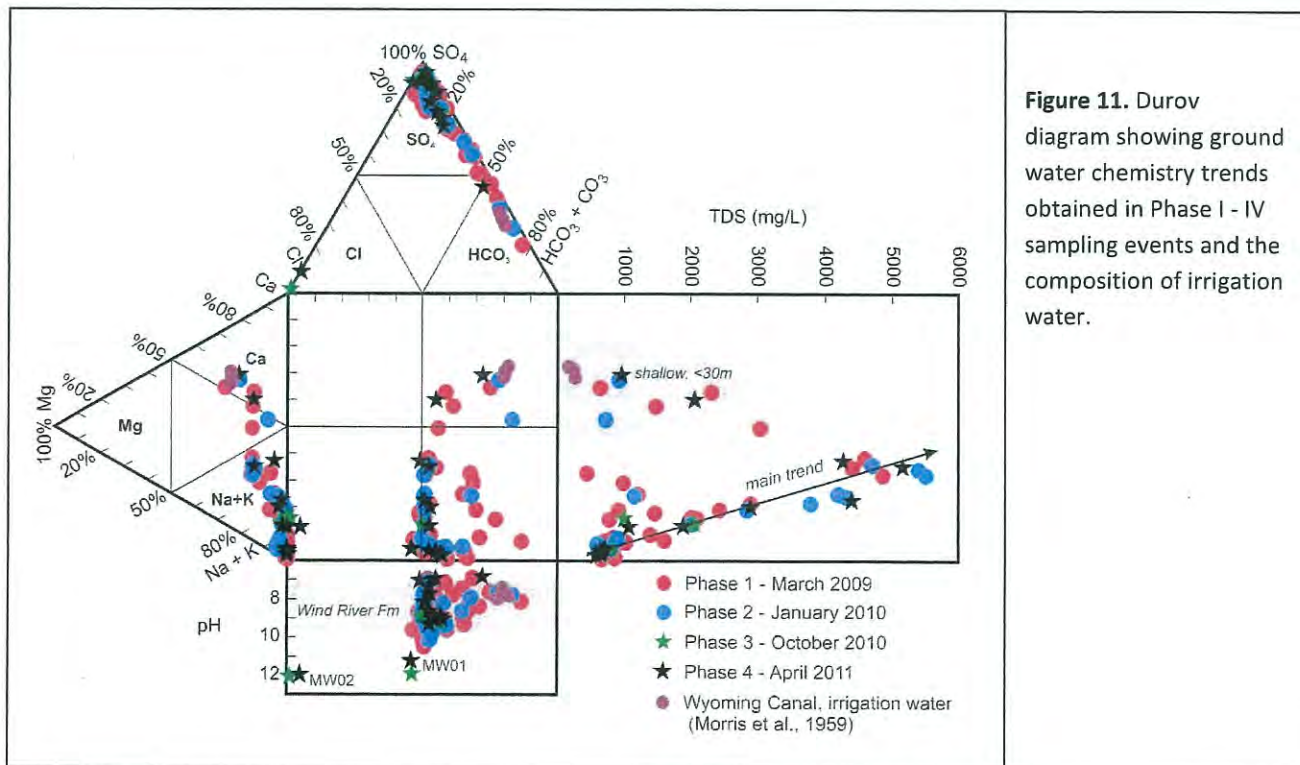
### Ground Water and Soil Sample Results Near Three Pits

There are at least 33 pits previously used for storage/disposal of drilling wastes, produced water, and flowback fluids in the area of investigation. Discussions are ongoing with stakeholders to determine the location, delineate the boundaries, and extent (areal and vertical) of contamination associated with these pits. The operator has initiated remediation of selected pit areas. Concentrations of DRO, gasoline range organics (GRO), and total purgeable hydrocarbons (TPH) detected in soil samples adjacent to three pits investigated in Phase II were as high as 5010, 1760, and 6600 mg/kg, respectively (EPA 2010). Concentrations of GRO, DRO, and TPH in ground water samples from shallow (4.6 m bgs) monitoring wells were as high as 2.4, 39, and 3.8 mg/L, respectively (EPA 2010). A wide variety of

organic compounds including benzene and m, p-xylene were detected at concentrations up to 390 and 150 µg/L, respectively (EPA 2010), indicating pits as a source of shallow ground water contamination in the area of investigation. EPA's maximum concentration level (MCL) for benzene is 5 µg/L.

### Inorganic Geochemistry

Inorganic geochemical results for ground water (all phases) are summarized in **Table A2a** and **Figure 11**. Major ion chemistry of ground water in the Pavillion area varies as a function of aquifer depth. Shallow ground waters (< 31 m bgs) collected from drinking water wells and stock wells are near-neutral (pH 7.7 ± 0.4, n = 19) (**Figure 12**) and display calcium-bicarbonate composition. With increasing depth, ground water becomes moderately alkaline (pH 9.0 ± 1.0, n = 55) (**Figure 12**), and with only one exception (MW02), is dominated by sodium and sulfate as the major cation/anion pair (**Figures 11** and **12**, **Table A2a**). This gradient in pH and water chemistry likely arises from the wide-scale surface application of irrigation water from the Wind River to support



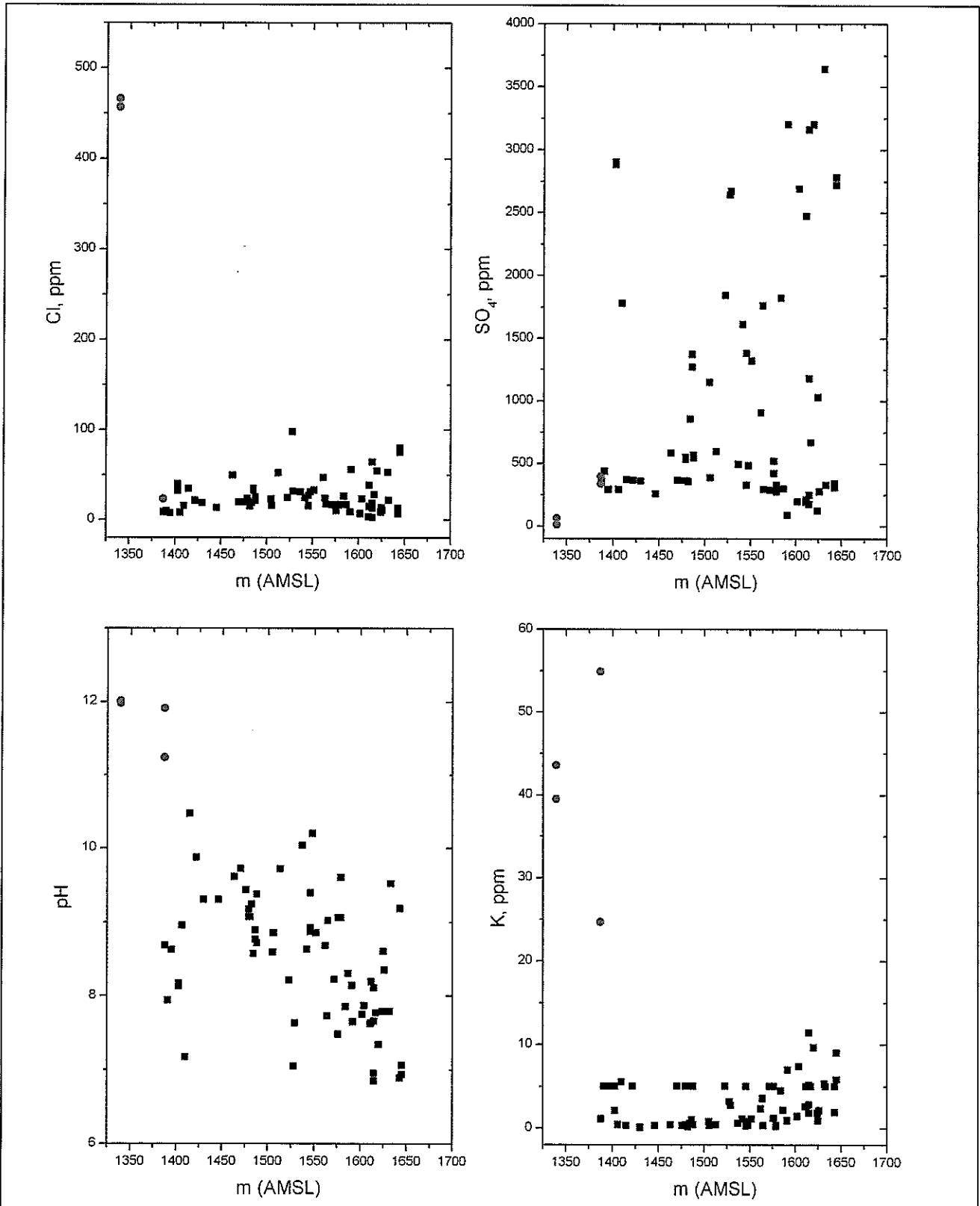


Figure 12. Depth trends of chloride, pH, sulfate, and potassium (filled black squares = domestic wells, filled red circles = monitoring wells).

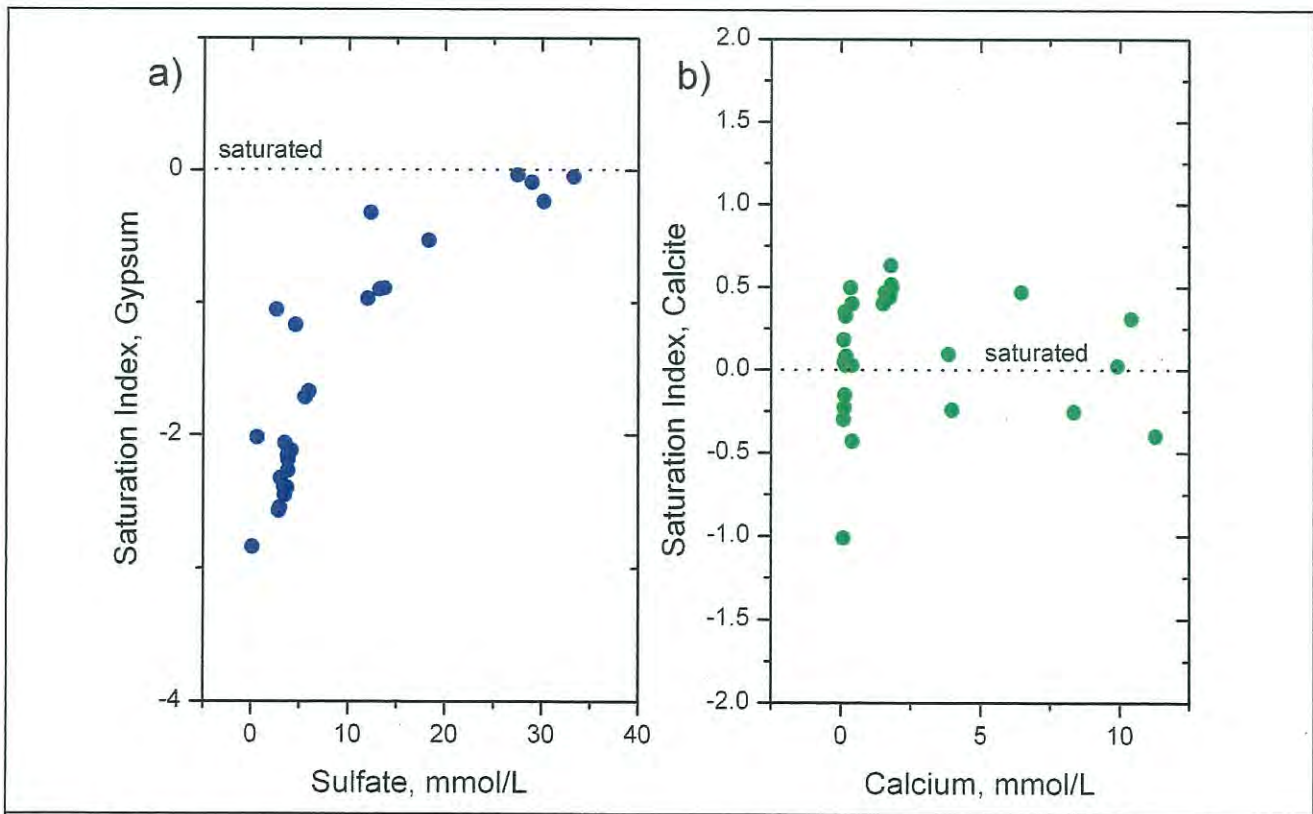
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crop growth since irrigation water appears to represent an endmember composition (**Figure 11**). The chemical alteration from bicarbonate-type recharge water to sulfate-type ground water involves multiple water-rock interactions, including salt dissolution, carbonate mineralization, and exchange of divalent cations for sodium (Morris et al. 1959). Total dissolved solids concentrations are <6000 mg/L in all ground water samples collected to depths up to 296 m (**Figure 11**).

Saturation indices of gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) and calcite ( $\text{CaCO}_3$ ), plotted against sulfate and calcium concentrations, are shown in **Figure 13**. The trend for gypsum saturation suggests that sulfate concentrations in the aquifer are limited by the solubility of gypsum. Ground water is also close to equilibrium with calcite which likely is an important control on pH and concentrations of calcium and

bicarbonate. Some residents have described the development of particulates in ground water samples collected and stored in glass jars. Precipitates that formed from PGDW05 ground water were analyzed by powder X-ray diffraction and found to be dominantly calcite. Because calcite has retrograde solubility, precipitation of calcite is possibly triggered by warming calcite-saturated ground water to ambient conditions.

The geochemistry of ground water from the deep monitoring wells is distinctive from that in the domestic wells. Chloride enrichment in monitoring well MW02 is 18 times the mean chloride concentration (25.6 mg/L) observed in ground water from domestic wells. Chloride enrichment in this well is significant because regional anion trends tend to show decreasing Cl concentrations with depth. The mean potassium concentration in domestic wells



**Figure 13.** Saturation indices for (a) gypsum versus sulfate concentration and (b) calcite versus calcium concentration. Saturation Index is equal to the logarithm of the ratio of the ion activity product to the mineral solubility product. A Saturation Index of 0 corresponds to chemical equilibrium; values less than 0 and greater than 0 correspond to undersaturated and oversaturated conditions, respectively.

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screened to 244 m bgs is 3 mg/L, with 99% of values <10 mg/L. Potassium enrichment in MW01 and MW02 is between 8.2 and 18.3 times the mean value of domestic wells (**Table A2a**). pH values in MW01 and MW02 are highly alkaline (11.2-12.0), above the pH range observed in domestic wells (6.9-10), and above the pH range previously reported for the Wind River Formation (Plafcan et al. 1995, Daddow 1996). In the deep monitoring wells, up to 94% of the total alkalinity is contributed by hydroxide. In addition, the monitoring wells show low calcium, sodium, and sulfate concentrations compared to the general trend observed in domestic well waters (**Figure 14**).

The high pH measured in the deep monitoring wells was unusual and unexpected. Although ground water pH in these wells was >11, total alkalinity was not particularly high (<500 mg/kg), and as already noted up to 94% of the total alkalinity was present as hydroxide (see charge balance calculations, **Table A2b**). Alkalinity contributed by carbonate/bicarbonate was less than the hydroxide component. In fact, inorganic carbon concentrations were so low in MW02 as to prevent the measurement of  $\delta^{13}\text{C}$  of dissolved inorganic carbon. Presence of hydroxide alkalinity suggests strong base addition as the causative factor for elevated pH in the deep monitoring wells. The possibility of cement/grout intrusion into the screened intervals was considered as a possibility for both monitoring wells, although precautions were taken to prevent downward migration of cement during well construction. Cement intrusion typically leads to pH values between 10 and 11, lower than the pH values measured in the deep monitoring wells (Gibb et al. 1987). Prolonged purging did not show decreasing pH trends (e.g., **Figure 9**) and water chemistry results indicate that ground water from the wells was highly undersaturated with respect to cement phases (e.g., portlandite), suggesting that cement was not the cause of elevated pH.

In order to gain additional insight, reaction path modeling was conducted to evaluate pH response to addition of strong base (potassium hydroxide, KOH).

Geochemical modeling was carried out by using ground water compositions for PGDW49, PGDW20, and PGDW32 (initial pH 7.3, 8.9, and 9.9, respectively). Modeled titration results are shown in **Figure 15a**; pH is plotted versus the mass of KOH added per kg of solution. Model titration results vary as a function of ground water composition. Samples PGDW20 and PGDW32 have Na-SO<sub>4</sub>-type compositions typical of deeper portions of the aquifer. In both of these cases, attainment of pH values between 11.2 and 12.0 requires small quantities of KOH addition (<250 mg KOH per kg of solution). Sample PGDW49 is elevated in Ca<sup>2+</sup> and Mg<sup>2+</sup>, lower in pH, and typical of shallower ground water compositions. In this case, significantly more KOH addition is required to attain pH values observed in the monitoring wells. The first derivative of the titration curve, or buffer intensity, is shown in **Figure 15b**. The buffer intensity indicates that ground water compositions like PGDW20 and PGDW32 inherently have little resistance to pH change up to about pH 12, at which point increased KOH additions are necessary to further increase pH. PGDW49 shows a broad peak on the buffer intensity diagram (pH 10 to 11) which reflects precipitation reactions to form calcium carbonate and magnesium hydroxide, reactions that consume hydroxide and therefore limit pH increases, until divalent cations are completely consumed. The model results clearly show that ground water typical of the Pavillion aquifer below 100 m depth (Na-SO<sub>4</sub>-type composition) is especially vulnerable to the addition of strong base, with small KOH additions driving significant upward pH changes.

Paired values of  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  in ground water samples plot below the Global Meteoric Water Line (**Figure 16**; -16.6 to -12.4‰  $\delta^{18}\text{O}$  and -129.2 to -97.4‰  $\delta^2\text{H}$ ). Shallow ground water samples generally tend to be depleted in <sup>18</sup>O and <sup>2</sup>H compared to deeper ground water samples and may be more reflective of local recharge. Ground water isotope data from the deep monitoring wells (red circles, **Figure 16**) follow along the same  $\delta^{18}\text{O}$  versus  $\delta^2\text{H}$  trajectory established by the domestic well data, suggesting similar recharge and evolutionary paths (e.g., Bartos et al. 2008).

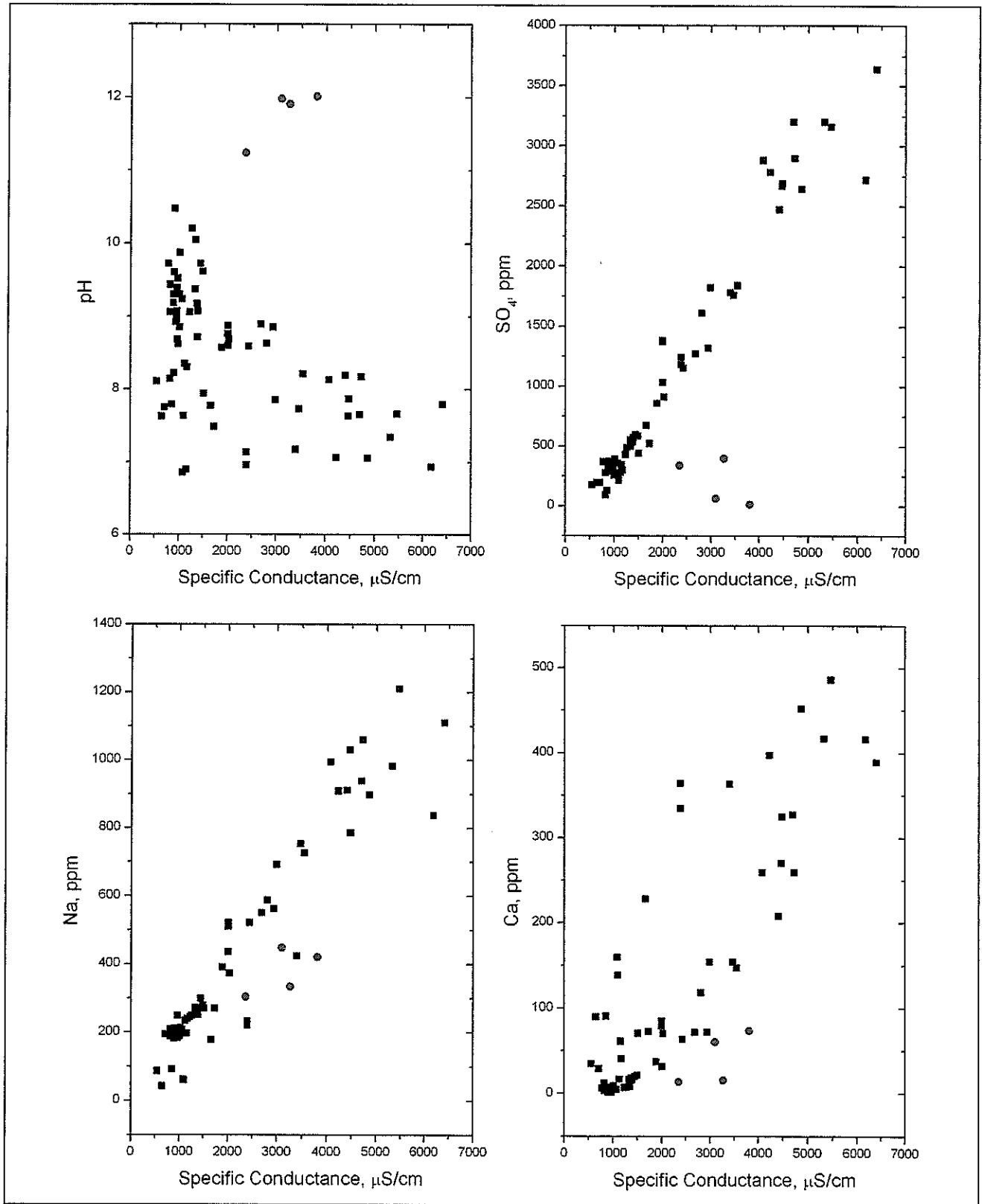
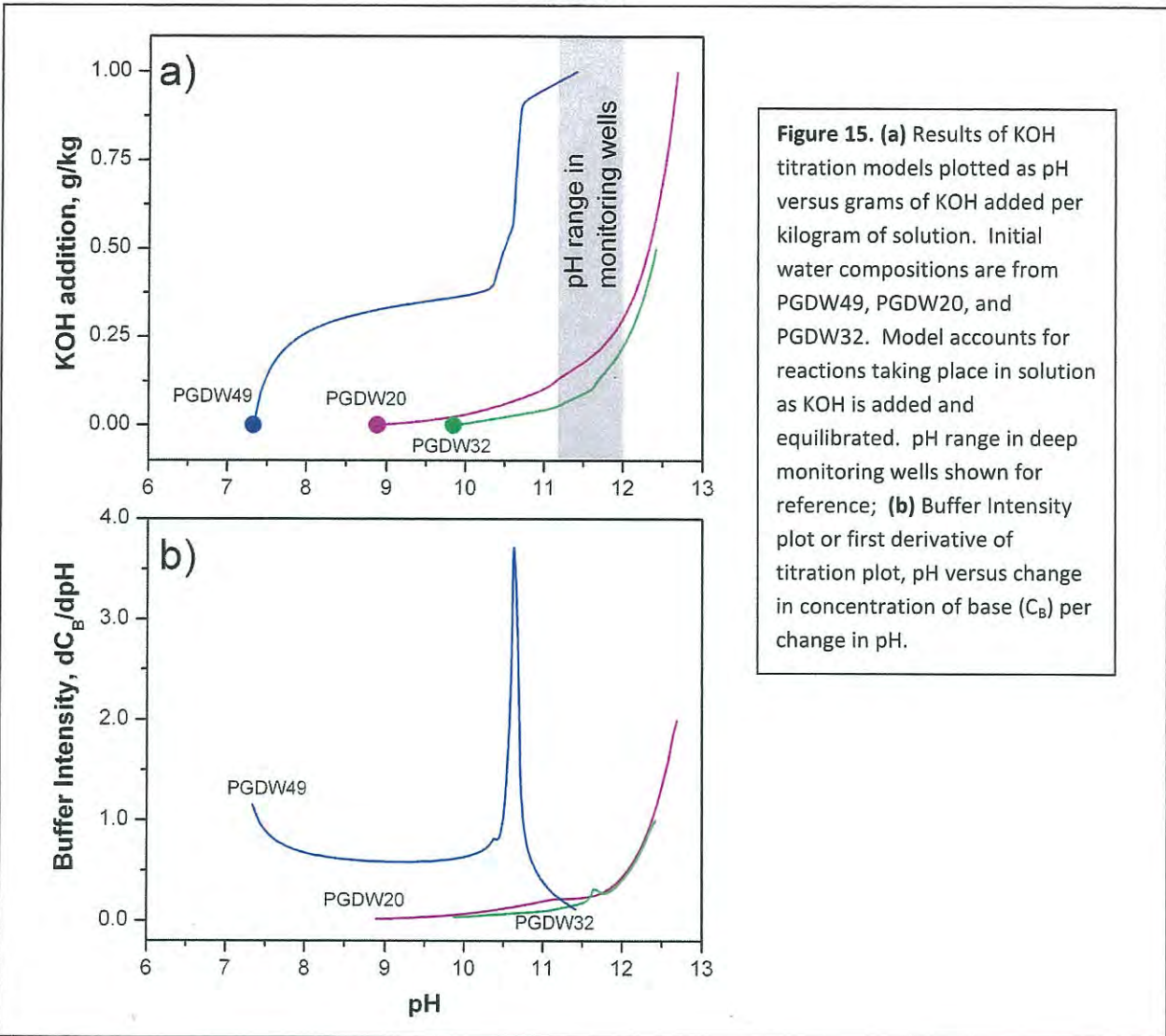
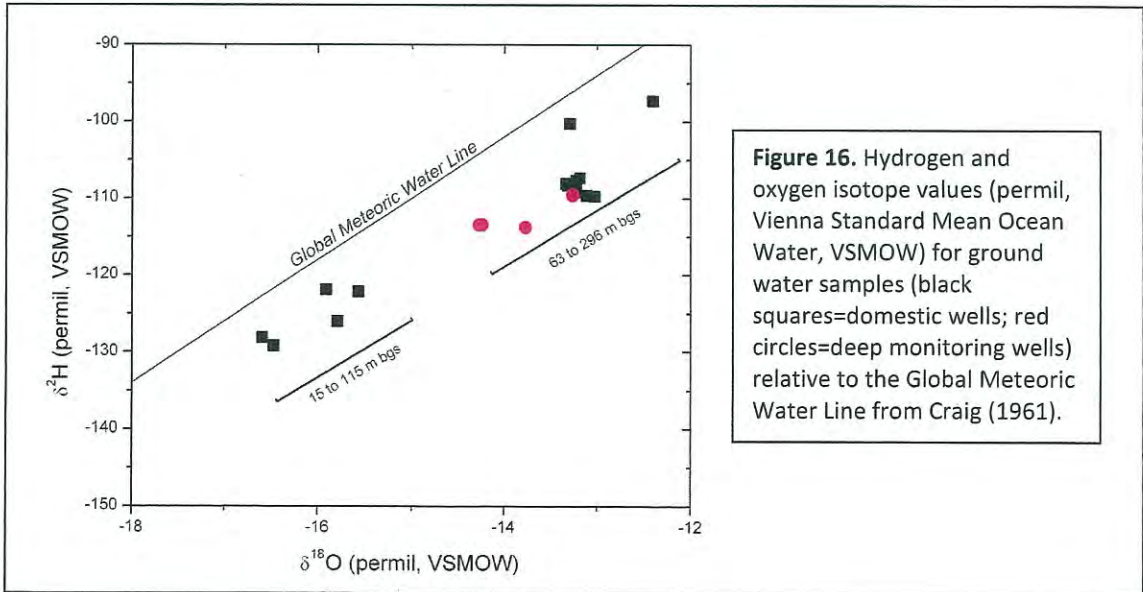


Figure 14. Concentration trends versus specific conductivity. Note the monitoring wells show high pH and low sulfate, calcium, and sodium relative to the general trend observed in the domestic wells (filled black squares = domestic wells, filled red circles = monitoring wells).



**Figure 15.** (a) Results of KOH titration models plotted as pH versus grams of KOH added per kilogram of solution. Initial water compositions are from PGDW49, PGDW20, and PGDW32. Model accounts for reactions taking place in solution as KOH is added and equilibrated. pH range in deep monitoring wells shown for reference; (b) Buffer Intensity plot or first derivative of titration plot, pH versus change in concentration of base ( $C_B$ ) per change in pH.



**Figure 16.** Hydrogen and oxygen isotope values (permil, Vienna Standard Mean Ocean Water, VSMOW) for ground water samples (black squares=domestic wells; red circles=deep monitoring wells) relative to the Global Meteoric Water Line from Craig (1961).

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### Organic Geochemistry

Organic and inorganic geochemical impacts in deep ground water monitoring wells (Phase III and IV) are summarized in **Table 3**. The monitoring wells produce ground water near-saturated in methane at ambient pressure, with concentrations up to 19.0 mg/L. Gas exsolution was observed while sampling at both MW01 and MW02. A wide variety of organic chemicals was detected in the monitoring wells including: GRO, DRO, BTEX, trimethylbenzenes, phenols, naphthalenes, acetone, isopropanol, TBA, 2-butoxyethanol, 2-butanone, diethylene glycol, triethylene glycol, and tetraethylene glycol (**Figure 17; Table 3**). Concentrations of these chemicals range from  $\mu\text{g/L}$  to  $\text{mg/L}$  levels. Concentrations of benzene in MW02 exceed EPA's MCL in drinking by a factor of 49 times. Detections of organic chemicals are more numerous and exhibit higher concentrations in the deeper of the two monitoring wells (**Figure 17, Table 3**). This observation, along with trends in methane, potassium, chloride, and pH, suggest a deep source (>299 m bgs) of contamination. Natural breakdown products of organic contaminants like BTEX and glycols include acetate and benzoic acid; these breakdown products are more enriched in the shallower of the two monitoring wells, suggesting upward/lateral migration with natural degradation and accumulation of daughter products (Corseuil et al. 2011, Caldwell and Suflita 2000, Dwyer and Tiedje 1983). Other trace-level detections of semi-volatile organic compounds included: bis(2-ethylhexyl) phthalate (MW01 and MW02, Phase III and IV), bis(2-chloroethyl) ether, bis(2-ethylhexyl) adipate (MW01, Phase IV), butyl benzyl phthalate, and 4-methyl-2-pentanone (MW02, Phase IV).

Well completion reports obtained online from WOGCC and Material Safety and Data Sheets (MSDSs) obtained from the operator were reviewed to examine inorganic and organic compounds in additives used for hydraulic fracturing and similarity with detected elements and compounds in ground water. Well completion reports were limited to a subset of production wells and included dates of injection, injection depths, pressure, flow, and volume

for slickwater and carbon dioxide foam fracture jobs. Some MSDSs list chemical formulation as proprietary (e.g., proprietary alcohols) or list a chemical family (e.g., blend of organic surfactants) rendering identification of constituents impossible. This review is summarized in **Table 4**. Inorganic additives are potential sources of elevated K, Cl, and OH in deep monitoring wells.

Detection of compounds associated with petroleum-based additives in ground water samples using analytical methods employed in this investigation would be manifested as GRO, DRO, BTEX, naphthalenes, and trimethylbenzenes observed in deep monitoring wells.

TBA was detected in MW02 during Phase 4 sampling at a concentration of 4470  $\mu\text{g/L}$ . Two possible formation pathways for TBA are: 1) biodegradation of methyl *tert*-butyl ether (MTBE, synthetic chemical used as a fuel additive) under methanogenic conditions (e.g., Mormile et al. 1994, Bradley et al. 2001); and 2) breakdown of *tert*-butyl hydroperoxide (a gel breaker used in hydraulic fracturing; e.g., Hiatt et al. 1964). TBA biodegradation is generally slow compared to the degradation of MTBE; this suggests that TBA could be present and persist even after complete MTBE removal from ground water impacted by fuel releases (Wilson et al. 2005). MTBE was not detected in either of the deep monitoring wells. A second pathway of TBA production is from the decomposition of the gel breaker *tert*-butyl hydroperoxide. Hiatt et al. (1964) found that decomposition of *tert*-butyl hydroperoxide yielded a 10-fold molar quantity of TBA, oxygen, *di-tert*-butyl peroxide, and acetone. Acetone was detected in MW02 during Phase 4 sampling at a concentration of 641  $\mu\text{g/L}$ . This breaker is used in hydraulic fracturing formulations; however, the MSDSs made available to EPA do not indicate whether *tert*-butyl hydroperoxide was used in the Pavillion gas field for well stimulation. Elevated concentrations of TBA are not expected in unimpacted aquifers and its presence in MW02 remains unresolved. Additional insight about the occurrence of TBA (and other organic compounds) might be obtained by conducting compound-specific isotope analyses.



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<b>Table 3. Geochemical impacts in deep ground-water monitoring wells</b>				
<b>Compound</b>	<b>MW01 Phase 3 10/6/2010</b>	<b>MW02 Phase 3 10/6/2010</b>	<b>MW01 Phase 4 4/20/2011</b>	<b>MW02 Phase 4 4/19/2011</b>
<b>pH</b>	11.9	12.0	11.2	11.8
<b>K, mg/L</b>	54.9	39.5	24.7	43.6
<b>Cl, mg/L</b>	23.3	466	23.1	457
<b>CH<sub>4</sub>, mg/L</b>	16.0	19.0	17.9	18.8
<b>Benzene †</b>	nd	246	nd	139
<b>Toluene</b>	0.75 <sup>d</sup>	617	0.56	336
<b>Ethylbenzene</b>	nd	67	nd	21.5
<b>Xylenes (total)</b>	nd	750	0.89 <sup>d</sup>	362
<b>1,2,4 Trimethylbenzene</b>	nd	69.2	nd	18.5
<b>1,3,5 Trimethylbenzene</b>	nd	35.5	nd	nd
<b>Diesel Range Organics</b>	634	1440	924	4050
<b>Gasoline Range Organics</b>	389	3710	592	2800
<b>Phenol<sup>a</sup></b>	11.1	56.1	20.9	64.9
<b>Naphthalene<sup>b</sup></b>	nd	6.06	nd	6.10
<b>Isopropanol</b>	-----	-----	212	581
<b>Tert-Butyl Alcohol</b>	-----	-----	nd	4470
<b>2-Butanone</b>	-----	-----	nd	120
<b>Diethylene Glycol</b>	-----	-----	226	1570
<b>Triethylene Glycol</b>	-----	-----	46	310
<b>Tetraethylene Glycol</b>	-----	-----	7.3 <sup>c, d</sup>	27.2
<b>2-Butoxyethanol<sup>*</sup></b>	-----	-----	nd	nd
<b>2-Butoxyethanol<sup>**</sup></b>	nd	nd	12.7	nd
<b>Acetone</b>	-----	-----	79.5	641
<b>Benzoic Acid</b>	212	244	457	209
<b>Acetate</b>	-----	-----	8050	4310
<b>Formate</b>	-----	-----	112	558
<b>Lactate</b>	-----	-----	69	213
<b>Propionate</b>	-----	-----	309	803

† All values in µg/L unless otherwise noted.

----- not analyzed.

nd - not detected.

<sup>a</sup> Includes phenol, 2,4-dimethylphenol, 2-methylphenol, 3&4 methylphenol.

<sup>b</sup> Includes naphthalene, 1-methylnaphthalene, and 2-methylnaphthalene.

<sup>c</sup> Value below quantitation limit of 10 µg/L.

<sup>d</sup> Chemical detected in a blank sample at a similar level

<sup>\*</sup> 2-Butoxyethanol determined by HPLC-MS-MS.

<sup>\*\*</sup> 2-Butoxyethanol determined by GC-MS.

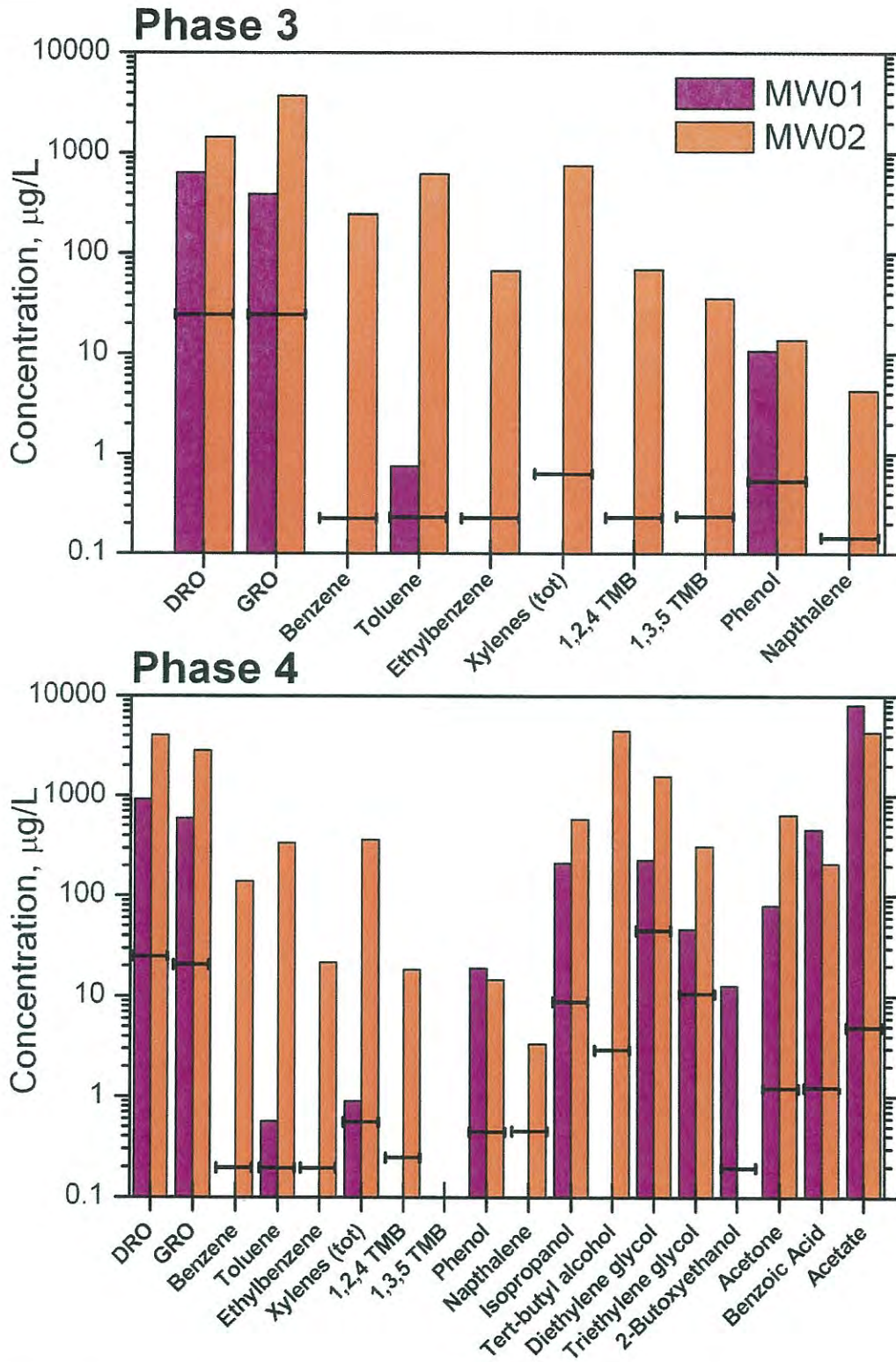


Figure 17. Organic compounds detected in deep monitoring wells MW01 and MW02 during Phase III and IV sampling events. Horizontal bars show method reporting limits for the individual analytes.

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<b>Table 4. Association of inorganic and organic anomalies with compounds used for hydraulic fracturing</b>	
<b>Compound/ Compound Class</b>	<b>Information from MSDSs and Well Completion Reports</b>
<b>pH</b>	KOH was used in a crosslinker (<5%) and in a solvent (85-100%).
<b>K, Cl</b>	The formulation of fracture fluid provided for foam jobs typically consisted of CO <sub>2</sub> , 6% KCl, 10% methanol, and "clean" fluid and "additives." Potassium metaborate was used in crosslinkers (5-10%, 30-60%). KOH was used in a crosslinker (<5%) and in a solvent (85-100%).
<b>Cl</b>	Ammonium chloride was used in crosslinker (1-27%).
<b>BTEX</b>	Aromatic solvent (typically BTEX mixture) was used in a breaker (<75%). Diesel oil (mixture of saturated and aromatic hydrocarbons including naphthalenes and alkylbenzenes) was used in a guar polymer slurry/liquid gel concentrate (30-60%) and in a solvent (60-100%). Petroleum raffinates (mixture of paraffinic, cycloparaffinic, olefinic, and aromatic hydrocarbons) was used in a breaker (<30-60%). Heavy aromatic petroleum naphtha (mixture of paraffinic, cycloparaffinic and aromatic hydrocarbons) was used in surfactants (5-10%, 10-30%, 30-60%) and in a solvent (10-50%). Toluene was used in a flow enhancer (3-7%). Xylenes were used in a flow enhancer (40-70%) and a breaker (confidential percentage).
<b>Trimethylbenzenes</b>	1,2,4-trimethylbenzene was used in surfactants (0-1%). Diesel oil (mixture of saturated and aromatic hydrocarbons including naphthalenes and alkylbenzenes) was used in a guar polymer slurry/liquid gel concentrate (30-60%) and in a solvent (60-100%). Petroleum raffinates (mixture of paraffinic, cycloparaffinic, olefinic, and aromatic hydrocarbons) was used in a breaker (<30-60%). Heavy aromatic petroleum naphtha (mixture of paraffinic, cycloparaffinic and aromatic hydrocarbons) was used in surfactants (5-10%, 10-30%, 30-60%) and in a solvent (10-50%).
<b>DRO and GRO</b>	Diesel oil (mixture of saturated and aromatic hydrocarbons including naphthalenes and alkylbenzenes) was used in a guar polymer slurry/liquid gel concentrate (30-60%) and in a solvent (60-100%). Petroleum raffinates (mixture of paraffinic, cycloparaffinic, olefinic, and aromatic hydrocarbons) was used in a breaker (<30-60%). Heavy aromatic petroleum naphtha (mixture of paraffinic, cycloparaffinic and aromatic hydrocarbons) was used in surfactants (5-10%, 10-30%, 30-60%) and in a solvent (10-50%).
<b>Naphthalene</b>	Naphthalene was used in surfactants (0-1, 5-10%) and a breaker (confidential percentage). Hydrotreated light petroleum distillates (mixture of C10-C14 naphthenes, iso- and n-paraffins) were used in a guar polymer slurry/liquid gel concentrate (40-60%). Diesel oil (mixture of saturated and aromatic hydrocarbons including naphthalenes and alkylbenzenes) was used in a guar polymer slurry/liquid gel concentrate (30-60%) and in a solvent (60-100%).
<b>Isopropanol</b>	Isopropanol was used in a biocide (20-40%), in a surfactant (30-60%), in breakers (<1%, 10-30%), and in foaming agents (<3%, 1-5%, 10-30%).
<b>Tert-Butyl Alcohol</b>	No MSDS listing. Breakdown product of methyl <i>tert</i> -butyl ether and <i>tert</i> -butyl hydroperoxide - found in gel breakers. See discussion.
<b>Glycols</b>	Diethylene glycol was used in a foaming agent (5-10%) and in a solvent (0.1-5%). Triethylene glycol was used in a solvent (95-100%).
<b>2-Butoxyethanol</b>	2-butoxyethanol was used in a surfactant (10-30%), in foaming agents (<10%, <11%, <12%, 1-10%, 10-30%) and in solvents (15-40%, 60-100%).
<b>Acetone</b>	Breakdown product of <i>tert</i> -butyl hydroperoxide - found in gel breakers. See discussion.
<b>Benzoic Acid, Acetate, Formate, Lactate, Propionate, 2-Butanone, Phenols</b>	Natural breakdown products of organic contaminants (e.g., BTEX, glycols, etc.).

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Natural gas condensates are composed primarily of aliphatic hydrocarbons; however, condensates may contain low quantities of aromatic compounds, such as BTEX. Gas from the Fort Union and lower Wind River Formations is generally dry ( $C_1/C_{1-C_5} = 0.95 - 0.96$  where methane =  $C_1$ , ethane =  $C_2$ , propane =  $C_3$ , butane =  $C_4$ , pentane =  $C_5$ ) (Johnson and Rice 1993) and unlikely to yield liquid condensates at ground water pressure and temperature conditions. In addition, a condensate origin for BTEX compounds in ground water is doubtful because dissolved gas compositions and concentrations are similar between the two deep monitoring wells and therefore would yield similar liquid condensates, yet the compositions and concentrations of organic compounds detected in these wells are quite different (**Figure 17**) further suggesting a deep source of BTEX in MW02. The presence of synthetic compounds such as glycol ethers, along with enrichments in K, Cl, pH, and the assortment of other organic components is explained as the result of direct mixing of hydraulic fracturing fluids with ground water in the Pavillion gas field.

As noted previously, this investigation was prompted by homeowner complaints over perceived changes in water quality. Domestic well results showed: the presence of DRO and GRO (in 23 of 28 samples), and trace levels of exotic organic compounds in some domestic wells including adamantanes, 2-butoxyethanol phosphate, phenols, naphthalene, and toluene (EPA 2009, EPA 2010). Methane was detected in 10 of 28 samples at concentration levels below 0.8 mg/L. Foul odors associated with some domestic wells correlate with detections of GRO and DRO.

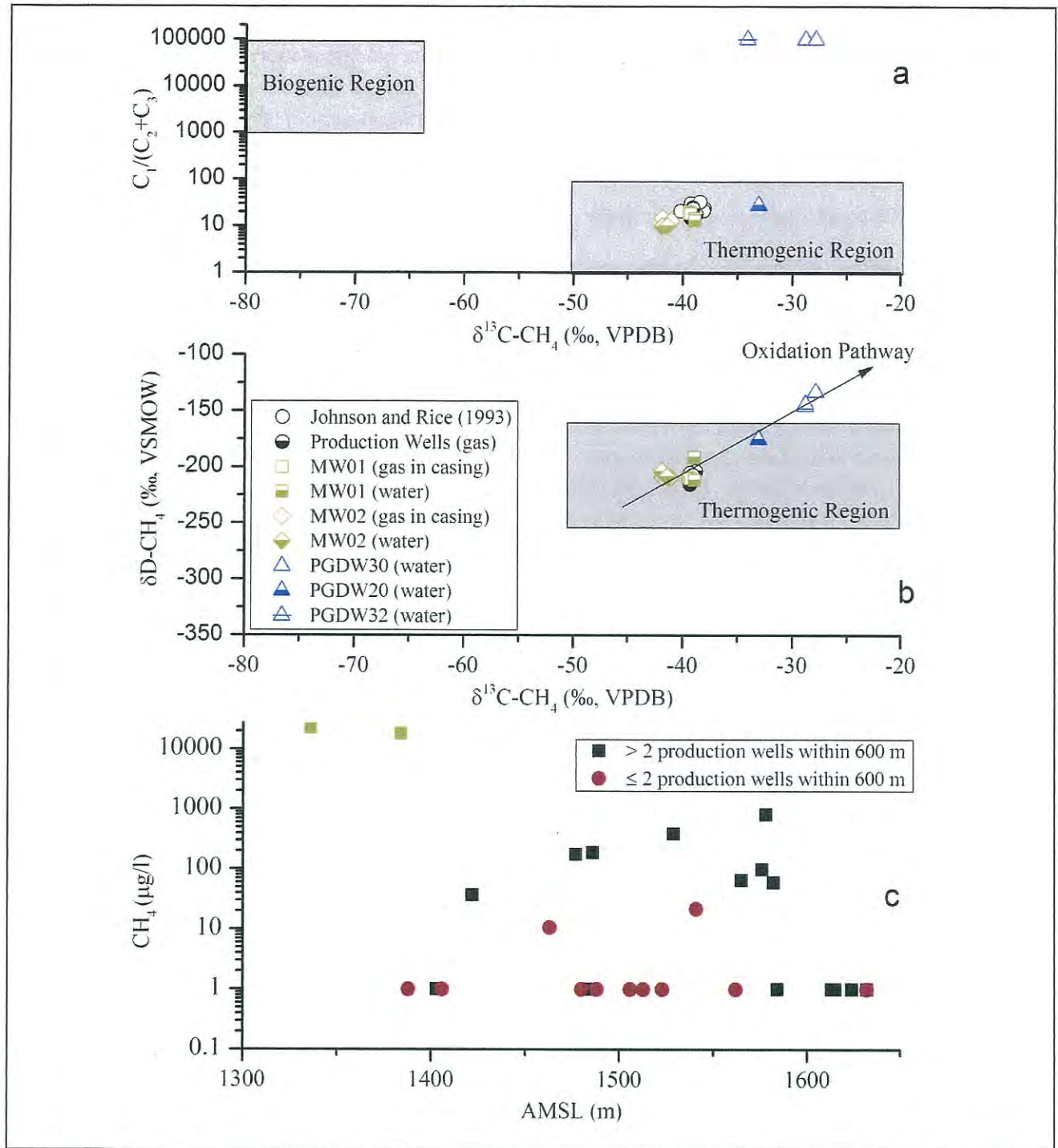
Anomalous trends in inorganic constituents observed in the deep monitoring wells (e.g., K, Cl, pH) were not revealed in domestic well waters. In several instances, glycols were detected in domestic wells using gas chromatography with flame ionization detection (GC-FID; EPA Standard Method 8015). However, glycol analysis using liquid chromatography with tandem mass spectroscopy (GC/MS/MS) failed to replicate these glycol detections, even though the method

reporting limit was over an order of magnitude lower, suggesting that Method 8015 is prone to false positive results (possibly due to interactions between the chromatographic column and organic compounds in sample water). This result points to the need for continued and future improvements of analytical methods to detect and quantitate low levels of organic chemicals that may be associated with hydraulic fracturing fluids. Although contamination was detected in some domestic wells proximal to the deep monitoring wells, underscoring potential future risk, the existing data at this time do not establish a definitive link between deep and shallow contamination of the aquifer. An increased number of sampling points (monitoring wells) with vertical profiling in targeted locations are necessary to better define transport and fate characteristics of organic and inorganic contaminants in the ground water system and impact on domestic wells.

### Natural Gas Migration

A review of open-hole geophysical logs obtained from the WOGCC internet site indicates the presence of gas-filled porosity at three locations at 198, 208, and 252 m bgs between the years 1965 - 1973 suggesting the presence of natural gas in ground water at depths used for domestic water supply prior to extensive commercial development. However, a review of 10 mud-gas logs recorded in the mid-1970s and early 1980s obtained on line from WOGCC, do not indicate gas shows within 300 m of the surface at any location.

Aqueous analysis of light hydrocarbons, gas and headspace analysis of light hydrocarbons, and isotopic data for dissolved, gas phase, and headspace analysis are summarized in **Tables A3a, A3b, and A3c** respectively (all investigative phases). Elevated levels of dissolved methane in domestic wells generally increase in those wells in proximity to gas production wells (**Figure 18c**). Methane was not detected in shallow domestic wells (e.g., < 50 m) regardless of proximity to production wells (**Figure 18c**). With the exception of two domestic wells where methane was



**Figure 18. (a)** Stable isotope ratios of carbon of methane versus ratio of methane ( $C_1$ ) to ethane ( $C_2$ ) and propane ( $C_3$ ) in gas from production wells, monitoring wells, and domestic wells. Values of 100,000 are used to denote non detection of ethane and propane in samples. **(b)** Stable isotope ratios of carbon versus hydrogen of methane in gas from production wells (both literature and measured values), monitoring wells, and domestic wells.  $\delta D$  was not determined for PGDW32. Oxidation pathway (enrichment of  $^{13}C$  of remaining  $CH_4$  with biodegradation) is illustrated. **(c)** Methane concentration in domestic (red circles and black squares) and monitoring wells (green squares) as a function of proximity to production wells and AMSL. Values of 1.0 were used for non-detection (detection limit 5  $\mu g/L$ ).

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detected at less than 22 µg/L, methane was not detected in domestic wells with 2 or less production wells within 600 m (**Figure 18c**). All domestic wells with the exception of PGDW25 with 2 or less production wells within 600 m are located on the periphery of the gas field (**Figure 5**). PGDW25 is located within 1600 m of 15 gas production wells.

Of particular interest is the area encompassing MW01, PGDW30, and PGDW05 (**Figure 19**). Ground water is saturated with methane at MW01 which is screened at a depth (239 m bgs) typical of deeper domestic wells in the area. Methane was detected in PGDW30 at 808 µg/L at a depth of only 80 m, the highest level in any domestic well. A blowout occurred during drilling at a depth of only 159 m bgs in December 2005 adjacent to PGDW05. Natural gas exited the borehole for three days until the gas field operator was ordered to plug the borehole with a dense mud. The owner of PGDW05 was attempting at the time to replace this well due to taste, odor, and yield reduction he stated occurred after hydraulic fracturing at nearby production wells. A mud-gas log conducted on 11/16/1980 at Tribal Pavillion 14-2 (illustrated on **Figure 19** as 14-2) located only 300 m from the location of the uncontrolled release does not indicate a gas show (distinctive peaks on a gas chromatograph) within 300 m of the surface. The owner of PGDW05 complained that well yield decreased after hydraulic fracturing at nearby production wells. Records obtained from the Wyoming State Engineer's office dated January 1973 indicate a yield of 30 to 38 L/min with 1.2 meters of drawdown after 10 hours of pumping. During a sampling event in April 2005, PGDW05 became dry after pumping at a rate of 21.6 L/min for 14 minutes. The cause of reduced well yield requires further investigation.

Similarity of  $\delta^{13}\text{C}$  values for methane, ethane, propane, isobutane, and butane between gas production and monitoring wells and plots of  $\delta^{13}\text{C}-\text{CH}_4$  versus  $\delta\text{D}-\text{CH}_4$  (**Figure 18b**) and  $\delta^{13}\text{C}-\text{CH}_4$  versus  $\text{C}_1/(\text{C}_2 + \text{C}_3)$  (**Figure 18a**) indicate that light hydrocarbons in casing and dissolved gas in deep monitoring wells are

similar to produced gas and have undergone little oxidation or biodegradation. These observations combined with radiocarbon analysis of  $\text{CH}_4$  (< 0.2% percent modern carbon) obtained from gas in casing of both MW01 and MW02 indicate that methane in deep monitoring wells is of thermogenic origin. Gas from the Fort Union and lower Wind River Formations is isotopically heavy ( $\delta^{13}\text{C}-\text{CH}_4$  from to -40.24 to -38.04‰) and as previously stated, dry (Johnson and Rice 1993, Johnson and Keighin 1998). Values of  $\delta^{13}\text{C}-\text{CH}_4$  and  $\delta\text{D}-\text{CH}_4$  more negative than -64‰ and -175‰, respectively, are indicative of microbial origin (Schoell 1980). The absence of ethane and propane in three of four domestic wells having sufficient methane to allow isotopic analysis and a shift of  $\delta^{13}\text{C}-\text{CH}_4$  and  $\delta\text{D}-\text{CH}_4$  values in a positive direction relative to produced gas suggests the presence of gas of thermogenic origin in domestic wells undergoing biodegradation and subsequent enrichment of  $\delta^{13}\text{C}$  and  $\delta\text{D}$ . This observation is consistent with a pattern of dispersion and degradation with upward migration observed for organic compounds. Values of  $\delta^{13}\text{C}-\text{CH}_4$  more positive than -64‰ and  $\text{C}_1/(\text{C}_2 + \text{C}_3)$  ratios above 1000 are often interpreted to indicate gas of mixed biogenic-thermogenic origin or gas of biogenic origin undergoing biodegradation (Whiticar 1999, Whiticar and Faber 1986) since neither ethane nor propane are biogenically generated in significant amounts. However, preferential loss of ethane and propane relative to methane in thermogenic gas produces a similar response (Valentine 2010, Kinnaman et al. 2007).

### Evaluation of Cement Bond/Variable Density Logs Along Transect

CBL/VDLs and lithology were examined along a transect (**Figure 19**) which included the deep monitoring wells and three domestic wells where elevated levels of methane were detected. At Pavillion Fee 34-03B, a CBL/VDL conducted on 10/22/2004 indicates no cement below surface casing until 802 m msl (**Figure 20**) and sporadic bonding to 604 m msl (not illustrated). The well completion

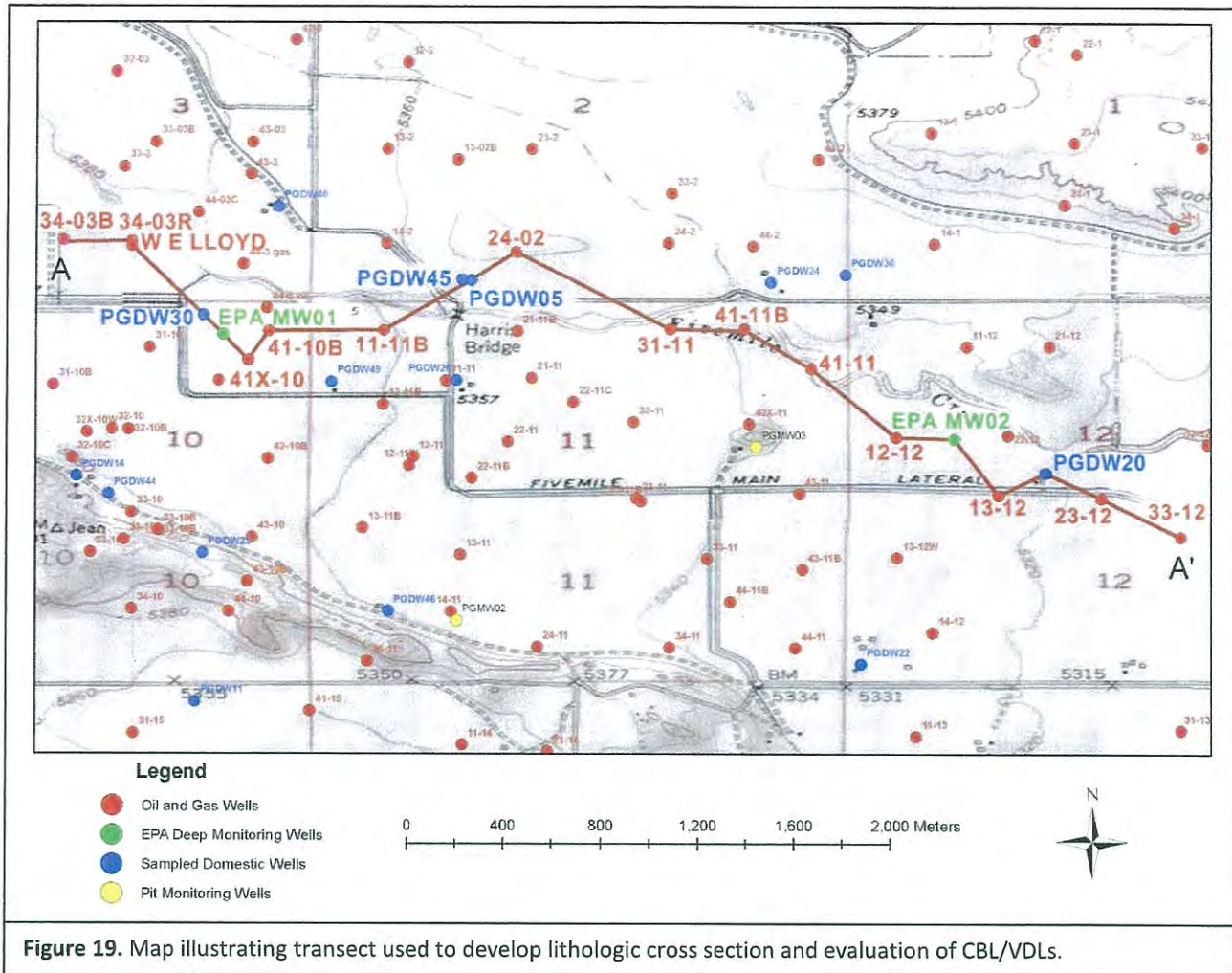
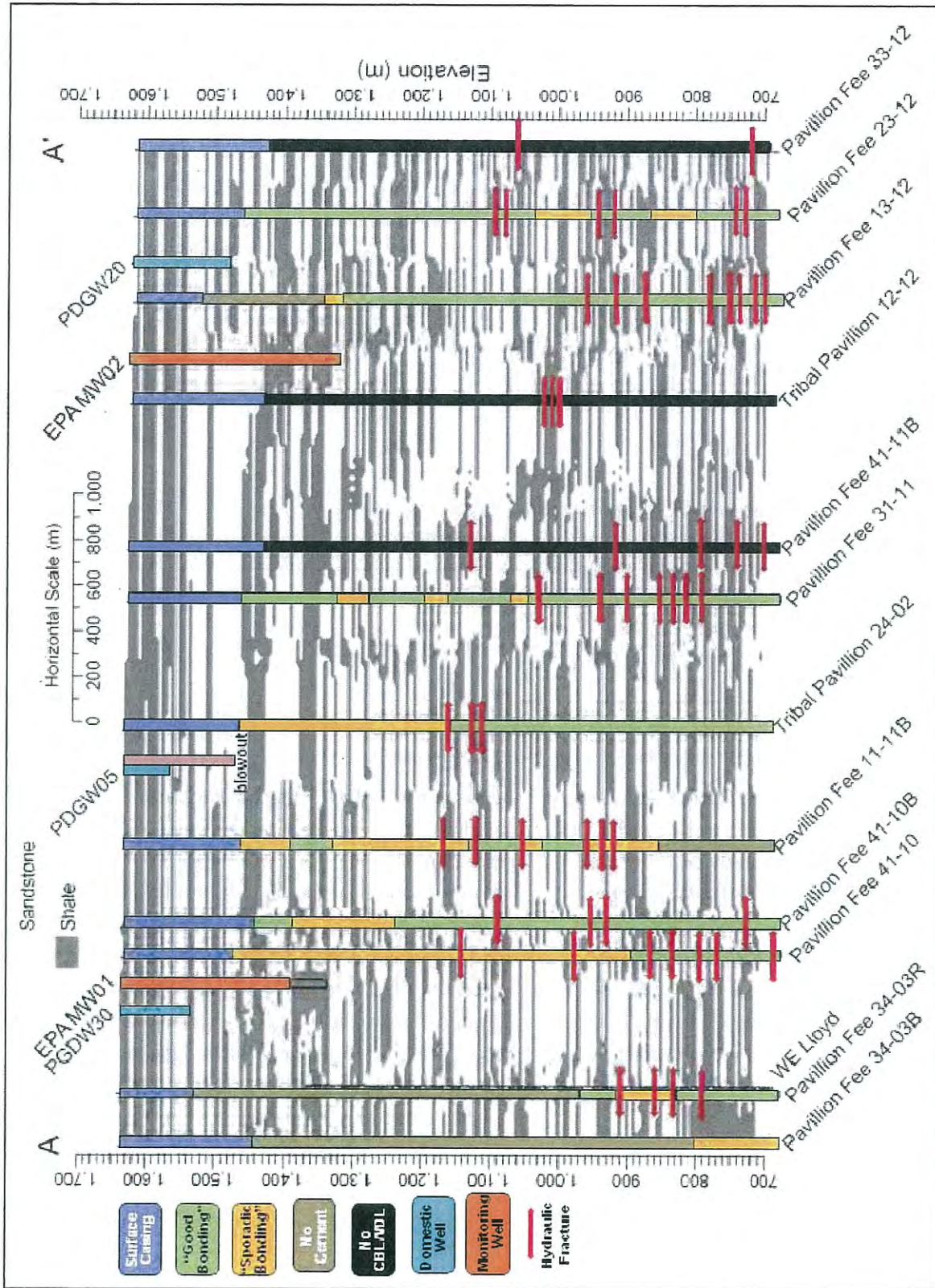


Figure 19. Map illustrating transect used to develop lithologic cross section and evaluation of CBL/VDLs.

report for this production well indicates that hydraulic fracturing was performed at 601 m msl on 11/9/2004. A cement squeeze was subsequently performed at 802 m msl on 4/1/2005 (no CBL/VDL after cement squeeze) with hydraulic fracturing at 689 m msl on 4/19/2005. At Pavillion Fee 34-03R, the CBL/VDL indicates no cement below surface casing until 968 m msl (Figure 20). At Tribal Pavillion 41-10 and 41-10B, CBL/VDLs indicate sporadic bonding over extensive intervals. A CBL/VDL conducted on 4/20/2005 at Tribal Pavillion 24-02 after a squeeze perforation at the base of the surface casing indicates poor bonding outside production casing below surface casing to the first perforation interval (Figure 20). At Tribal Pavillion 11-11B, a CBL/VDL indicates poor or sporadic bonding to 991 m bgs and no cement or cement bridging from 675 - 857 m msl. Thus, a review of well completion

reports and CBL/VDLs indicates instances of sporadic bonding directly above intervals of hydraulic fracturing. This review also indicates instances where cement outside production casing is lacking over an extensive interval providing a potential conduit for fluid migration to within 300 m of the surface. As graphically illustrated in Figure 20, production wells having no or sporadic cement outside production casing are located in proximity to deep monitoring wells where aqueous constituents consistent with hydraulic fracturing were detected and methane exsolved from solution during sampling and locations of domestic wells where elevated levels of methane were detected and where an uncontrolled release of natural gas occurred.



**Figure 20.** Lithologic cross-section along transect illustrating production wells (with evaluation of CBL/VDLs), domestic wells, and blowout location. Red arrows denote depths of hydraulic fracturing of unknown areal extent. Sandstone units are undifferentiated between fine, medium and coarse-grained units.



## Potential Migration Pathways

Further investigation is necessary to determine mechanisms of aqueous and gas phase transport in the area of investigation. However, at least three mechanisms can be postulated at this time. The first mechanism is aqueous and/or gas transport via boreholes due to insufficient or inadequate cement outside production casing. Both aqueous (brine) and gas phase migration vertically up compromised wellbores have been simulated (Nordbotten et al. 2004, 2005a, 2005b) and indicate decreasing mass flux toward the surface with increasing number of permeable formations encountered along the way. Thus, the severity of ground water contamination increases with depth. Migration of gas via wellbores is well documented in the literature (e.g., Harrison 1983, Harrison 1985, Van Stempvoort et al. 2005, Taylor et al. 2000). In Bainbridge, Ohio, an operator initiated hydraulic fracturing despite knowing that only 24 m of cement was present above the perforation interval (Bair et al. 2010, ODNR 2008). Hydraulic fracturing fluid flowed to the surface via surface-production casing annulus which pressurized upon shut-in. Gas subsequently migrated through natural fractures to domestic wells eventually causing an explosion at one home. In northeastern Pennsylvania, two operators were fined for enhanced gas migration into domestic wells attributed to incomplete or inadequate cement outside production casing in wells used for hydraulic fracturing (PADEP 2009a, 2009b, 2010).

The second mechanism is fracture fluid excursion from thin discontinuous tight sandstone units into sandstone units of greater permeability. This would be accompanied by physical displacement of gas-rich solutions in both tight and more permeable sandstone formations. As illustrated in **Figure 20**, there is little lateral and vertical continuity to hydraulically fractured tight sandstones and no lithologic barrier (laterally continuous shale units) to upward vertical migration of aqueous constituents of hydraulic fracturing in the event of excursion from fractures. A third mechanism is that the process of hydraulic

fracturing generates new fractures or enlarges existing ones above the target formation, increasing the connectivity of the fracture system.

In all three transport pathways, a general correlation (spatial relationships ultimately determined by fault and fracture systems in addition to lithology) would exist between proximity to gas production wells and concentration of aqueous and gas phase constituents in ground water. For instance, Osborn et al. (2011) observed a correlation between methane concentration and proximity to hydraulically fractured gas production wells at locations above the Marcellus and Utica formations in Pennsylvania and New York. Isotopic data and other measurements for methane in the drinking water were consistent with gas found in deep reservoirs such as the Marcellus and Utica shales at the active sites and matched gas geochemistry from shale-gas wells sampled nearby. Also, in all three transport pathways, advective/dispersive transport would be accompanied by degradation causing a vertical chemical gradient as observed during sampling of MW01 and MW02. Reduced mass flux to the near surface environment and subsequent degradation along vertical and lateral transport pathways would explain lack of detection in domestic wells of compounds observed in MW02.

## 4.0 Conclusions

The objective of this investigation was to determine the presence of ground water contamination in the Wind River Formation above the Pavillion gas field and to the extent possible, identify the source of contamination. The combined use of shallow and deep monitoring wells allowed differentiation between shallow sources of contamination (pits) and deep sources of contamination (production wells). Additional investigation is necessary to determine the areal and vertical extent of shallow and deep ground water contamination.

Detection of high concentrations of benzene, xylenes, gasoline range organics, diesel range organics, and total purgeable hydrocarbons in ground water samples from shallow monitoring wells near pits indicates that pits are a source of shallow ground water contamination in the area of investigation. Pits were used for disposal of drilling cuttings, flowback, and produced water. There are at least 33 pits in the area of investigation. When considered separately, pits represent potential source terms for localized ground water plumes of unknown extent. When considered as whole they represent potential broader contamination of shallow ground water. A number of stock and domestic wells in the area of investigation are fairly shallow (e.g., < 30 m) representing potential receptor pathways. EPA is a member of a stakeholder group working with the operator to determine the areal and vertical extent of shallow ground water contamination caused by these pits. The operator of the site is currently engaged in investigating and remediating several pit areas.

Detection of contaminants in ground water from deep sources of contamination (production wells, hydraulic fracturing) was considerably more complex than detection of contaminants from pits necessitating a multiple lines of reasoning approach common to

complex scientific investigations. In this approach, individual data sets and observations are integrated to formulate an explanation consistent with each data set and observation. While each individual data set or observation represents an important line of reasoning, taken as a whole, consistent data sets and observations provide compelling evidence to support an explanation of data. Using this approach, the explanation best fitting the data for the deep monitoring wells is that constituents associated with hydraulic fracturing have been released into the Wind River drinking water aquifer at depths above the current production zone.

Lines of reasoning to support this explanation consist of the following.

1. High pH values

pH values in MW01 and MW02 are highly alkaline (11.2-12.0), above the pH range observed in domestic wells (6.9-10), and above the pH range previously reported for the Wind River Formation with up to 94% of the total alkalinity contributed by hydroxide. The presence of hydroxide alkalinity suggests addition of base as the causative factor for elevated pH in the deep monitoring wells. Reaction path modeling indicates that sodium-sulfate composition ground water typical of deeper portions of the Wind River Formation provides little resistance to elevation of pH with small addition of potassium hydroxide.

With the exception of soda ash, the pH of drilling additives in concentrated aqueous solution was well below that observed in the deep monitoring wells. Dense soda ash was added to the drilling mud which varied between pH 8 - 9.

The possibility of cement/grout intrusion into the screened intervals was considered as a possibility for elevated pH in both monitoring

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wells. However, cement intrusion typically leads to pH values between 10 and 11 – below that observed in deep monitoring wells. Prolonged purging did not show decreasing pH trends. Water chemistry results indicate that ground water from the wells was highly undersaturated with respect to cement phases (e.g., portlandite).

Material Safety Data Sheets indicate that potassium hydroxide was used in a crosslinker (<5%) and in a solvent.

### 2. Elevated potassium and chloride

The inorganic geochemistry of ground water from the deep monitoring wells is distinctive from that in the domestic wells and expected composition in the Wind River formation. Potassium concentration in MW02 (43.6 mg/L) and MW01 (54.9 mg/L) is between 14.5 and 18.3 times the mean value of levels observed in domestic wells (3 mg/L, 99% of values < 10 mg/L). Chloride enrichment in monitoring well MW02 (466 mg/L) is 18 times the mean chloride concentration (25.6 mg/L) observed in ground water from domestic wells. Chloride concentration in this well is significant because regional anion trends show decreasing chloride concentrations with depth. In addition, the monitoring wells show low calcium, sodium, and sulfate concentrations compared to the general trend observed in domestic well waters.

Potassium levels in concentrated solutions of drilling additives were all less than 2 mg/L. One additive (Aqua Clear used during well development) contained 230 mg/L chloride in a concentrated solution. Information from well completion reports and Material Safety Data Sheets indicate that the formulation of fracture fluid provided for foam jobs typically consisted of 6% potassium chloride.

Potassium metaborate was used in crosslinkers (5-10%, 30-60%). Potassium hydroxide was used in a crosslinker (<5%) and in a solvent. Ammonium chloride was used in crosslinker (1-27%).

Alternative explanations for inorganic geochemical anomalies observed in deep monitoring wells have been provided and considered. These alternate explanations include contamination from drilling fluids and additives, well completion materials, and surface soil, with contamination from all these sources exacerbated by poor well development. Contamination by drilling fluids and additives is inconsistent with analysis of concentrated solutions of bentonite and additives. Well construction materials (screen and sections of casing) consisted of stainless steel and were power-washed on site with detergent-free water prior to use. Sections of tremie pipe used to inject cement above screened intervals were also power washed with detergent-free water prior to use. Stainless-steel screens and sections of casing and tremie pipe remained above ground level (did not touch soil) prior to use. Both deep monitoring wells were purposefully located away from the immediate vicinity of gas production wells, known locations of pits, and areas of domestic waste disposal (abandoned machinery) to minimize the potential of surface soil contamination. Conductor pipe installed over the first 30.5 m (100 ft) of drilling at both deep monitoring wells eliminated the possibility of surface soil entry into the borehole. Turbidity measurements in MW01 during sampling ranged from 7.5 and 7.9 Nephelometric Turbidity Units (NTUs). Turbidity measurements in MW02 during sampling ranged from 24.0 to 28.0 NTUs, slightly above the stated goal of 10.0 NTUs but nevertheless was clear water typical of domestic wells during sampling. A low

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recharge rate in MW02 necessitated a prolonged period of well development which was likely due in part to gas flow (reduced relative permeability to water) into the well during development.

### 3. Detection of synthetic organic compounds

Isopropanol was detected in MW01 and MW02 at 212 and 581 µg/L, respectively. Diethylene glycol was detected in MW01 and MW02 at 226 and 1570 µg/L, respectively. Triethylene glycol was detected in MW01 and MW02 at 46 and 310 µg/L, respectively. Another synthetic compound, *tert*-butyl alcohol, was detected in MW02 at a concentration of 4470 µg/L. *Tert*-butyl alcohol is a known breakdown product of methyl *tert*-butyl ether (a fuel additive) and *tert*-butyl hydroperoxide (a gel breaker used in hydraulic fracturing). EPA methods were utilized for analysis when applicable for compounds or classes of compounds. Detection of synthetic organic compounds in MW01 and MW02 was made in part through the use of non-commercially available modified EPA analytical methods. For instance, high performance liquid chromatography/mass spectrometry/mass spectrometry was utilized for analysis of diethylene, triethylene and tetraethylene glycols. Ethylene glycol, which was widely used for well stimulation, required additional method modification and was not analyzed during this investigation.

Isopropanol was detected in concentrated solutions of drilling additives at a maximum concentration of 87 µg/L, well below that detected in deep monitoring wells. Glycols were not detected in concentrated solutions of drilling additives.

Material Safety Data Sheets indicate that isopropanol was used in a biocide (20-40%), in

a surfactant (30-60%), in breakers (<1%, 10-30%), and in foaming agents (<3%, 1-5%, 10-30%). Diethylene glycol was used in a foaming agent (5-10%) and in a solvent (0.1-5%). Triethylene glycol was used in a solvent (95-100%). Material Safety Data Sheets do not indicate that *tert*-butyl hydroperoxide was used in the Pavillion gas field. The source of this compound remains unresolved. However, *tert*-butyl alcohol is not expected to occur naturally in ground water. Material Safety Data Sheets do not contain proprietary information and the chemical ingredients of many additives.

Alternative explanations provided to date and considered by EPA for detection of synthetic organic compounds in deep monitoring wells include arguments previously listed and addressed.

### 4. Detection of petroleum hydrocarbons

Benzene, toluene, ethylbenzene, and xylenes (BTEX) were detected in MW02 at concentrations of 246, 617, 67, and 750 µg/L respectively. Trimethylbenzenes were detected in MW02 at 105 µg/L. Gasoline range organics were detected in MW01 and MW02 at 592 and 3710 µg/L, respectively. Diesel range organics were detected in MW01 and MW02 at 924 and 4050 µg/L respectively. Naphthalene was detected in MW02 at 6 µg/L. EPA methods were utilized for analysis.

BTEX and trimethylbenzenes were not detected in concentrated solutions of drilling additives.

Material Safety Data Sheets indicate that aromatic solvent (typically BTEX mixture) was used in a breaker (<75%). Diesel oil (mixture of saturated and aromatic hydrocarbons including naphthalenes and alkylbenzenes) was used in a guar polymer slurry/liquid gel

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concentrate (30-60%) and in a solvent (60-100%). Petroleum raffinates (a mixture of paraffinic, cycloparaffinic, olefinic, and aromatic hydrocarbons) were used in a breaker (<30-60%). Heavy aromatic petroleum naphtha (mixture of paraffinic, cycloparaffinic and aromatic hydrocarbons) was used in surfactants (5-10%, 10-30%, 30-60%) and in a solvent (10-50%). Toluene was used in a flow enhancer (3-7%). Xylenes were used in a flow enhancer (40-70%) and a breaker (confidential percentage). Gasoline range organics correspond to a hydrocarbon range of C6 – C10. It includes a variety of organic compounds ketones, ethers, mineral spirits, stoddard solvents, and naphthas. Detection of gasoline range organics does not infer the use of gasoline for hydraulic fracturing.

Alternative explanations provided to date and considered by EPA for detection of petroleum compounds in deep monitoring wells include arguments previously listed and addressed. An additional alternate explanation for detection of petroleum compounds includes use of lubricants on the drillstem and well casing, use of electrical tape on submersible pumps, and components of submersible pumps. Jet Lube Well Guard hydrocarbon free lubricant specifically designed for monitoring well installation was used for drillstem connections. No lubricants were used to attach sections of casing or sections of tremie pipe during cementation. Clamps, not electrical tape, were used to bind electrical wires for submersible pumps. Water collected for samples during recharge at MW01 and MW02 would have a short contact time with components of submersible pumps. For components of submersible pumps to be a causative factor of high concentrations of petroleum hydrocarbons observed in MW01 and MW02, components of submersible

pumps would have to contain high levels of water extractable petroleum compounds and consist of a matrix allowing rapid mass transfer, neither of which is plausible.

Another alternate explanation is that detection of petroleum hydrocarbons in ground water is expected above a natural gas field. Gas from Fort Union and Wind River Formations is dry and unlikely to yield liquid condensates at ground water pressure and temperature conditions. In addition, a condensate origin for petroleum hydrocarbons in ground water is doubtful because dissolved hydrocarbon gas compositions and concentrations are similar between the two deep monitoring wells and therefore would yield similar liquid condensates, yet the compositions and concentrations of organic compounds detected in these wells are quite different.

### 5. Breakdown products of organic compounds

Detections of organic chemicals were more numerous and exhibited higher concentrations in the deeper of the two monitoring wells. Natural breakdown products of organic contaminants like BTEX and glycols include acetate and benzoic acid. These breakdown products are more enriched in the shallower of the two monitoring wells, suggesting upward/lateral migration with natural degradation and accumulation of daughter products.

Hydraulic gradients are currently undefined in the area of investigation. However, there are flowing stock wells (e.g., PGDW44 - one of the deepest domestic wells in the area of investigation at 229 m below ground surface) suggesting that upward gradients exist in the area of investigation. In the Agency's report on evaluation of impacts to USDWs by hydraulic fracturing of coalbed methane

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reservoirs (EPA, 2004), hypothetical conceptual models were presented on contaminant migration in a USDW during injection of fracturing fluids into a USDW. In these conceptual models, highly concentrated contaminant plumes exist within the zone of injection with dispersed lower concentration areas vertically and laterally distant from injection points. Data from deep monitoring wells suggests that this conceptual model may be appropriate at this site.

6. Sporadic bonding outside production casing directly above intervals of hydraulic fracturing

It is possible that wellbore design and integrity issues were one causative factor in deep ground water contamination at this site (surface casing of production wells not extending below deepest domestic wells, little vertical separation between fractured zones and domestic wells, no cement or sporadic bonding outside production casing).

A review of well completion reports and cement bond/variable density logs in the area around MW01 and MW02 indicates instances of sporadic bonding outside production casing directly above intervals of hydraulic fracturing. For instance, at Pavillion Fee 34-03B, a cement bond/variable density log conducted on 10/22/2004 indicated no cement until 838 m (2750 ft) and sporadic bonding to 1036 m (3400 ft) below ground surface. The well completion report for this production well indicates that hydraulic fracturing was performed at 1039 m (3409 ft) below ground surface on 11/9/2004 prior to cement squeeze jobs at 823 m (2700 ft) and 256 m (840 ft) below ground surface in April 2005. At Tribal Pavillion 41-10 a cement bond/variable density log indicates sporadic bonding directly above the interval of hydraulic fracturing at 493 m (1618 ft) below ground surface. A cement bond/variable density log conducted

on Tribal Pavillion 24-02 after a squeeze job at the base of the surface casing indicates sporadic bonding outside production casing below surface casing to the interval of hydraulic fracturing at 469 m (1538 ft) below ground surface. At Tribal Pavillion 11-11B, a cement bond/variable density log indicates sporadic bonding between 305 to 503 m (1000 to 1650 ft) below ground surface with hydraulic fracturing occurring at 463 m (1516 ft) below ground surface.

7. Hydraulic fracturing into thin discontinuous sandstone units

There is little lateral and vertical continuity to hydraulically fractured tight sandstones and no lithologic barrier (laterally continuous shale units) to stop upward vertical migration of aqueous constituents of hydraulic fracturing in the event of excursion from fractures. Sandstone units are of variable grain size and permeability indicating a potentially tortuous path for upward migration.

In the event of excursion from sandstone units, vertical migration of fluids could also occur via nearby wellbores. For instance, at Pavillion Fee 34-03R, the cement bond/variable density log indicates no cement until 671 m (2200 ft) below ground surface. Hydraulic fracturing occurred above this depth at nearby production wells.

Although some natural migration of gas would be expected above a gas field such as Pavillion, data suggest that enhanced migration of gas has occurred to ground water at depths used for domestic water supply and to domestic wells. Lines of reasoning to support this explanation consist of following.

1. Hydrocarbon and isotopic composition of gas

The similarity of  $\delta^{13}\text{C}$  values for methane, ethane, propane, isobutane, and butane

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between gas production and monitoring wells and plots of  $\delta^{13}\text{C}-\text{CH}_4$  versus  $\delta\text{D}-\text{CH}_4$  and  $\delta^{13}\text{C}-\text{CH}_4$  versus methane/(ethane + propane) indicate that light hydrocarbons in casing and dissolved gas in deep monitoring wells are similar to produced gas and have undergone little oxidation or biodegradation indicative of advective transport. The absence of ethane and propane in three of four domestic wells having sufficient methane to allow isotopic analysis and a shift of  $\delta^{13}\text{C}-\text{CH}_4$  and  $\delta\text{D}-\text{CH}_4$  values in a positive direction relative to produced gas suggests the presence of gas of thermogenic origin in domestic wells undergoing biodegradation. This observation is consistent with a pattern of dispersion and degradation with upward migration observed for organic compounds.

### 2. Elevation of dissolved methane concentrations in proximity to production wells

Levels of dissolved methane in domestic wells generally increase in those wells in proximity to gas production wells. With the exception of 2 domestic wells where methane was detected at less than 22  $\mu\text{g}/\text{L}$ , methane was not detected in domestic wells with 2 or less production wells within 600 m.

### 3. Spatial anomaly near PGDW05

Methane concentrations in ground water appear highest in the area encompassing MW01, PGDW30, and PGDW05. Ground water is saturated with methane at MW01 which is screened at a depth (239 m bgs) typical of deeper domestic wells in the area. Methane was detected in PGDW30 at 808  $\mu\text{g}/\text{L}$  at a depth of only 80 m, the highest level in any domestic well. A blowout occurred during drilling at a depth of only 159 m bgs in December 2005 adjacent to PGDW05.

An alternative explanation of high methane concentrations in this area is that it is close to the top of the dome comprising the Pavillion gas field which may facilitate natural gas migration toward the surface. However, this geologic feature would also facilitate enhanced gas migration. Also, a mud-gas log conducted on 11/16/1980 (prior to intensive gas production well installation) at Tribal Pavillion 14-2 located only 300 m from the location of the uncontrolled release does not indicate a gas show (distinctive peaks on a gas chromatograph) within 300 m of the surface.

### 4. Shallow surface casing and lack of cement or sporadic bonding outside production casing

With the exception of two production wells, surface casing of gas production wells do not extend below the maximum depth of domestic wells in the area of investigation. Shallow surface casing combined with lack of cement or sporadic bonding of cement outside production casing would facilitate migration of gas toward domestic wells.

The discussion on migration of fluids associated with hydraulic fracturing is relevant for gas migration and is not repeated here for brevity. Of particular concern are wellbores having no or little cement over large vertical instances. For instance, at Pavillion Fee 34-03R, the cement bond/variable density log indicates no cement until 671 m (2200 ft) below ground surface. At Pavillion Fee 34-03B, a cement bond/variable density log conducted on 10/22/2004 indicated no cement until 838 m (2750 ft) below ground surface. Migration of gas via wellbores having no cement or poor cement bonding outside production casing is well documented in the literature.

An alternative explanation of wellbore gas migration provided to EPA and considered is that domestic wells are poorly sealed and thus

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constitute a potential gas migration pathway. However, lack of cement and sporadic bonding outside casing in production constitutes a major potential gas migration pathway to the depth of deep monitoring and domestic wells. It is possible that domestic wells could subsequently facilitate gas migration toward the surface.

### 5. Citizens' complaints

Finally, citizens' complaints of taste and odor problems concurrent or after hydraulic fracturing are internally consistent. Citizens' complaints often serve as the first indication of subsurface contamination and cannot be dismissed without further detailed evaluation, particularly in the absence of routine ground water monitoring prior to and during gas production.

An alternate explanation provided and considered by EPA is that other residents in the Pavillion area have always had gas in their wells. Unfortunately, no baseline data exists to verify past levels of gas flux to the surface or domestic wells.

A lines of reasoning approach utilized at this site best supports an explanation that inorganic and organic constituents associated with hydraulic fracturing have contaminated ground water at and below the depth used for domestic water supply. However, further investigation would be needed to determine if organic compounds associated with hydraulic fracturing have migrated to domestic wells in the area of investigation. A lines of evidence approach also indicates that gas production activities have likely enhanced gas migration at and below depths used for domestic water supply and to domestic wells in the area of investigation.

Hydraulic fracturing in the Pavillion gas field occurred into zones of producible gas located within an Underground Source of Drinking Water (USDW).

Hydraulic fracturing for coal-bed methane recovery is often shallow and occurs directly into USDWs (EPA 2004). TDS less than 10,000 mg/L in produced water is common throughout the Rocky Mountain portion of the United States (USGS 2011; Dahm et al. 2011). Ground water contamination with constituents such as those found at Pavillion is typically infeasible or too expensive to remediate or restore (GAO 1989). Collection of baseline data prior to hydraulic fracturing is necessary to reduce investigative costs and to verify or refute impacts to ground water.

Finally, this investigation supports recommendations made by the U.S. Department of Energy Panel (DOE 2011a, b) on the need for collection of baseline data, greater transparency on chemical composition of hydraulic fracturing fluids, and greater emphasis on well construction and integrity requirements and testing. As stated by the panel, implementation of these recommendations would decrease the likelihood of impact to ground water and increase public confidence in the technology.



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# Appendix A

## Summary of Analytical Results

Table A1. Summary of subsurface sample locations, depth of sample collection, times (phases) of sampling, target analytes, laboratories utilized, and analytical methods

Sample	Latitude	Longitude	Depth (m bgs)	Type	Media	Major anions and alkalinity phase(lab)	Metals phase(lab)	Alcohols and VOCs phase(lab)	Low molecular weight acids, glycols phase(lab)	SVOCS Pesticides PCBs, TICs phase(lab)	GRO, DRO, THE, TPH phase(lab)	Bacteria phase(lab)	Fixed gases, C <sub>1</sub> -C <sub>4</sub> , δ <sup>13</sup> C and δD C <sub>1</sub> -C <sub>4</sub> , DOC DIC, δ <sup>13</sup> C DIC δ <sup>18</sup> O and δD water phase(lab)
PGPP01 (Tribal Pavillion 14-10)	43.24578857	-108.6356735		PG	gas/ fluid	-----	-----	II(R8 <sup>2</sup> )	-----	II(R8 <sup>3</sup> )	II(R8 <sup>4</sup> )	-----	II(I <sup>1</sup> )
PGPP02	43.2486496	-108.6274796		PG	gas	-----	-----	-----	-----	-----	-----	-----	II(I <sup>1</sup> )
PGPP04 (Tribal Pavillion 24-02)	43.25984955	-108.6116409		PG	gas/ fluid	-----	-----	II(R8 <sup>2</sup> )	-----	II(R8 <sup>3</sup> )	II(R8 <sup>4</sup> )	-----	II(I <sup>1</sup> )
PGPP05 (Tribal Pavillion 33-10)	43.2486496	-108.6274796		PG	gas/ fluid	-----	-----	II(R8 <sup>2</sup> )	-----	II(R8 <sup>3</sup> )	II(R8 <sup>4</sup> )	-----	II(I <sup>1</sup> )
PGPP06 (Tribal Pavillion 14-2)	43.26016998	-108.6165009		PG	gas/ fluid	-----	-----	II(R8 <sup>2</sup> )	-----	II(R8 <sup>3</sup> )	II(R8 <sup>4</sup> )	-----	II(I <sup>1</sup> )
MNW01	43.25682	-108.62185	233 - 239	MW	gas/ water	III(O <sup>1</sup> ) IV(O <sup>1</sup> )	III(S <sup>1</sup> ) IV(S <sup>1</sup> )	III(R8 <sup>2</sup> , S <sup>2</sup> ) IV(R8 <sup>2</sup> , S <sup>2</sup> )	IV(S <sup>4</sup> , R3)	III(R8 <sup>3</sup> ) IV(R8 <sup>3</sup> )	III(R8 <sup>4</sup> ) IV(R8 <sup>4</sup> )	-----	III(O <sup>2</sup> , I <sup>2</sup> , O <sup>2</sup> , S <sup>2</sup> , S <sup>2</sup> ) IV(I <sup>2</sup> , I <sup>2</sup> , O <sup>2</sup> , S <sup>2</sup> , S <sup>2</sup> )
MNW02	43.25293	-108.59468	293 - 299	MW	gas/ water	III(O <sup>1</sup> ) IV(O <sup>1</sup> )	III(S <sup>1</sup> ), IV(S <sup>1</sup> )	III(R8 <sup>2</sup> , S <sup>2</sup> ) IV(R8 <sup>2</sup> , S <sup>2</sup> )	IV(S <sup>4</sup> , R3)	III(R8 <sup>3</sup> ) IV(R8 <sup>3</sup> )	III(R8 <sup>4</sup> ) IV(R8 <sup>4</sup> )	-----	III(O <sup>2</sup> , I <sup>2</sup> , O <sup>2</sup> , S <sup>2</sup> , S <sup>2</sup> ) IV(I <sup>2</sup> , I <sup>2</sup> , O <sup>2</sup> , S <sup>2</sup> , S <sup>2</sup> )
PGMW01 (Pit 24-3#1)	43.26172665	-108.6316147	4.6	PGM	water	II(R8 <sup>1</sup> )	II(A4)	II(A, R8 <sup>2</sup> )	-----	II(A, R8 <sup>3</sup> )	II(F <sup>2</sup> , R8 <sup>4</sup> )	II(F <sup>1</sup> )	II(R8 <sup>5</sup> )
PGMW02 (Pit 14X-11#6)	43.24616241	-108.613205	4.6	PGM	water	II(R8 <sup>1</sup> )	II(A4)	II(A, R8 <sup>2</sup> )	-----	II(A, R8 <sup>3</sup> )	II(E <sup>2</sup> , R8 <sup>4</sup> )	II(E <sup>1</sup> )	II(R8 <sup>5</sup> )
PGMW03 (Pit 42X-11#4)	43.25263977	-108.6020584	4.6	PGM	water	II(R8 <sup>1</sup> )	II(A4)	II(A, R8 <sup>2</sup> )	-----	II(A, R8 <sup>3</sup> )	II(E <sup>2</sup> , R8 <sup>4</sup> )	II(E <sup>1</sup> )	II(R8 <sup>5</sup> )
PGS001 (Pit 24-3)	43.26117325	-108.6316071	< 5	PGS	soil	-----	-----	-----	-----	II(R8 <sup>3</sup> )	II(E <sup>2</sup> , R8 <sup>4</sup> )	-----	-----
PGS002 (Pit 14X-11)	43.24636841	-108.6135254	< 5	PGS	soil	-----	-----	-----	-----	II(R8 <sup>3</sup> )	II(E <sup>2</sup> , R8 <sup>4</sup> )	-----	-----
PGS003 (Pit 42X-11)	43.25279504	-108.6022339	< 5	PGS	soil	-----	-----	-----	-----	II(R8 <sup>3</sup> )	II(E <sup>2</sup> , R8 <sup>4</sup> )	-----	-----
PGDW01	unknown	unknown	-----	DW	water	II(R8 <sup>1</sup> )	(K)	(L)	-----	I(L, R8 <sup>3</sup> )	-----	-----	-----
PGDW02	43.21848912	-108.5783117	15.2	DW	water	II(R8 <sup>1</sup> )	(K)	(L)	-----	I(L, R8 <sup>3</sup> )	-----	-----	-----
PGDW03	43.22721318	-108.6584107	152.4	DW	water	II(R8 <sup>1</sup> )	(K), II(A4)	I(L) II(A, R8 <sup>2</sup> )	-----	I(L, R8 <sup>3</sup> ) II(A, R8 <sup>3</sup> )	II(E <sup>2</sup> , R8 <sup>4</sup> )	II(E <sup>1</sup> )	II(I <sup>1</sup> , R8 <sup>5</sup> )
PGDW04	43.22790981	-108.6542063	152.4	DW	water	II(R8 <sup>1</sup> ) II(R8 <sup>1</sup> )	(K), II(A4)	I(L) II(A, R8 <sup>2</sup> )	-----	I(L, R8 <sup>3</sup> ) II(A, R8 <sup>3</sup> )	II(F <sup>1</sup> ) II(F <sup>2</sup> , R8 <sup>4</sup> )	II(E <sup>1</sup> ) II(E <sup>1</sup> ) II(E <sup>2</sup> )	II(R8 <sup>5</sup> ) II(I, R8 <sup>5</sup> )
PGDW05	43.25884666	-108.6126481	64.0	DW	water	II(R8 <sup>1</sup> ), II(R8 <sup>1</sup> ) IV(O <sup>1</sup> )	II(K) II(A4) IV(S <sup>1</sup> )	I(L) II(A, R8 <sup>2</sup> ) IV(R8 <sup>2</sup> , S <sup>2</sup> )	IV(S <sup>4</sup> , R3)	I(L, R8 <sup>3</sup> ) II(A, R8 <sup>3</sup> ) IV(R8 <sup>3</sup> )	II(E <sup>2</sup> , R8 <sup>4</sup> )	II(E <sup>1</sup> ) II(E <sup>2</sup> )	II(R8 <sup>5</sup> ) II(R8 <sup>5</sup> ) IV(I <sup>2</sup> , O <sup>2</sup> , S <sup>2</sup> , S <sup>2</sup> )

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Sample	Latitude	Longitude	Depth (m, lgs)	Type	Media	Major anions and alkalinity phase(lab)	Metals phase(lab)	Alcohols and VOCs phase(lab)	Low molecular weight acids, glycols phase(lab)	SVOCs Pesticides PCBs, TICs phase(lab)	GRO, DRO, THE, TPH phase(lab)	Bacteria phase(lab)	Fixed gases, C <sub>2</sub> -C <sub>4</sub> , δ <sup>13</sup> C and δD C <sub>1</sub> -C <sub>4</sub> DOC DIC, δ <sup>13</sup> C DIC δ <sup>18</sup> O and δD water phase(lab)
PGDW06	43.27110813	-108.5599211	115.8	DW	water	(R8 <sup>+</sup> )	(K)	(L)	-----	(L,R8 <sup>+</sup> )	-----	-----	-----
PGDW07	43.24678442	-108.6879085	154.2	PGP	water	(R8 <sup>+</sup> )	(K)	(L)	-----	(L,R8 <sup>+</sup> )	-----	-----	(R8 <sup>+</sup> )
PGDW08	43.24697265	-108.6840567	157.0	PGP	water	(R8 <sup>+</sup> )	(K)	(L)	-----	(L,R8 <sup>+</sup> )	-----	-----	-----
PGDW09	43.27211644	-108.615144	9.1	DW	water	(R8 <sup>+</sup> )	(K)	(L)	-----	(L,R8 <sup>+</sup> )	-----	-----	-----
PGDW10	43.23574855	-108.6563896	227.1	DW	water	(R8 <sup>+</sup> ) (R8 <sup>+</sup> )	(K) (A4)	(L) (A,R8 <sup>+</sup> )	-----	(L,R8 <sup>+</sup> ) (A,R8 <sup>+</sup> )	(E <sup>+</sup> ) (E <sup>+</sup> ,R8 <sup>+</sup> )	(E <sup>+</sup> )	(R8 <sup>+</sup> ) (R8 <sup>+</sup> )
PGDW11	43.24312049	-108.6228628	227.1	DW	water	(R8 <sup>+</sup> )	(K)	(L)	-----	(L,R8 <sup>+</sup> )	-----	-----	-----
PGDW12	43.27628977	-108.5661502	115.8	DW	water	(R8 <sup>+</sup> )	(K)	(L)	-----	(L,R8 <sup>+</sup> )	-----	-----	-----
PGDW13	43.2444467	-108.6772771	-----	DW	water	(R8 <sup>+</sup> )	(K)	(L)	-----	(L,R8 <sup>+</sup> )	-----	-----	-----
PGDW14	43.25154027	-108.6273311	57.9	DW	water	(R8 <sup>+</sup> )	(K)	(L) IV(R8 <sup>+</sup> ,S <sup>+</sup> )	IV(S <sup>+</sup> ,R3)	(L,R8 <sup>+</sup> )	-----	-----	IV(O <sup>+</sup> ,S <sup>+</sup> )
PGDW15	43.24312129	-108.6671791	30.5	DW	water	(R8 <sup>+</sup> )	(K)	(L)	-----	(L,R8 <sup>+</sup> )	-----	-----	-----
PGDW16	43.20381363	-108.6405183	161.5	DW	water	(R8 <sup>+</sup> )	(K)	(L)	-----	(L,R8 <sup>+</sup> )	-----	-----	-----
PGDW17	43.20416653	-108.6368713	152.4	DW	water	(R8 <sup>+</sup> )	(K)	(L)	-----	(L,R8 <sup>+</sup> )	-----	-----	(R8 <sup>+</sup> )
PGDW18	43.22491388	-108.569651	67.1	DW	water	(R8 <sup>+</sup> )	(K)	(L)	-----	(L,R8 <sup>+</sup> )	-----	-----	-----
PGDW19	43.21382469	-108.651274	19.8	DW	water	(R8 <sup>+</sup> )	(K)	(L)	-----	(L,R8 <sup>+</sup> )	-----	-----	-----
PGDW20	43.25166961	-108.5912756	140.2	DW	water	(R8 <sup>+</sup> ) (R8 <sup>+</sup> ) (O <sup>+</sup> ) IV(O <sup>+</sup> )	(K) (A4) (S) IV(S)	(L) (A,R8 <sup>+</sup> ) (R8 <sup>+</sup> ,S <sup>+</sup> ) IV(R8 <sup>+</sup> ,S <sup>+</sup> )	IV(S <sup>+</sup> ,R3)	(L,R8 <sup>+</sup> ) (A,R8 <sup>+</sup> ) (R8 <sup>+</sup> ) IV(R8 <sup>+</sup> )	(E <sup>+</sup> ) (E <sup>+</sup> ,R8 <sup>+</sup> ) (R8 <sup>+</sup> ) IV(R8 <sup>+</sup> )	(E <sup>+</sup> ) (E <sup>+</sup> ) (E <sup>+</sup> ) (E <sup>+</sup> )	(R8 <sup>+</sup> ) (R8 <sup>+</sup> ) (R8 <sup>+</sup> ) III(O <sup>+</sup> ,S <sup>+</sup> ,S <sup>+</sup> ) IV(O <sup>+</sup> ,S <sup>+</sup> ,S <sup>+</sup> )
PGDW21	43.25167095	-108.5912762	140.2	DW	water	(R8 <sup>+</sup> )	(K)	(L)	-----	(L,R8 <sup>+</sup> )	-----	-----	(R8 <sup>+</sup> )
PGDW22	43.24452934	-108.5981513	-----	DW	water	(R8 <sup>+</sup> ) (R8 <sup>+</sup> )	(K) (A4)	(L) (A,R8 <sup>+</sup> )	-----	(L,R8 <sup>+</sup> ) (A,R8 <sup>+</sup> )	(E <sup>+</sup> ) (E <sup>+</sup> ,R8 <sup>+</sup> )	(F <sup>+</sup> ) (F <sup>+</sup> )	(R8 <sup>+</sup> ) (R8 <sup>+</sup> )
PGDW23	43.24866472	-108.6275943	152.4	DW	water	(R8 <sup>+</sup> ) (R8 <sup>+</sup> )	(K) (A4)	(L) (A,R8 <sup>+</sup> ) IV(R8 <sup>+</sup> ,S <sup>+</sup> )	IV(S <sup>+</sup> ,R3)	(L,R8 <sup>+</sup> ) (A,R8 <sup>+</sup> ) IV(R8 <sup>+</sup> )	(F <sup>+</sup> ) (E <sup>+</sup> ,R8 <sup>+</sup> )	(L <sup>+</sup> ) (L <sup>+</sup> )	(R8 <sup>+</sup> ) (R8 <sup>+</sup> ) IV(S <sup>+</sup> ,S <sup>+</sup> )
PGDW24	43.25877211	-108.6015039	30.5	DW	water	(R8 <sup>+</sup> )	(K)	(L)	-----	(L,R8 <sup>+</sup> )	-----	-----	-----
PGDW25	43.25558722	-108.5694867	243.8	DW	water	(R8 <sup>+</sup> ) (R8 <sup>+</sup> )	(K) (A4)	(L) (A,R8 <sup>+</sup> )	-----	(L,R8 <sup>+</sup> ) (A,R8 <sup>+</sup> )	(E <sup>+</sup> ,R8 <sup>+</sup> )	(E <sup>+</sup> )	(R8 <sup>+</sup> ) (R8 <sup>+</sup> )
PGDW26	43.25512275	-108.6132115	19.8	DW	water	(R8 <sup>+</sup> ) IV(O <sup>+</sup> )	(K)	(L) IV(R8 <sup>+</sup> ,S <sup>+</sup> )	IV(S <sup>+</sup> ,R3)	(L,R8 <sup>+</sup> ) IV(R8 <sup>+</sup> )	IV(R8 <sup>+</sup> )	-----	(R8 <sup>+</sup> ) IV(O <sup>+</sup> ,O <sup>+</sup> ,S <sup>+</sup> )
PGDW28	43.23993143	-108.6465688	25.9	DW	water	(R8 <sup>+</sup> )	(K)	(L)	-----	(L,R8 <sup>+</sup> )	-----	-----	-----
PGDW29	43.21773909	-108.6288449	121.9	DW	water	(R8 <sup>+</sup> )	(K)	(L)	-----	(L,R8 <sup>+</sup> )	(E <sup>+</sup> )	-----	(R8 <sup>+</sup> )

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Sample	Latitude	Longitude	Depth (m bgs)	Type	Media	Major anions and alkalinity phase(lab)	Metals phase(lab)	Alcohols and VOCs phase(lab)	Low molecular weight acids, glycols phase(lab)	SVOCs Pesticides PCBs, TICs phase(lab)	GRO, DRO, THE, TPH phase(lab)	Bacteria phase(lab)	Fixed gases, C <sub>1</sub> -C <sub>4</sub> , δ <sup>13</sup> C and δD C <sub>1</sub> -C <sub>4</sub> , DOC DIC, δ <sup>13</sup> C DIC δ <sup>18</sup> O and δD water phase(lab)
PGDW30	43.25753218	-108.6275755	79.2	DW	water	II(R8) II(R8) III(O) IV(O)	II(K), II(A4) III(S <sup>1</sup> ), IV(S <sup>1</sup> )	II(L, RR <sup>1</sup> ) III(RR <sup>1</sup> , S <sup>1</sup> ) IV(RR <sup>1</sup> , S <sup>1</sup> )	IV(S <sup>1</sup> , R3)	II(L, RR <sup>1</sup> ) II(A, RR <sup>1</sup> ) III(RR <sup>1</sup> ) IV(RR <sup>1</sup> )	II(E <sup>1</sup> ) III(RR <sup>1</sup> ) IV(RR <sup>1</sup> )	III(F)	II(RR <sup>1</sup> ) II(RR <sup>1</sup> ) III(F <sup>1</sup> , O <sup>1</sup> , S <sup>1</sup> , S <sup>1</sup> ) IV(F <sup>1</sup> , O <sup>1</sup> , S <sup>1</sup> , S <sup>1</sup> )
PGDW31	43.27302485	-108.6615302	-----	DW	water	II(R8)	II(K)	II(L)	-----	II(L, RR <sup>1</sup> )	-----	-----	-----
PGDW32	43.24075756	-108.5941561	205.7	DW	water	II(R8) II(RR <sup>1</sup> ) IV(O)	II(K), II(A4), IV(S <sup>1</sup> )	II(L, II(A) IV(RR <sup>1</sup> , S <sup>1</sup> )	IV(S <sup>1</sup> , R3)	II(L, RR <sup>1</sup> ) II(A, RR <sup>1</sup> ) IV(RR <sup>1</sup> )	II(E <sup>1</sup> , RR <sup>1</sup> ) IV(RR <sup>1</sup> )	III(F)	II(RR <sup>1</sup> ) II(RR <sup>1</sup> ) IV(F <sup>1</sup> , O <sup>1</sup> , S <sup>1</sup> )
PGDW33	43.23855527	-108.5964146	9.1	DW	water	II(R8)	II(K)	II(L)	-----	II(L, RR <sup>1</sup> )	-----	-----	-----
PGDW34	43.23605297	-108.6058086	30.5	DW	water	II(R8)	II(K)	II(L)	-----	II(L, RR <sup>1</sup> )	-----	-----	-----
PGDW35	43.23021564	-108.6241763	88.4	DW	water	II(R8)	II(K)	II(L)	-----	II(L, RR <sup>1</sup> )	-----	-----	II(RR <sup>1</sup> )
PGDW36	43.25905726	-108.5987059	30.5	DW	water	II(R8)	II(K)	II(L)	-----	II(L, RR <sup>1</sup> )	II(E <sup>1</sup> )	-----	-----
PGDW37	43.24016136	-108.6585376	24.4	DW	water	II(R8)	II(K)	II(L)	-----	II(L, RR <sup>1</sup> )	II(E <sup>1</sup> )	-----	-----
PGDW38	43.2296703	-108.572037	48.8	DW	water	II(R8)	II(K)	II(L)	-----	II(L, RR <sup>1</sup> )	II(E <sup>1</sup> )	-----	II(RR <sup>1</sup> )
PGDW39	43.23750687	-108.5781708	6.1	DW	water	II(L), II(R8)	II(L), II(A4)	II(L), II(A, RR <sup>1</sup> )	-----	II(L, RR <sup>1</sup> ) II(A, RR <sup>1</sup> )	-----	II(E <sup>1</sup> )	-----
PGDW40	43.26156616	-108.6198273	67.1	DW	water	II(R8)	II(A4)	II(A, RR <sup>1</sup> )	-----	II(A, RR <sup>1</sup> )	II(E <sup>1</sup> , RR <sup>1</sup> )	II(E <sup>1</sup> )	II(F <sup>1</sup> , RR <sup>1</sup> )
PGDW41	43.262146	-108.6378479	114.6	DW	water	II(R8), IV(O)	II(A4) IV(S <sup>1</sup> )	II(A, RR <sup>1</sup> ) IV(RR <sup>1</sup> , S <sup>1</sup> )	IV(S <sup>1</sup> , R3)	II(A, RR <sup>1</sup> ) IV(RR <sup>1</sup> )	II(E <sup>1</sup> , RR <sup>1</sup> ) IV(RR <sup>1</sup> )	II(E <sup>1</sup> )	II(F <sup>1</sup> , RR <sup>1</sup> ) IV(F <sup>1</sup> , S <sup>1</sup> , S <sup>1</sup> )
PGDW42	43.25574493	-108.6473116	61.0	DW	water	II(R8)	II(A4)	II(A, RR <sup>1</sup> )	-----	II(A, RR <sup>1</sup> )	II(F <sup>1</sup> , RR <sup>1</sup> )	II(F <sup>1</sup> )	II(F <sup>1</sup> , RR <sup>1</sup> )
PGDW43	43.25749207	-108.64151	-----	DW	water	II(R8)	II(A4)	II(A, RR <sup>1</sup> )	-----	II(A, RR <sup>1</sup> )	II(E <sup>1</sup> , RR <sup>1</sup> )	II(E <sup>1</sup> )	II(F <sup>1</sup> , RR <sup>1</sup> )
PGDW44	43.25056975	-108.6261292	238.6	DW	water	II(R8)	II(A4)	II(A, RR <sup>1</sup> ) IV(RR <sup>1</sup> , S <sup>1</sup> )	IV(S <sup>1</sup> , R3)	II(A, RR <sup>1</sup> ) IV(RR <sup>1</sup> )	II(E <sup>1</sup> , RR <sup>1</sup> )	II(E <sup>1</sup> )	II(RR <sup>1</sup> ) IV(F <sup>1</sup> , O <sup>1</sup> , S <sup>1</sup> )
PGDW45	43.25888062	-108.6130142	-----	DW	water	II(R8), IV(O)	II(A4) IV(S <sup>1</sup> )	II(A, RR <sup>1</sup> ) IV(RR <sup>1</sup> , S <sup>1</sup> )	IV(S <sup>1</sup> , R3)	II(A, RR <sup>1</sup> ) IV(RR <sup>1</sup> )	II(F <sup>1</sup> , RR <sup>1</sup> ) IV(RR <sup>1</sup> )	II(E <sup>1</sup> )	II(RR <sup>1</sup> ) IV(F <sup>1</sup> , O <sup>1</sup> , S <sup>1</sup> )
PGDW46	43.24651337	-108.6157684	14.6	DW	water	II(R8)	II(A4)	II(A, RR <sup>1</sup> )	-----	II(A, RR <sup>1</sup> )	II(F <sup>1</sup> , RR <sup>1</sup> )	II(E <sup>1</sup> )	II(F <sup>1</sup> , RR <sup>1</sup> )
PGDW47	43.24520493	-108.6319885	147.5	DW	water	II(R8)	II(A4)	II(A, RR <sup>1</sup> )	-----	II(A, RR <sup>1</sup> )	II(F <sup>1</sup> , RR <sup>1</sup> )	II(E <sup>1</sup> )	II(RR <sup>1</sup> )
PGDW48	43.2295881	-108.6235733	-----	DW	water	II(R8)	II(A4)	II(A, RR <sup>1</sup> )	-----	II(A, RR <sup>1</sup> )	II(F <sup>1</sup> , RR <sup>1</sup> )	II(E <sup>1</sup> )	II(RR <sup>1</sup> )
PGDW49	43.25505829	-108.6178741	-----	DW	water	II(R8)	II(A4)	II(A, RR <sup>1</sup> ) IV(RR <sup>1</sup> , S <sup>1</sup> )	-----	II(A, RR <sup>1</sup> ) IV(RR <sup>1</sup> )	II(E <sup>1</sup> , RR <sup>1</sup> )	II(E <sup>1</sup> )	II(RR <sup>1</sup> ) IV(F <sup>1</sup> , O <sup>1</sup> , S <sup>1</sup> )
PGPW01	43.24678802	-108.6879349	~ 154	PGP	water	II(R8)	II(A4)	II(A, RR <sup>1</sup> )	-----	II(A, RR <sup>1</sup> )	II(F <sup>1</sup> , RR <sup>1</sup> )	II(F <sup>1</sup> )	II(F <sup>1</sup> , RR <sup>1</sup> )
PGPW02	43.24697113	-108.6840515	~ 154	PGP	water	II(R8)	II(A4)	II(A, RR <sup>1</sup> )	-----	II(A, RR <sup>1</sup> )	II(F <sup>1</sup> , RR <sup>1</sup> )	II(F <sup>1</sup> )	II(F <sup>1</sup> , RR <sup>1</sup> )
LD-02	43.25167095	-108.5912762	185.9	DW	water	III(O)	III(S <sup>1</sup> )	III(S <sup>1</sup> )	-----	III(RR <sup>1</sup> )	-----	-----	III(F <sup>1</sup> , O <sup>1</sup> , S <sup>1</sup> , S <sup>1</sup> )



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### Laboratories, Analytes, and Methods

A - ALS Laboratory Group, Salt Lake City, UT. VOCs, SVOCs, pesticides, TCBS, TICs determined using methods specified under the CLP.

A4 - A4 Scientific, The Woodlands, TX. TAL metals determined using methods specified under the CLP.

E<sup>1</sup> - Energy Laboratories Inc., Billings, MT. Heterotrophic plate counts, iron reducing bacteria, sulfur reducing bacteria.

E<sup>2</sup> - Energy Laboratories Inc., Billings, MT. GRO, DRO, THE, and TPH.

I<sup>1</sup> - Isotech Laboratories, Champaign, IL under contract by EnCana. Fixed gases and light hydrocarbons determined using ASTM D1945-03 in gas samples and headspace of aqueous samples.  $\delta^{13}\text{C}$  and  $\delta\text{D}$  for  $\text{C}_1$  determined using gas stripping and IRMS in aqueous samples.  $\delta^{13}\text{C}$  and  $\delta\text{D}$  for  $\text{C}_1$ - $\text{C}_4$  determined using IRMS for gas samples.

I<sup>2</sup> - Isotech Laboratories, Champaign, IL. Fixed gases and light hydrocarbons determined using ASTM D1945-03 in headspace of aqueous samples.  $\delta^{13}\text{C}$  and  $\delta\text{D}$  for  $\text{C}_1$  and  $\delta^{13}\text{C}$  for  $\text{C}_2$  and  $\text{C}_3$  determined using gas stripping and IRMS in aqueous samples.  $\delta^{13}\text{C}$  DIC using gas stripping and IRMS.

I<sup>3</sup> - Isotech Laboratories, Champaign, IL. Fixed gases and light hydrocarbons determined using ASTM D1945-03 in headspace of aqueous samples.  $\delta^{13}\text{C}$  and  $\delta\text{D}$  for  $\text{C}_1$ ,  $\delta^{13}\text{C}$  for  $\text{C}_2$  -  $\text{C}_5$ , and  $\delta^{13}\text{C}$  for DIC gas stripping and IRMS in aqueous samples.

I<sup>4</sup> - Isotech Laboratories, Champaign, IL. Fixed gases and light hydrocarbons determined using ASTM D1945-03 in gas samples.  $\delta^{13}\text{C}$  and  $\delta\text{D}$  for  $\text{C}_1$  -  $\text{C}_3$  using IRMS in gas samples.

I<sup>5</sup> - Isotech Laboratories, Champaign, IL. Fixed gases and light hydrocarbons determined using ASTM D1945-03 in gas samples.  $\delta^{13}\text{C}$  and  $\delta\text{D}$  for  $\text{C}_1$  -  $\text{C}_3$  using IRMS in gas samples.  $^{14}\text{C}$  using AMS in gas samples.

K - KAP Laboratories, Vancouver, WA. TAL metals determined under the CLP.

L - Liberty Analytical, Salt Lake City, UT. VOCs, SVOCs, PCBs, and TICs determined under the CLP.

O<sup>1</sup> - EPA, ORD, Ada, OK.  $\text{SO}_4$ , Cl, F, and Br determined using RSKSOP 276v3 and EPA Method 6500.  $\text{NO}_3$  +  $\text{NO}_2$  and  $\text{NH}_4$  determined using RSKSOP 214v5 and EPA Method 350.1 and 353.2

O<sup>2</sup> - EPA, ORD, Ada, OK. DIC and DOC determined using RSKSOP-330v0 and EPA Method 9060A.

O<sup>3</sup> - EPA, ORD, Ada, OK.  $\text{C}_1$  determined using RSKSOP 175v5 and Cali-5 gas sampling bags.

R3 - U.S. EPA Region 3 Laboratory, Fort Mead, MD. Diethylene glycol, triethylene glycol, tetraethylene glycol, and 2-butoxyethanol analysis by LC/MS/MS. This method is under development with no finalized SOP. EPA Methods 8000C and 8321 were followed for method development and QA/QC limits where applicable.

R8<sup>1</sup> - U.S. EPA Region 8 Laboratory, Golden, CO (fluoride, chloride, nitrite-N, nitrate-N, orthophosphate-P, and sulfate determined using EPA Method 300.0 and EPA Region SOP 310. Alkalinity determined using EPA Method 310.0).

R8<sup>2</sup> - U.S. EPA Region 8 Laboratory, Golden, CO. VOCs determined using EPA Method 8260B.

R8<sup>3</sup> - U.S. EPA Region 8 Laboratory, Golden, CO. SVOCs determined using ORGM-515 r1.1 and EPA Method 8270D.

R8<sup>4</sup> - U.S. EPA Region 8 Laboratory, Golden, CO. GRO determined using ORGM-506 r1.0 and EPA Method 8015D. DRO determined using ORGM-508 r1.0 and EPA Method 8015D.

R8<sup>5</sup> - U.S. EPA Region 8 Laboratory, Golden, CO. Dissolved  $\text{C}_1$  in Phase I and dissolved  $\text{C}_1$ - $\text{C}_3$  in Phase II using EPA Method 524.2.

S<sup>1</sup> - Shaw Inc, Ada, OK in Phases III and IV. Metals and metals speciation determined using RSKSOP 213v4 and 257v2, or 332V0 and EPA Methods 200.7 and 6020.

S<sup>2</sup> - Shaw Inc, Ada, OK in Phases III and IV. Aromatics and chlorinated hydrocarbons determined using method RSKSOP-259v1 and EPA Method 5021A plus 8260C.

S<sup>3</sup> - Shaw Inc, Ada, OK. Alcohols, aromatics, and chlorinated hydrocarbons determined using method RSKSOP-259v1.

S<sup>4</sup> - Shaw Inc, Ada, OK. Low molecular weight acids determined using RSKSOP-112v6.

S<sup>5</sup> - Shaw Inc, Ada, OK. Dissolved gases  $\text{C}_1$ - $\text{C}_4$  determined using RSKSOP 194v4 and 175v5.

S<sup>6</sup> - Shaw Inc, Ada, OK. Hydrogen and oxygen isotope ratios of water determined using RSKSOP-296v0.

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## Abbreviations

I () - Phase I(laboratory/method). Samples collected March, 2009	VOCs - volatile organic compounds
II() - Phase II(laboratory/method). Samples collected January, 2010	SVOCs - semivolatile organic compounds
III() - Phase III(laboratory/method). Samples collected September and October 2010	PCBs - polychlorinated biphenyls
IV() - Phase IV(laboratory/method). Samples collected April 2011.	TICs - tentatively identified compounds
PG - gas production well	DRO - diesel range organics
MW - deep monitoring wells	GRO - gasoline range organics
PGM - shallow monitoring wells near pits	TEH - total extractable hydrocarbons
PGS - soil samples near pits	TPH - total purgeable hydrocarbons
DW - domestic wells	DIC - dissolved inorganic carbon
PGP - municipal wells in the Town of Pavillion	TAL - target analyte list
IRMS - isotope-ratio mass spectrometry	CLP - U.S. EPA Contract Laboratory Program
AMS - accelerated mass spectrometry	
C <sub>1</sub> (methane), C <sub>2</sub> (ethane), C <sub>3</sub> (propane), iC <sub>4</sub> (isobutane), nC <sub>4</sub> (normal butane), iC <sub>5</sub> (isopentane), nC <sub>5</sub> (normal pentane), C <sub>6</sub> <sup>+</sup> (hexanes + other light hydrocarbons)	

## Analytical Methods

- ORGM-506 r1.0 - Region 8 Standard Operating Procedure.
- ORGM-508 r1.0 - Region 8 Standard Operating Procedure. .
- ORGM-515 r1.1 - Region 8 Standard Operating Procedure.
- 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.
- RSKSOP-314v1 - Determination of Fixed Gases using the GEM2000 and GEM2000 Plus Gas Analyzers & Extraction Monitors, 13 p.
- RSKSOP-320v1 - Determination of Organic and Inorganic Vapors Using the TVA-1000B Toxic Vapor Analyzer, 18 p.
- RSKSOP-330v0 – Determination of Various Fractions of Carbon in Aqueous Samples Using the Shimadzu TOC-VCPH Analyzer, 16 p.
- U.S. EPA Method 200.7 - Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Spectrometry, Rev. 5, Jan 2001.
- U.S. EPA Method 300.0 - Determination of Inorganic Anions by Ion Chromatography, Rev. 2.1, Aug. 1993.
- U.S. EPA method 310.1 - Alkalinity (Titrimetric, pH 4.5), Rev. 1978.
- U.S. EPA Method 350.1 - Determination of Ammonia Nitrogen by Semi-Automated Colorimetry, Rev. 2, Aug. 1993.

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- U.S. EPA Method 5021A - Volatile Organic Compounds in Various Sample Matrices Using Equilibrium Headspace Analysis, Rev. 1, June 2003.
- U.S. EPA Method 6020 - Inductively Coupled Plasma-Mass Spectrometry, Rev. 1, Feb. 2007.
- U.S. EPA Method 6500 - Dissolved Inorganic Anions in Aqueous Matrices by Capillary Electrophoresis, Rev. 0, Feb. 2007.
- U.S. EPA Method 8260C - Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), Rev. 3, Aug. 2006.
- U.S. EPA Method 8015B - Determination of Nonhalogenated Organics Using GC/FID, Rev. 2, Dec. 1996.
- U.S. EPA Method 8015D - Nonhalogenated Organics Using GC/FID, Rev. 4, May 2003.
- U.S. EPA Method 8270D - Determination of Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), Rev. 4, Feb. 2007.
- U.S. EPA Method 8000C - Determinative Chromatographic Separations, Rev. 3, Mar. 2003.
- U.S. EPA Method 8260C - Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), Rev. 3, Aug. 2006.
- U.S. EPA Method 8270D - Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), Rev. 4, Feb. 2007.
- U.S. EPA Method 9060A - Total Organic Carbon, Rev. 1, Nov. 2004.

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**Table A2a. Geochemical results for Pavillion ground water**

Sample ID	T (°C)	pH	SC (µS/cm)	Alkalinity (mg/kg)	Na (ppm)	K (ppm)	Ca (ppm)	Mg (ppm)	Cl (ppm)	SO <sub>4</sub> (ppm)	F (ppm)	NO <sub>3</sub> (N) (ppm)
PGDW01	-----	-----	-----	234	808	6.2	398	93.6	34.3	1860	0.4	6.2
PGDW02	13.4	8.11	551	108	86	1.8	34.8	5.3	2.6	175	0.7	<0.5
PGDW03	11.1	9.37	1333	40	272	0.4	16.3	0.3	25.1	549	0.9	<0.5
PGDW04	11.8	9.17	1370	29	270	0.4	18.0	0.1	21.6	551	0.9	<0.5
PGDW05	12.0	9.02	956	93	192	0.3	3.6	0.1	17	295	0.9	<0.5
PGDW06	13.8	10.20	1262	35	249	0.3	7.1	<0.1	31	485	1.3	<0.5
PGDW07	12.4	8.85	1016	61	213	0.3	8.9	0.1	15.7	390	1.2	<0.5
PGDW08	12.4	8.57	1883	83	390	0.6	36.7	0.2	18.9	857	0.5	<0.5
PGDW09	12.4	8.35	1128	254	233	2.1	16.6	4.1	10.5	279	2.4	3.2
PGDW10	12.2	8.95	948	147	204	0.4	6.1	0.1	8.0	293	0.9	<0.5
PGDW11	13.1	7.17	3400	312	423	5.5	363	80.9	15.3	1780	0.2	1.3
PGDW12	12.4	10.04	1344	37	256	0.6	7.8	0.4	30.8	497	1.5	<0.5
PGDW13	10.9	6.89	1155	303	196	1.9	61.0	19.9	6.2	343	0.7	1.0
PGDW14	10.8	7.85	2990	159	690	4.5	154	18.1	26.1	1820	0.4	0.7
PGDW15	11.4	7.48	1728	277	269	1.2	72.2	10.2	9.9	520	0.6	1.8
PGDW16	13.2	9.30	1011	145	188	0.3	6.4	0.1	13.4	258	0.8	<0.5
PGDW17	12.7	9.61	1490	21	278	0.4	21.2	0.5	49.5	583	2.0	<0.5
PGDW18	10.3	8.87	2002	21	509	0.8	84.5	0.3	27	1380	1.8	0.5
PGDW19	11.8	7.75	707	291	194	1.4	29.0	3.2	6.9	196	0.9	2.6
PGDW20	9.3	8.76	2005	70	520	1.0	79.3	9.3	34.5	1370	0.8	<0.5
PGDW22	8.3	6.93	6180	332	837	9.0	416	126	79.9	2720	<0.2	43.6
PGDW23	11.5	9.43	816	61	208	0.3	6.5	0.1	19.8	365	1.2	<0.5
PGDW24	9.7	7.65	4700	165	938	7.0	327	131	55.7	3200	0.6	<0.5
PGDW25	13.3	8.68	972	205	249	1.1	1.1	1.1	8.4	355	4.1	<0.5
PGDW26	9.2	7.13	2390	337	220	6.8	364	57.7	14.6	1240	0.7	1.5
PGDW28	10.7	8.30	1170	258	239	2.2	40.6	12.9	16.7	298	0.5	3.7
PGDW29	11.5	9.72	1442	52	298	0.4	19.7	0.5	52.3	596	0.9	<0.5
PGDW30	10.4	9.60	902	96	210	0.3	0.9	0.1	16.3	331	0.9	<0.5
PGDW31	9.0	8.60	2006	83	435	0.9	31.2	0.8	13.3	1030	0.4	0.5
PGDW32	9.5	10.47	908	34	199	0.3	7.2	<0.1	34.1	373	2.3	<0.5
PGDW33	3.7	7.77	1662	276	178	5.0	228	40.9	28	670	0.2	2.1
PGDW34	8.3	7.87	4480	373	786	7.4	325	113	23	2690	0.5	3.5
PGDW35	10.6	8.63	2810	84	587	1.1	118	1.1	24.1	1610	0.3	0.5
PGDW36	9.8	7.62	649	232	42	2.6	89.5	28.9	3.2	195	1.0	1.2
PGDW37	10.5	8.14	819	342	187	0.9	12.1	1.3	8.7	89.9	0.9	1.2
PGDW38	9.5	8.68	2030	47	373	2.3	70.0	2.3	46.9	908	1.3	5.9
PGDW39	6.7	7.79	6410	127	1110	5.3	389	147	52.9	3640	0.4	0.6
PGDW40	11.5	9.06	1229	86	244	5.0	6.6	5.0	13.1	426	-----	<0.3
PGDW41	7.2	7.63	4470	108	1030	2.7	270	57.5	31.4	2670	0.5	<0.3
PGDW42	12.1	9.18	888	89	181	5.0	5.1	5.0	13.2	311	1.0	<0.3
PGDW43	0.2	8.19	4410	113	911	5.0	208	13.7	38.4	2470	0.4	<0.3
PGDW44	9.4	8.13	4080	100	994	5.0	259	28.3	39.5	2880	0.3	<0.3
PGDW45	9.3	7.63	1103	379	59	2.6	138	31.2	14.5	213	1.9	0.3
PGDW46	7.9	7.79	855	329	91	1.8	90.3	9.9	8.4	126	0.5	2.3
PGDW47	8.2	9.52	970	44	183	5.0	6.9	5.0	21.6	330	1.5	<0.3
PGDW48	8.7	8.21	3550	90	725	5.0	147	4.4	24.1	1840	0.3	<0.3
PGDW49	7.8	7.66	5470	243	1210	11.4	486	153	64.3	3160	0.4	7.7
PGDW03-0110	8.3	8.71	1390	28	251	5.0	16.3	5.0	20.7	570	0.8	<0.3
PGDW04-0110	8.3	9.07	1388	38	265	5.0	15.5	5.0	23.3	532	0.9	-----
PGDW05-0110	9.4	8.22	900	88	188	5.0	3.3	5.0	16.5	287	0.9	<0.3
PGDW10-0110	10.4	8.62	985	147	195	5.0	5.8	5.0	7.5	293	0.9	<0.3
PGDW20-0110	9.3	8.89	2690	68	550	5.0	71.7	8.1	32.6	1270	0.8	<0.3
PGDW22-0110	8.2	7.06	4230	337	908	5.8	397	130	74.6	2780	-----	40.7
PGDW23-0110	8.2	9.72	780	54	194	5.0	5.8	5.0	19.7	368	1.5	<0.3
PGDW25-0110	7.2	7.94	1511	295	269	5.0	70.1	9.6	9.5	441	-----	1.7
PGDW30-0110	9.2	9.39	967	94	195	5.0	4.1	5.0	15.5	333	0.9	<0.3
PGDW32-0110	8.3	9.87	1018	32	193	5.0	6.9	5.0	21.4	368	2.4	<0.3

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Sample ID	T (°C)	pH	SC (µS/cm)	Alkalinity mg/kg	Na (ppm)	K (ppm)	Ca (ppm)	Mg (ppm)	Cl (ppm)	SO <sub>4</sub> (ppm)	F (ppm)	NO <sub>3</sub> (N) (ppm)
MW01	11.8	11.91	3265	430	334	54.9	15.6	0.05	23.3	398	1.6	0.15
MW02	12.3	12.01	3812	456	420	39.5	73.3	0.03	466	12.1	1.0	0.38
RD01	11.5	9.24	1068	78	208	0.2	4.3	0.10	15.2	357	1.0	0.23
LD01	10.9	8.85	2940	54	562	1.1	71.9	8.1	33.0	1320	0.9	0.35
PGDW05-0411	10.5	9.06	820	80	190	0.24	3.35	0.08	16.8	276	1.2	ND
PGDW14-0411	8.5	7.73	3473	156	753	3.52	154	18.6	23.7	1760	<0.05	0.36
PGDW20-0411	8.3	8.59	2430	102	520	0.78	63	6.86	22.9	1150	1.3	<0.03
PGDW23-0411	11.0	9.07	959	72	208	0.31	6.7	0.17	19.9	365	1.6	<0.03
PGDW26-0411	8.3	6.95	2390	196	232	5.15	334	56	13.2	1180	1.0	1.37
PGDW30-0411	10.4	8.92	938	82	210	0.29	4.5	0.09	16.1	327	1.1	<0.03
PGDW32-0411	11.1	9.30	885	46	198	0.09	7.2	0.03	18.8	361	2.0	<0.03
PGDW41-0411	8.2	7.05	4866	112	896	3.18	452	46.9	97.6	2640	<0.05	17.5
PGDW44-0411	10.0	8.17	4730	94	1060	2.09	259	19.2	32.1	2900	<0.05	<0.03
PGDW45-0411	9.1	6.85	1085	364	61.6	2.81	159	34.5	18.4	251	1.7	0.64
PGDW49-0411	10.4	7.34	5333	296	982	9.66	417	127	54.3	3200	<0.05	8.75
MW01-0411	11.2	11.24	2352	388	304	24.7	13.6	0.12	23.1	339	1.9	<0.03
MW02-0411	12.0	11.78	3099	482	448	43.6	60.5	0.03	457	63	1.5	<0.03

----- not measured. SC – specific conductance. Alkalinity – mg/kg CaCO<sub>3</sub>. Other cations detected include Al (0.05 to 0.74 ppm), Ba (0.01 to 0.21 ppm), Fe (<0.02 to 2.4 ppm), Mn (<0.01 to 0.23 ppm), NH<sub>4</sub><sup>+</sup> (0.4 to 4.6 ppm), and Sr (0.06 to 8.4 ppm). Sulfide was detected in LD01 (0.16 ppm, Phase III, same location as PGDW20), PGDW20 (0.12 ppm, Phase IV), and MW01 (1.1 ppm Phase III, 1.8 ppm Phase IV). Turbidity ranged from 1.7 to 29.7 in domestic wells (Phase III and IV). Turbidity in MW01 was 7.5 (Phase III) and 7.9 (Phase IV). Turbidity in MW02 was 28.8 (Phase III) and 24.0 (Phase IV). All turbidity values are in Nephelometric Turbidity Units (NTUs). Turbidity measurements in MW01 and MW02 could be impacted by gas exsolution.

**Table A2b. Charge balance calculations for deep monitoring wells**

Well	Phase	Ca, meq	Mg, meq	Na, meq	K, meq	SO <sub>4</sub> , meq	CO <sub>3</sub> , meq	Cl, meq	F, meq	OH, meq	Σcat, meq	Σan, meq	Balance, %
		<i>cations</i>				<i>anions</i>							
MW01	III	0.78	0.00	14.53	1.40	8.29	4.48	0.66	0.08	9.56	16.71	23.08	16.0
MW02	III	3.66	0.00	18.27	1.01	0.25	3.40	13.14	0.05	12.04	22.94	28.89	11.5
MW01	IV	0.68	0.01	13.22	0.63	7.06	2.12	0.65	0.10	1.97	14.54	11.90	10.0
MW02	IV	3.02	0.00	19.49	1.12	1.30	0.23	12.89	0.08	7.01	23.62	21.52	4.7

Balance (%) = |(Σcat-Σan)/(Σcat+Σan)\*100|. meq OH is calculated as 1000\*[α<sub>OH-</sub>/γ<sub>OH-</sub>], where α<sub>OH-</sub> = 10<sup>-(14-pH)</sup> and γ<sub>OH-</sub> = 0.85 to 0.88. meq CO<sub>3</sub> is estimated from measurements of Dissolved Inorganic Carbon (DIC) as 2\*[DIC/12], where DIC is in mg/L.

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Table A3a. Summary of aqueous analysis of light hydrocarbons						
Sample (matrix)	Phase	Date	C <sub>1</sub> (ug/l)	C <sub>2</sub> (ug/l)	C <sub>3</sub> (ug/l)	C <sub>4</sub> (ug/l)
MW01(w)	III	10/6/2010	15950	2230	790	158
MW01(w)	IV	4/20/2011	17930	2950	1250	172
MW02(w)	III	10/6/2010	18990	3290	1820	355
MW02(w)	IV	4/19/2011	18820	2550	2260	276
MW02(w)-dup	IV	4/19/2011	22620	3120	2770	356
PGMW01(w)	II	01/21/10	474	nd(10)	nd(15)	-----
PGMW02(w)	II	01/21/10	361	299	43.8	-----
PGMW03(w)	II	01/21/10	528	nd(10)	nd(15)	-----
PGDW03(w)	II	01/20/10	nd(5.0)	nd(10)	nd(15)	-----
PGDW04(w)	I	03/03/09	nd(5.0)	-----	-----	-----
PGDW04(w)	II	01/21/10	nd(5.0)	nd(10)	nd(15)	-----
PGDW05(w)	I	03/03/09	16.6	-----	-----	-----
PGDW05(w)	II	01/18/10	5.44	nd(10)	nd(15)	-----
PGDW05(w)	IV	04/19/11	65*	discarded	nd(1.3)	nd(1.6)
PGDW07(w)	I	03/03/09	nd(5.0)	-----	-----	-----
PGDW10(w)	I	03/03/09	nd(5.0)	-----	-----	-----
PGDW10(w)	II	01/18/10	nd(5.0)	nd(10)	nd(15)	-----
PGDW14(w)	IV	04/20/11	discarded	nd(1.3)	nd(1.4)	nd(1.7)
PGDW17(w)	I	03/04/09	10.6	-----	-----	-----
PGDW20(w)	I	03/04/09	137	-----	-----	-----
PGDW20(w)	III	10/06/10	189	24.3	nd(0.22)	nd(0.21)
PGDW20(w)-dup	III	10/06/10	168	17.4	nd(0.22)	nd(0.21)
PGDW20(w)	IV	04/18/11	137	discarded	nd(1.43)	2.93
PGDW21(w)	I	03/04/09	54.3	-----	-----	-----
PGDW22(w)	I	03/04/09	nd(5.0)	-----	-----	-----
PGDW22(w)	II	01/18/10	nd(5.0)	nd(10)	nd(15)	-----
PGDW23(w)	I	03/04/09	146	-----	-----	-----
PGDW23(w)	II	01/18/10	149	nd(10)	nd(15)	-----
PGDW23(w)	IV	04/21/11	176	nd(5.7)	nd(6.6)	nd(6.9)
PGDW25(w)	II	01/19/10	nd(5.0)	nd(10)	nd(15)	-----
PGDW26(w)	I	03/05/09	nd(5.0)	-----	-----	-----
PGDW26(w)	IV	04/18/11	nd(2.2)*	nd(1.4)	nd(1.5)	nd(1.8)
PGDW29(w)	I	03/05/09	nd(5.0)	-----	-----	-----
PGDW30(w)	I	03/05/09	558	-----	-----	-----
PGDW30(w)	II	01/19/10	808	nd(10)	nd(15)	-----
PGDW30(w)	III	10/05/10	762	nd(0.19)	nd(0.23)	nd(0.21)
PGDW30(w)	IV	04/18/11	644	discarded	nd(1.5)	4.6
PGDW32(w)	I	03/05/09	21.4	-----	-----	-----

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Sample (matrix)	Phase	Date	C <sub>1</sub> (ug/l)	C <sub>2</sub> (ug/l)	C <sub>3</sub> (ug/l)	C <sub>4</sub> (ug/l)
PGDW32(w)	II	01/20/10	36.3	nd(10.0)	nd(15.0)	-----
PGDW32(w)	IV	04/18/11	nd(2.2)*	nd(1.2)	nd(1.3)	nd(1.5)
PGDW32(w)-dup	IV	04/18/11	discarded	discarded	nd(1.4)	discarded
PGDW35(w)	I	03/05/09	21.6	-----	-----	-----
PGDW38(w)	I	03/05/09	nd(5.0)	-----	-----	-----
PGDW39(w)	II	01/19/10	nd(5.0)	nd(10.0)	nd(15.0)	-----
PGDW40(w)	II	01/22/10	98.9	nd(10.0)	nd(15.0)	-----
PGDW41(w)	II	01/21/10	nd(5.0)	nd(10.0)	nd(15.0)	-----
PGDW41(w)	IV	04/20/11	385	142	nd(1.35)	discarded
PGDW42(w)	II	01/19/10	60	nd(10.0)	nd(15.0)	-----
PGDW43(w)	II	01/21/10	nd(5.0)	nd(10.0)	nd(15.0)	-----
PGDW44(w)	II	01/18/10	nd(5.0)	nd(10.0)	nd(15.0)	-----
PGDW44(w)	IV	4/21/2011	nd(2.2)*	nd(1.3)	nd(1.4)	nd(1.7)
PGDW45(w)	II	01/18/10	nd(5.0)	nd(10.0)	nd(15.0)	-----
PGDW45(w)	IV	04/19/11	nd(2.2)*	discarded	nd(1.3)	nd(1.6)
PGDW46(w)	II	01/20/10	nd(5.0)	nd(10.0)	nd(15.0)	-----
PGDW47(w)	II	01/19/10	nd(5.0)	nd(10.0)	nd(15.0)	-----
PGDW48(w)	II	01/20/10	nd(5.0)	nd(10.0)	nd(15.0)	-----
PGDW49(w)	II	01/20/10	nd(5.0)	nd(10.0)	nd(15.0)	-----
PGDW49(w)	IV	4/20/2011	nd(2.2)*	discarded	nd(1.3)	nd(1.6)
LD02(w)	III	10/20/2010	229	21	nd(0.24)	nd(0.23)
PGPW01(w)	II	01/20/10	nd(5.0)	nd(10.0)	nd(15.0)	-----
PGPW02(w)	II	01/20/10	nd(5.0)	nd(10.0)	nd(15.0)	-----
Travel Blank(w)	III	10/6/2010	23.3	nd(2.0)	nd(0.24)	nd(0.23)
Equipment Blank(w)	III	10/6/2010	23.0	nd(2.0)	nd(0.29)	nd(0.27)
Field Blank(w)	III	10/6/2010	76.4	nd(2.0)	nd(0.28)	nd(0.26)
Travel Blank(w)	IV	4/14/2011	18.5	56.4	nd(1.63)	nd(1.6)
Field Blank(w)	IV	4/18/2011	45.0	67.9	nd(1.36)	nd(1.66)
equipment blank(w) (on-site GC analysis)	IV	4/18/2011	nd(2.2)	-----	-----	-----
equipment blank(w) (on-site GC analysis)	IV	4/19/2011	nd(2.2)	-----	-----	-----
equipment blank(w) (on-site GC analysis)	IV	4/20/2011	nd(2.2)	-----	-----	-----
equipment blank(w) (on-site GC analysis)	IV	4/20/2011	nd(2.2)	-----	-----	-----
field blank(w)	IV	4/21/2011	nd(0.32)	nd(1.18)	nd(1.27)	nd(1.54)

\* Determined by on-site GC analysis in Phase IV. Fixed laboratory analysis rejected in Phase IV if detection of methane and ethane less than 100 µg/L.

All values of methane in Phase III greater than 100 µg/L accepted.

Ultrapure nitrogen was used for equipment and travel blanks for on-site GC analysis.

nd() - not detected(detection limit) ----- not analyzed

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Table A3b. Summary of gas and headspace analysis of light hydrocarbons											
Sample (matrix)	Phase	Date	C <sub>1</sub> (%)	C <sub>2</sub> (%)	C <sub>2</sub> H <sub>4</sub> (%)	C <sub>3</sub> (%)	iC <sub>4</sub> (%)	nC <sub>4</sub> (%)	iC <sub>5</sub> (%)	nC <sub>5</sub> (%)	C <sub>6</sub> + (%)
Tribal Pavillion 14-6(g) (WR)	----	Johnson and Rice (1993)	95.28	2.83	----	0.3	0.11	0.18	0.05	0.02	----
Govt 21-5(g) (WR)	----	Johnson and Rice (1993)	93.24	3.75	----	0.73	0.33	0.22	0.16	0.09	----
Tribal Pavillion 41-09(g) (FU)	----	Johnson and Rice (1993)	88.17	3.35	----	0.36	0.14	0.09	nd	nd	----
Tribal Pavillion 14-11(g) (FU)	----	Johnson and Rice (1993)	66.00	1.96	----	0.06	0.054	0.006	0.006	0.002	----
Blankenship 4-8(g) (FU)	----	Johnson and Rice (1993)	93.38	4.00	----	0.41	0.05	0.06	0.07	0.01	----
Tribal Pavillion 14-10(g) (WR)(PGPP01)	II	01/21/10	92.47	4.04	0.001	1.21	0.415	0.372	0.183	0.114	0.486
Tribal Pavillion 43-10(g) (FU)(PGPP02)	II	01/21/10	94.86	3.48	0.0001	0.356	0.143	0.0618	0.0501	0.0194	0.18
Tribal Pavillion 24-2(g) (WR)(PGPP04)	II	01/21/10	90.16	4.64	0.0017	1.46	0.581	0.512	0.335	0.211	1.39
Tribal Pavillion 33-10(g) (FU)(PGPP05)	II	01/21/10	94.68	3.64	nd	0.373	0.131	0.055	0.0427	0.014	0.107
Tribal Pavillion 14-2(g) (FU)(PGPP06)	II	01/21/10	93.23	3.93	0.0012	0.903	0.321	0.25	0.151	0.0905	0.506
MW01(g)	III	9/23/2010	84.22	3.43	0.0007	0.791	0.327	0.191	0.143	0.0632	0.111
MW01(w)	III	10/6/2010	35.11	2.02	0.0008	0.414	0.114	0.0871	0.0499	0.0241	0.0539
MW01(g)	IV	4/18/2011	89.43	3.92	0.0013	0.907	0.298	0.211	0.109	0.0574	0.0972
MW01(g)-dup	IV	4/18/2011	89.49	3.91	0.0013	0.902	0.295	0.206	0.103	0.0533	0.0804
MW01(w)	IV	4/20/2011	38.33	2.46	0.0016	0.504	0.113	0.101	0.0422	0.0229	0.0566
MW02(g)	III	9/24/2010	1.05	0.048	nd	0.022	0.0089	0.0053	0.0020	0.0008	0.0012
MW02(g)-dup	III	9/24/2010	1.04	0.048	nd	0.022	0.0089	0.0053	0.0020	0.0008	0.0009
MW02(w)	III	10/6/2010	28.03	2.16	nd	0.693	0.128	0.101	0.0185	0.0067	0.0174
MW02(g)	IV	4/18/2011	6.74	0.383	nd	0.142	0.0401	0.026	0.0070	0.0025	0.0034
MW02(g)-dup	IV	4/18/2011	7.41	0.422	nd	0.156	0.0439	0.0284	0.0077	0.0027	0.0035
MW02(w)	IV	4/19/2011	26.17	1.80	nd	0.765	0.259	0.147	0.0416	0.0141	0.0237
MW02(w)-dup	IV	4/19/2011	21.32	1.49	nd	0.623	0.204	0.118	0.0324	0.011	0.018
PGMW01(w)	II	01/21/10	2.47	nd	nd	nd	0.0054	0.005	0.0287	0.0092	0.537
PGMW02(w)	II	01/21/10	3.57	1.13	nd	0.103	0.402	0.0134	0.13	0.0003	0.398
PGDW03(w)	II	01/20/10	0.0122	nd	nd	nd	nd	nd	nd	nd	nd
PGDW04(w)	II	01/21/10	0.0036	nd	nd	nd	nd	nd	nd	nd	nd
PGDW05(w)	IV	04/19/11	0.0966	nd	nd	nd	nd	nd	nd	nd	nd
PGDW10(w)	II	01/18/10	0.0266	nd	nd	nd	nd	nd	nd	nd	nd
PGDW14(w)	IV	04/20/11	0.0005	nd	nd	nd	nd	nd	nd	nd	nd



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Sample (matrix)	Phase	Date	C <sub>1</sub> (%)	C <sub>2</sub> (%)	C <sub>2</sub> H <sub>4</sub> (%)	C <sub>3</sub> (%)	iC <sub>4</sub> (%)	nC <sub>4</sub> (%)	iC <sub>5</sub> (%)	nC <sub>5</sub> (%)	C <sub>6</sub> + (%)
PGDW20 (w)	III	10/06/10	0.191	0.007	nd	0.0006	nd	nd	nd	nd	nd
PGDW20(w)-dup	III	10/06/10	0.134	0.005	nd	nd	nd	nd	nd	nd	nd
PGDW20(w)	IV	04/18/11	0.221	0.007	nd	0.0007	nd	nd	nd	nd	nd
PGDW22(w)	II	01/18/10	nd	nd	nd	nd	nd	nd	nd	nd	nd
PGDW23(w)	IV	04/21/11	0.248	nd	nd	nd	nd	0.0015	nd	nd	0.0008
PGDW25(w)	II	01/19/10	nd	nd	nd	nd	nd	nd	nd	nd	nd
PGDW26(w)	IV	04/18/11	nd	nd	nd	nd	nd	nd	nd	nd	nd
PGDW30(w)	II	01/19/10	5.99	nd	nd	nd	nd	nd	nd	nd	nd
PGDW30(g)	III	09/23/10	0.0123	nd	nd	nd	nd	nd	nd	nd	nd
PGDW30(w)	III	10/05/10	1.19	nd	nd	nd	nd	nd	nd	nd	nd
PGDW30(w)	IV	04/18/11	1.46	nd	nd	nd	nd	nd	nd	nd	nd
PGDW32(w)	II	01/20/10	0.197	nd	nd	nd	nd	nd	nd	nd	0.0085
PGDW32(w)	IV	04/18/11	0.0752	nd	nd	nd	nd	nd	nd	nd	0.0019
PGDW32(w)-dup	IV	04/18/11	0.0522	nd	nd	nd	nd	nd	nd	nd	0.0013
PGDW39(w)	II	01/19/10	nd	nd	nd	nd	nd	nd	nd	nd	nd
PGDW40(w)	II	01/22/10	0.418	nd	nd	nd	nd	nd	nd	nd	nd
PGDW41(w)	II	01/21/10	0.0091	nd	nd	nd	nd	nd	nd	nd	nd
PGDW41(w)	IV	04/20/11	0.0005	nd	nd	nd	nd	nd	nd	nd	nd
PGDW42(w)	II	01/19/10	0.291	nd	nd	nd	nd	nd	nd	nd	nd
PGDW43(w)	II	01/21/10	0.0016	nd	nd	nd	nd	nd	nd	nd	nd
PGDW44(w)	IV	4/21/11	0.0022	nd	nd	nd	nd	nd	nd	nd	nd
PGDW45(w)	II	01/18/10	nd	nd	nd	nd	nd	nd	nd	nd	nd
PGDW45(w)	IV	04/19/11	nd	nd	nd	nd	nd	nd	nd	nd	nd
PGDW46(w)	II	01/20/10	0.0016	nd	nd	nd	nd	nd	nd	nd	nd
PGDW47(w)	II	01/19/10	0.0428	nd	nd	nd	nd	nd	nd	nd	nd
PGDW47(w)-dup	II	01/19/10	0.0365	nd	nd	nd	nd	nd	nd	nd	nd
PGDW49(w)	IV	4/20/11	nd	nd	nd	nd	nd	nd	nd	nd	nd
LD02(w)	III	10/20/10	0.12	0.007	nd	0.001	0.0008	0.0007	nd	0.0005	nd
PGPW01(w)	II	01/20/10	0.0253	nd	nd	nd	nd	nd	nd	nd	nd
PGPW02(w)	II	01/20/10	0.0389	nd	nd	nd	nd	nd	nd	nd	nd
field blank(w)	II	01/21/10	0.0068	nd	nd	nd	nd	nd	nd	nd	0.0021
field blank(w)	II	01/22/10	nd	nd	nd	nd	nd	nd	nd	nd	nd
travel blank(g)	III	9/23/10	nd	nd	nd	nd	nd	nd	nd	nd	nd
equipment blank(g)	III	9/23/10	0.0029	nd	nd	nd	nd	nd	nd	nd	nd
travel blank(g)	III	9/24/10	nd	nd	nd	nd	nd	nd	nd	nd	nd
equipment blank(g)	III	9/24/10	nd	nd	nd	nd	nd	nd	nd	nd	nd
travel blank(g)	IV	4/18/11	nd	nd	nd	nd	nd	nd	nd	nd	nd
equipment blank(g)	IV	4/18/11	nd	nd	nd	nd	nd	nd	nd	nd	nd
equipment blank(g)	IV	4/18/11	nd	nd	nd	nd	nd	nd	nd	nd	nd

WR - Wind River Formation

FU - Fort Union Formation

---- not analyzed

nd () not detected

Table A3c. Summary of isotopic data for dissolved, gas phase, and headspace analysis

Sample (matrix)	Phase	Date	$\delta^{13}C_{C_1}$ (‰)	$\delta D_{C_1}$ (‰)	$\delta^{13}C_{C_2}$ (‰)	$\delta D_{C_2}$ (‰)	$\delta^{13}C_{C_3}$ (‰)	$\delta D_{C_3}$ (‰)	$\delta^{13}C_{C_4}$ (‰)	$\delta^{13}C_{C_5}$ (‰)	$\delta^{13}C_{n-C_4}$ (‰)	$\delta D_{n-C_4}$ (‰)	$\delta^{13}C_{i-C_4}$ (‰)	$\delta^{13}C_{n-C_5}$ (‰)	$\delta^{13}C_{i-C_5}$ (‰)	$\delta^{13}C_{DIC}$ (‰)	$\delta^{18}O_{H_2O}$ (‰)	$\delta D_{H_2O}$ (‰)
Tribal Pavilion 14-6(g) (WR)	----	Johnson and Rice (1993)	-39.24	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
Govt 21-5(g) (WR)	----	Johnson and Rice (1993)	-40.2	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
Tribal Pavilion 41-09(g) (FU)	----	Johnson and Rice (1993)	-38.04	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
Tribal Pavilion 14-11(g) (FU)	----	Johnson and Rice (1993)	-38.4	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
Blankenship 4-8(g) (FU)	----	Johnson and Rice (1993)	-38.08	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
Tribal Pavilion 14-10(g) (WR)(PGPP01)	II	01/21/10	-38.75	-203.4	-26.93	-162.5	-24.93	-147.2	-25.83	-152.4	-25.26	-151.3	-----	-----	-----	-----	-----	-----
Tribal Pavilion 43-10(g) (FU)(PGPP02)	II	01/21/10	-39.07	-212.9	-25.99	-157.5	-19.4	-----	-----	-----	-23.87	-----	-----	-----	-----	-----	-----	-----
Tribal Pavilion 24-2(g) (WR)(PGPP04)	II	01/21/10	-39.26	-204.9	-26.79	-166.2	-25.33	-148.0	-25.66	-155.5	-25.05	-154	-----	-----	-----	-----	-----	-----
Tribal Pavilion 33-10(g) (FU)(PGPP05)	II	01/21/10	-39.05	-207.3	-26.21	-161.1	-18.46	-101.7	-23.96	-----	-23.64	-----	-----	-----	-----	-----	-----	-----
Tribal Pavilion 14-2(g) (FU)(PGPP06)	II	01/21/10	-39.28	-215.3	-26.42	-162.3	-24.01	-145.2	-25.33	-150.1	-24.87	-152	-----	-----	-----	-----	-----	-----
MW01(g)	III	9/23/2010	-39.44	-209.1	-26.63	-165.0	-23.76	-143.7	-----	-----	-----	-----	-----	-----	-----	<0.2	-----	-----
MW01(w)	III	10/6/2010	-38.89	-191.3	-26.55	-----	-23.85	-----	-----	-----	-----	-----	-----	-----	-----	-12.18	-13.77	-113.77
MW01(g)	IV	4/18/2011	-39.25	-211.2	-26.67	-166.8	-23.74	-146.1	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
MW01(g)-dup	IV	4/18/2011	-39.28	-210.1	-26.67	-167.4	-23.91	-146.6	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
MW01(w)	IV	4/20/2011	-38.88	-211.6	-26.70	-----	-24.40	-----	-25.3	-----	-24.4	-----	-----	-----	-----	-12.01	-13.26	-109.53
MW02(g)	III	9/24/2010	-41.85	-209.4	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
MW02(g)-dup	III	9/24/2010	-41.72	-209.2	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----

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Sample (matrix)	Phase	Date	$\delta^{13}C_{C_1}$ (‰)	$\delta D-C_1$ (‰)	$\delta^{13}C_{C_2}$ (‰)	$\delta D-C_2$ (‰)	$\delta^{13}C_{C_3}$ (‰)	$\delta D-C_3$ (‰)	$\delta^{13}C_{C_4}$ (‰)	$\delta D-C_4$ (‰)	$\delta^{13}C-nC_5$ (‰)	$\delta^{13}C-nC_6$ (‰)	$\delta D-nC_6$ (‰)	$\delta^{13}C-nC_7$ (‰)	$\delta^{13}C-nC_8$ (‰)	$\delta^{13}C$ DIC (‰)	$\delta^{18}O_{H_2O}$ (‰)	$\delta D_{H_2O}$ (‰)
MW02(w)	III	10/6/2010	-41.83	-203.8	-26.4	-24.28	-----	-----	-----	-----	-----	-----	-----	-----	-----	Low DIC	-15.55	-117.41
MW02(g)	IV	4/18/2011	-41.05	-208.9	-26.10	-24.05	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
MW02(g)-dup	IV	4/18/2011	-41.01	-210.8	-26.09	-24.06	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
MW02(w)	IV	4/19/2011	-41.30	-210.7	-26.25	-24.29	-----	-25.3	-----	-----	-----	-----	-----	-24.3	-----	Low DIC	-14.24	-113.42
MW02(w)-dup	IV	4/19/2011	-41.37	-208.2	-26.28	-24.28	-----	-25.3	-----	-----	-----	-----	-----	-24.5	-----	Low DIC	-14.27	-113.46
PGDW05(w)	IV	04/19/11	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
PGDW14(w)	IV	04/20/11	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
PGDW20 (w)	III	10/06/10	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
PGDW20(w)-dup	III	10/06/10	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
PGDW20(w)	IV	04/18/11	-33.1	-175	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-13.18	-107.38
PGDW23(w)	IV	04/21/11	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-13.31	-108.35
PGDW30(w)	II	01/19/10	-28.77	-143.6	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-12.40	-97.35
PGDW30(w)	III	10/05/10	-28.76	-145.8	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
PGDW30(w)	IV	04/18/11	-27.8	-133	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-13.02	-109.78
PGDW32(w)	IV	04/18/11	-34.2	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-13.23	-108.11
PGDW32(w)-dup	IV	04/18/11	-34.0	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-13.28	-108.24
PGDW41(w)	IV	04/20/11	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-12.31	-121.93
PGDW44(w)	IV	4/21/2011	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-10.35	-100.29
PGDW45(w)	IV	04/19/11	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-14.18	-128.18
PGDW49(w)	IV	4/20/2011	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-11.05	-122.19
LD02(w)	III	10/20/2010	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-18.58	-109.20

WR - Wind River Formation

FU - Fort Union Formation

----- not analyzed

nd () - not detected

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## Appendix B

# Quality Assurance and Quality Control (QA/QC) for Analysis

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**Table B1.** Sample collection containers, preservation, and holding times for ground-water samples for Phase III and IV

Sample Type	Analysis Method (EPA Method)	Sample Bottles/# of bottles*	Preservation/Storage	Holding Time(s)
Dissolved gases	RSKSOP-194v4 &-175v5 (No EPA Method)	60 mL serum bottles/2	No Headspace TSP <sup>†</sup> , pH>10; refrigerate 4°C <sup>††</sup>	14 days
Metals (filtered)	RSKSOP-213v4 &-257v3 (EPA Methods 200.7 and 6020)	125 mL plastic bottle/1	HNO <sub>3</sub> , pH<2; room temperature	6 months (Hg 28 days)
SO <sub>4</sub> , Cl, F, Br	RSKSOP-276v3 (EPA Method 6500)	30 mL plastic/1	Refrigerate ≤4°C	28 days
NO <sub>3</sub> + NO <sub>2</sub> , NH <sub>4</sub>	RSKSOP-214v5 (EPA Method 350.1 and 353.2)	30 mL plastic/1	H <sub>2</sub> SO <sub>4</sub> , pH<2; refrigerate ≤4°C	28 days
DIC	RSKSOP-102v5 or 330v0 (EPA Method 9060A)	40 mL clear glass VOA vial/2	refrigerate ≤4°C	14 days
DOC	RSKSOP-102v5 or 330v0 (EPA Method 9060A)	40 mL clear glass VOA vial/2	H <sub>3</sub> PO <sub>4</sub> , pH<2; refrigerate ≤4°C	28 days
VOCs	RSKSOP-299v1 or 259v1 (EPA Method 5021A plus 8260C)	40 mL amber glass VOA vial/2	No Headspace TSP <sup>†</sup> , pH>10; refrigerate ≤4°C	14 days
Low Molecular Weight Acids	RSKSOP-112V6 (No EPA Method)	40 mL glass VOA vial/2	TSP <sup>†</sup> , pH>10; refrigerate ≤4°C	30 days
O, H stable isotopes of water	RSKSOP-296v0 (No EPA Method)	20 mL glass VOA vial/1	Refrigerate at ≤4°C	Stable
δ <sup>13</sup> C DIC	Isotech: gas stripping and IRMS (No EPA Method)	60 mL plastic bottle/1	Refrigerate ≤4°C	No information
δ <sup>13</sup> C and δD of methane	Isotech: gas stripping and IRMS (No EPA Method)	1 L plastic bottle/1	Caplet of benzalkonium chloride; refrigerate ≤4°C	No information
SVOCs	ORGM-515 r1.1, EPA Method 8270D	1L amber glass bottle/2 and for every 10 samples of ground water need 2 more bottles for one selected sample, or if <10 samples collected, collect 2 more bottles for one select sample	Refrigerate ≤4°C	7 days until extraction, 30 days after extraction
DRO	ORGM-508 r1.0, EPA Method 8015D	1L amber glass bottle/2 and for every 10 samples of ground water need 2 more bottles for one selected sample, or if <10 samples collected, collect 2 more bottles for one select sample	HCl, pH<2; refrigerate ≤4°C	7 days until extraction, 40 days after extraction
GRO	ORGM-506 r1.0, EPA Method 8015D	40 mL amber glass VOA vial/2 and for every 10 samples of ground water need 2 more bottles for one selected sample, or if <10 samples collected, collect 2 more bottles for one select sample	No headspace; HCl, pH<2; refrigerate ≤4°C	14 days
Glycols	Region III method** (No EPA Method)	40 mL amber glass VOA vial/2	Refrigerate ≤4°C	14 days

<sup>†</sup> Trisodium phosphate

<sup>††</sup> Above freezing point of water

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

\*\*EPA Methods 8000C and 8321 were followed for method development and QA/AC limits were applicable.

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QC Sample	Purpose	Method	Frequency
<b>Trip Blanks (VOCs and Dissolved Gases only)</b>	Assess contamination during transportation.	Fill bottles with reagent water and preserve, take to field and returned without opening.	One in an ice chest with VOA and dissolved gas samples.
<b>Equipment Blanks</b>	Assess contamination from field equipment, sampling procedures, decontamination procedures, sample container, preservative, and shipping.	Apply only to samples collected via equipment, such as filtered samples: Reagent water is filtered and collected into bottles and preserved same as filtered samples.	One per day of sampling with submersible pumps
<b>Field Duplicates</b>	Represent precision of field sampling, analysis, and site heterogeneity.	One or more samples collected immediately after original sample.	One in every 10 samples, or if <10 samples collected for a water type (ground or surface), collect a duplicate for one sample.
<b>Temperature Blanks</b>	Measure temperature of samples in the cooler.	Water sample that is transported in cooler to lab.	One per cooler.
<b>Field Blanks**</b>	Assess contamination introduced from sample container with applicable preservative.	In the field, reagent water is collected into sample containers with preservatives.	One per day of sampling.

\* Reporting limit or Quantitation Limit

\*\* Blank samples were not collected for isotope measurements, including O, H, C.

Measurement	Analysis Method	Blanks (Frequency)	Calibration Checks (Frequency)	Second Source (Frequency)	Duplicates (Frequency)	Matrix Spikes (Frequency)
<b>Metals</b>	RSKSOP-213v4 (EPA Methods 200.7 and 6020)	<QL for 80% of metals; (Beginning and end of each sample queue, 10-15 samples)	90-110% of known value ( Beginning and end of each sample queue, 10-15 samples)	PE sample acceptance limits or 90-110% of known value (Immediately after first calibration check)	RPD<10 for 80% of metals; for results <5x QL, difference of ≤QL.(Every 15 samples)	90-110% Rec. for 80% of metals w/ no individual exceeding 50-150% Rec. (one per sample set, 10-15 samples)
<b>Metals</b>	RSKSOP-257v3 (EPA Methods 200.7 and 6020)	<QL for 80% of metals; none>10xMDL (Beginning and end of each sample queue, 10-15 samples)	90-110% of known value ( Beginning and end of each sample queue, 10-15 samples)	PE sample acceptance limits or 90-110% of known value (Immediately after first calibration check)	RPD<10 for 80% of metals; for results <5xQL, difference of <QL (Every 15 samples)	90-110% Rec. for 80% of metals w/ no individual exceeding 70-130% (one per sample set, 10-15 samples)
<b>SO<sub>4</sub>, Cl, F, Br</b>	RSKSOP-2 (EPA Method 6500)76v3	<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)
<b>NO<sub>3</sub> + NO<sub>2</sub>, NH<sub>4</sub></b>	RSKSOP-214v5 (EPA Method 350.1 and 353.2)	<½ lowest calib. std. (Beginning and end of each sample queue)	90-110% Rec. (Beginning, end, and every 10 samples)	PE sample acceptance limits (One per sample set)	RPD<10 (every 10 samples)	80-120% Rec (one per every 20 samples)

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<b>Table B4. QA/QC requirements for analysis of dissolved gases, DIC/DOC, VOCs, low molecular weight acids and stable isotopes of water</b>						
<b>Measurement</b>	<b>Analysis Method</b>	<b>Blanks (Frequency)</b>	<b>Calibration Checks (Frequency)</b>	<b>Second Source (Frequency)</b>	<b>Duplicates (Frequency)</b>	<b>Matrix Spikes (Frequency)</b>
<b>Dissolved gases</b>	RSKSOP-194v4 &-175v5 (No EPA Method)	≤MDL (He/Ar blank, first and last in sample queue; water blank before samples)	85-115% of known value (After helium/Ar blank at first of analysis queue, before helium/Ar blank at end of sample set, and every 15 samples)	85-115% of known value (After first calibration check)	RPD≤20 (Every 15 samples)	NA
<b>DIC/DOC</b>	RSKSOP-102v5 (Phase III) or 330v0 (Phase IV) (EPA Method 9060A)	- 102v5: <½QL (after initial calib., every 10-15 samples, and at end) -330v0: < MDL (Beginning and end of sample set)	-102v5: 80-120% of known value (after initial calib., every 10-15 samples, and at end-330v0: 90-100% of known value (Beginning and end of sample set and every 10 samples)	-102v5: 80-120% of known value (Immediately after calibration) -330v0: PE sample reported acceptance limits. Others: 90-100% recovery (one per sample set)	-102v5: RPD<10 (every 15 samples) -330v0: RPD<10 (every 10 samples)	-102v5:80-120% Rec. (one per 20 or every set) -330v0:80-120% Rec.
<b>Volatile organic compounds (VOC)**</b>	RSKSOP-299v1 and -259v1 (EPA Method 5021A plus 8260C)	<MDL (Beginning and end of each sample set)	80-120% Rec. (Beginning, end, and every 20 samples)	80-120% of known value Once at beginning (and at end for -259v1)	-299v1 RPD<20 -259v1 RPD<25 (every 20 samples)	70-130% Rec. (every 20 samples)
<b>Low Molecular Weight Acids</b>	RSKSOP-112v6 (No EPA Method)	<MDL (Beginning of a sample queue; every 10 samples; and end of sample queue)	85-115% of the recovery (Prior to sample analysis; every 10 samples; end of sample queue)	85-115% of recovery (Prior to sample analysis)	< 15 RPD (Every 20 samples through a sample queue)	80-120 % recovery (Every 20 samples through a sample queue)
<b>O, H stable isotopes of water***</b>	RSKSOP-296v1 (No EPA Method)	NA	Difference of calibrated/true < 1‰ for δ <sup>2</sup> H & < 0.2‰ for δ <sup>18</sup> O (Beginning, end and every tenth sample)	Working stds calibrated against IAEAstds.† (Beginning, end, and every tenth sample)	Standard deviation ≤ 1‰ for δ <sup>2</sup> H and < 0.2‰ for δ <sup>18</sup> O (every sample)	NA

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

\*\*Surrogate compounds spiked at 100 ug/L: p-bromofluorobenzene and 1,2-dichlorobenzene-d4, 85-115% recovery.

\*\*\*Additional checks: internal reproducibility prior to each sample set, std dev≤ 1‰ for δ<sup>2</sup>H and ≤ 1‰ for δ<sup>18</sup>O

†International Atomic Energy Agency (VSMOW, GISP, and SLAP)

Corrective actions are outlined in the SOPs.

MDL = Method Detection Limit

QL = Quantitation Limit

PE = Performance Evaluation



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<b>Table B5. QA/QC requirements for analysis of semi-volatiles, GRO, and DRO</b>				
<b>QC Type</b>	<b>Semivolatiles</b>	<b>DRO</b>	<b>GRO</b>	<b>Frequency</b>
<b>Method Blanks</b>	<RL Preparation or Method Blank, one with each set of extraction groups. Calibration Blanks are also analyzed	<RL Preparation or Method Blank	<RL Preparation or Method Blank and IBL	At least one per sample set
<b>Surrogate Spikes</b>	Limits based upon DoD statistical study (rounded to 0 or 5) for the target compound analyses.	60-140% of expected value	70-130% of expected value	Every field and QC sample
<b>Internal Standards Verification</b>	Every sample, EICP area within -50% to +100% of last ICV or first CCV.	NA	NA	Every field and QC sample
<b>Initial multilevel calibration</b>	ICAL: minimum of 6 levels (0.25 -12.5 ug/L) , one is at the MRL (0.50 ug/L), prior to sample analysis (not daily) RSD≤20%, r <sup>2</sup> ≥0.990	ICAL: 10-500 ug/L RSD≤20% or r <sup>2</sup> ≥0.990	ICAL: .25-12.5 ug/L for gasoline (different range for other compounds)  RSD≤20% or r <sup>2</sup> ≥0.990	As required (not daily if pass ICV)
<b>Initial and Continuing Calibration Checks</b>	80-120% of expected value	80-120% of expected value	80-120% of expected value	At beginning of sample set, every tenth sample, and end of sample set
<b>Second Source Standards</b>	ICV1 70-130% of expected value	ICV1 80-120% of expected value	ICVs 80-120% of expected value	Each time calibration performed
<b>Laboratory Control Samples (LCS)</b>	Statistical Limits from DoD LCS Study (rounded to 0 or 5) or if SRM is used based on those certified limits	Use an SRM: Values of all analytes in the LCS should be within the limits determined by the supplier.  Otherwise 70-130% of expected value	Use and SRM: Values of all analytes in the LCS should be within the limits determined by the supplier.  Otherwise 70-130% of expected value	One per analytical batch or every 20 samples, whichever is greater
<b>Laboratory Control Samples (LCS)</b>	Statistical Limits from DoD LCS Study (rounded to 0 or 5) or if SRM is used based on those certified limits	Use an SRM: Values of all analytes in the LCS should be within the limits determined by the supplier.  Otherwise 70-130% of expected value	Use and SRM: Values of all analytes in the LCS should be within the limits determined by the supplier.  Otherwise 70-130% of expected value	One per analytical batch or every 20 samples, whichever is greater
<b>Matrix Spikes (MS)</b>	Same as LCS	Same as LCS	70-130% of expected value	One per sample set or every 20 samples, whichever is more frequent
<b>MS/MSD</b>	% Recovery same as MS RPD ≤ 30	% Recovery same as MS RPD ≤ 25	% Recovery same as MS RPD ≤ 25	One per sample set or every 20 samples, whichever is more frequent
<b>Reporting Limits*</b>	0.1 µg/L (generally) <sup>1</sup> for target compounds HF special compounds are higher	20 µg/L <sup>1</sup>	20 µg/L <sup>2</sup>	NA

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

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

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<b>Table B6. QA/QC requirements for LC/MS/MS analysis of glycols</b>		
<b>QC Type</b>	<b>Performance Criteria</b>	<b>Frequency</b>
<b>Method Blanks</b>	<RL	One per every 20 samples
<b>Solvent Blanks</b>	<RL	One per every 10 samples
<b>Initial and Continuing Calibration Checks</b>	80-120% of expected value	At beginning of sample set, after every tenth sample, and end of sample set
<b>Second Source Standards</b>	80-120% of expected value	Each time calibration performed
<b>Laboratory Control Samples (LCS)</b>	80-120% of expected value	One per analytical batch or every 20 samples, whichever is greater
<b>Matrix Spikes (MS)</b>	70-130% of expected value	One per sample set or every 20 samples, whichever is more frequent
<b>MS/MSD</b>	RPD $\leq$ 25	One per sample set or every 20 samples, whichever is more frequent

RL = Reporting Limit

Corrective Actions: If re-analysis was not possible (such as lack of sample volume), the data was qualified with a determination about the impact on the sample data.

Table B7a. ICP-OES blank results for Phase III and Phase IV sampling

Label	Date	Al	Ag	B	Ba	Be	Ca	Co	Fe	K	Mg
		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Trip Blank	10/6/2010	nd	nd	nd	nd	nd	nd	BQL 0.001	nd	nd	nd
EQ Blank	10/7/2010	nd	nd	nd	nd	nd	BQL 0.009	nd	nd	nd	BQL 0.017
Field Blank	10/5/2010	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Trip Blank	4/14/2011	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Field Blank	4/18/2011	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Field Blank	4/21/2011	nd	nd	nd	nd	nd	nd	nd	nd	BQL 0.096	nd
Equip Blank	4/21/2011	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
MDL		0.045	0.015	0.006	0.001	0.001	0.007	0.001	0.019	0.038	0.015
QL		0.149	0.051	0.018	0.004	0.004	0.023	0.004	0.063	0.127	0.049
Detections in samples		17/21	0/21	21/21	21/21	7/21	21/21	2/21	12/21	21/21	21/21
Concentration min		0.054	nd	0.103	0.006	0.001	3.35	0.001	0.019	0.089	0.019
Concentration max		0.736	nd	0.378	0.210	0.003	452	0.002	2.41	54.9	56.0

BQL – below quantitation level. Units are mg/L. nd – not detected. MDL – method detection level. QL – quantitation level. Detections in samples: the number of times the analyte was detected in Phase III and Phase IV sampling. Minimum and maximum sample concentration in Phase III /Phase IV sampling activities in mg/L.

Table B7b. ICP-OES blank results for Phase III and Phase IV sampling

Label	Date	Mn	Mo	Na	Sb	Sr	Ti	Zn	Si	S	P
		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Trip Blank	10/6/2010	nd	nd	nd	nd	nd	nd	nd	BQL 0.077	nd	nd
EQ Blank	10/7/2010	BQL 0.001	nd	nd	nd	nd	nd	BQL 0.017	nd	2.04	nd
Field Blank	10/5/2010	nd	nd	nd	nd	nd	nd	BQL 0.011	nd	1.2	nd
Trip Blank	4/14/2011	nd	nd	nd	nd	nd	nd	nd	nd	nd	BQL 0.007
Field Blank	4/18/2011	nd	nd	nd	nd	nd	nd	nd	nd	nd	BQL 0.009
Field Blank	4/21/2011	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Equip Blank	4/21/2011	nd	nd	nd	nd	nd	nd	nd	nd	nd	BQL 0.011
MDL		0.001	0.002	0.040	0.006	0.001	0.001	0.007	0.037	0.121	0.004
QL		0.004	0.007	0.134	0.019	0.004	0.004	0.024	0.122	0.403	0.013
Detections in samples		16/21	14/21	21/21	11/21	21/21	4/21	15/21	21/21	21/21	5/21
Concentration min		0.001	0.006	61.6	0.007	0.058	0.001	0.009	2.93	6.76	0.008
Concentration max		0.231	0.019	1060	0.033	8.44	0.004	0.201	10.2	1140	0.024

BQL – below quantitation level. Units are mg/L. nd – not detected. MDL – method detection level. QL – quantitation level. Detections in samples: the number of times the analyte was detected in Phase III and Phase IV sampling. Minimum and maximum sample concentration in Phase III /Phase IV sampling activities in mg/L.

Table B7c. ICP-MS blank results for Phase III and Phase IV sampling

Label	Date	As µg/L	Cd µg/L	Cr µg/L	Cu µg/L	Hg µg/L	Ni µg/L	Pb µg/L	Se µg/L	Tl µg/L	U µg/L
Trip Blank	10/6/2010	BQL 0.096	nd	nd	0.96	0.46	nd	0.981	nd	0.014	-----
EQ Blank	10/7/2010	0.258	nd	0.086	BQL 0.65	nd	0.34	nd	nd	BQL 0.004	-----
Field Blank	10/5/2010	0.263	nd	BQL 0.018	nd	nd	nd	nd	nd	0.014	-----
Trip Blank	4/14/2011	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Field Blank	4/18/2011	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Field Blank	4/21/2011	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Equip Blank	4/21/2011	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
MDL		0.052	0.020	0.008	0.287	0.019	0.048	0.043	0.044	0.004	0.002
QL		0.173	0.067	0.124	0.957	0.064	0.160	0.143	0.147	0.013	0.007
Detections in samples		18/21	3/21	19/21	19/21	5/21	19/21	11/21	21/21	5/21	15/15
Concentration min		0.255	0.028	0.010	0.380	0.117	0.060	0.123	0.337	0.014	0.005
Concentration max		4.96	0.089	0.864	18.9	0.614	9.62	2.37	16.4	0.125	80.1

BQL – below quantitation level. Units are µg/L. ----- not measured. nd – not detected. MDL – method detection level. QL – quantitation level. Detections in samples: the number of times the analyte was detected in Phase III and Phase IV sampling. Minimum and maximum sample concentration in Phase III/Phase IV sampling activities in µg/L.

Table B8. Blank results for Capillary Electrophoresis, Lachat Flow Injection Analysis, Dissolved Inorganic Carbon (DIC) and Dissolved Organic Carbon analyses for Phase III and Phase IV sampling

Label	Date	Cl mg/L	SO <sub>4</sub> mg/L	F mg/L	NO <sub>3</sub> +NO <sub>2</sub> mg/L	NH <sub>4</sub> mg/L	DIC mg/L	DOC mg/L
Trip Blank	10/6/2010	nd	nd	nd	nd	nd	BQL 0.51	BQL 0.06
EQ Blank	10/7/2010	nd	nd	nd	nd	nd	BQL 0.17	BQL 0.03
Field Blank	10/5/2010	nd	nd	nd	nd	nd	BQL 0.08	BQL 0.04
Trip Blank	4/14/2011	nd	nd	nd	nd	nd	BQL 0.09	BQL 0.29
Field Blank	4/18/2011	nd	nd	nd	nd	nd	BQL 0.29	BQL 0.24
Field Blank	4/21/2011	nd	nd	nd	nd	nd	BQL 0.20	BQL 0.17
Equip Blank	4/21/2011	nd	nd	nd	nd	nd	BQL 0.18	BQL 0.28
MDL		0.136	0.103	0.056	0.005	0.014	0.103	0.103
QL		1.00	1.00	0.200	0.100	0.100	0.500	0.500
Detections in samples		21/21	21/21	17/21	11/21	16/21	21/21	21/21
Concentration min		13.2	12.1	0.90	0.08	0.04	1.4	0.51
Concentration max		466	3200	2.02	17.5	4.61	89.1	19.7

BQL – below quantitation level. Units are mg/L. nd – not detected. MDL – method detection level. QL – quantitation level. Detections in samples: the number of times the analyte was detected in Phase III and Phase IV sampling. Minimum and maximum sample concentration in Phase III/Phase IV sampling activities in mg/L.

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**Table B9.** Blank results for Volatile Organic Compounds (µg/L) in Phase III and Phase IV sampling (Region 8 laboratory, Golden, CO)

	Trip Blank	EQ Blank	Field Blank	Trip Blank	Field Blank	Field Blank	RL
	10/6/2010	10/7/2010	10/5/2010	4/14/2011	4/18/2011	4/21/2011	
1,1,1,2-Tetrachloroethane	nd	nd	nd	nd	nd	nd	0.25
1,1,1-Trichloroethane	nd	nd	nd	nd	nd	nd	0.25
1,1,2,2-Tetrachloroethane	nd	nd	nd	nd	nd	nd	0.25
1,1,2-Trichloroethane	nd	nd	nd	nd	nd	nd	0.25
1,1-Dichloroethane	nd	nd	nd	nd	nd	nd	0.25
1,1-Dichloroethene	nd	nd	nd	nd	nd	nd	0.25
1,1-Dichloropropene	nd	nd	nd	nd	nd	nd	0.25
1,2,3-Trichlorobenzene	nd	nd	nd	nd	nd	nd	0.25
1,2,3-Trichloropropane	nd	nd	nd	nd	nd	nd	0.25
1,2,4-Trichlorobenzene	nd	nd	nd	nd	nd	nd	0.25
1,2,4-Trimethylbenzene	nd	nd	nd	nd	nd	nd	0.25
1,2-Dibromo-3-chloropropane	nd	nd	nd	nd	nd	nd	0.25
1,2-Dibromoethane (EDB)	nd	nd	nd	nd	nd	nd	0.25
1,2-Dichlorobenzene	nd	nd	nd	nd	nd	nd	0.25
1,2-Dichloroethane	nd	nd	nd	nd	nd	nd	0.25
1,2-Dichloropropane	nd	nd	nd	nd	nd	nd	0.25
1,3,5-Trimethylbenzene	nd	nd	nd	nd	nd	nd	0.25
1,3-Dichlorobenzene	nd	nd	nd	nd	nd	nd	0.25
1,3-Dichloropropane	nd	nd	nd	nd	nd	nd	0.25
1,3-Dimethyl adamantane	nd	nd	nd	nd	nd	nd	0.25
1,4-Dichlorobenzene	nd	nd	nd	nd	nd	nd	0.25
2,2-Dichloropropane	nd	nd	nd	nd	nd	nd	0.25
2-Butanone	----	----	----	nd	0.64	0.82	0.50
2-Chlorotoluene	nd	nd	nd	nd	nd	nd	0.25
4-Chlorotoluene	nd	nd	nd	nd	nd	nd	0.25
4-Methyl-2-pentanone	----	----	----	nd	nd	nd	0.25
2-Hexanone	----	----	----	nd	0.29	0.41	0.25
Acetone	----	----	----	nd	1.03	1.38	1.00
Acrylonitrile	nd	nd	nd	nd	nd	nd	0.25
Adamantane	nd	nd	nd	nd	nd	nd	0.25
Allyl chloride	nd	nd	nd	nd	nd	nd	0.25
Benzene	nd	nd	nd	nd	nd	nd	0.03
Bromobenzene	nd	nd	nd	nd	nd	nd	0.25
Bromochloromethane	nd	nd	nd	nd	nd	nd	0.25
Bromodichloromethane	nd	nd	nd	nd	nd	nd	0.25
Bromoform	nd	nd	nd	nd	nd	nd	0.25
Bromomethane	nd	nd	nd	nd	nd	nd	0.25
Carbon disulfide	nd	nd	nd	nd	nd	nd	0.25
Carbon tetrachloride	nd	nd	nd	nd	nd	nd	0.25
Chlorobenzene	nd	nd	nd	nd	nd	nd	0.25
Chlorodibromomethane	nd	nd	nd	nd	nd	nd	0.25
Chloroethane	nd	0.25	nd	nd	nd	nd	0.25
Chloroform	nd	nd	nd	nd	nd	nd	0.25
Chloromethane	nd	nd	nd	1.04	nd	nd	0.25
cis-1,2-Dichloroethene	nd	nd	nd	nd	nd	nd	0.25
cis-1,3-Dichloropropene	nd	nd	nd	nd	nd	nd	0.25
Dibromomethane	nd	nd	nd	nd	nd	nd	0.25
Dichlorodifluoromethane	nd	nd	nd	nd	nd	nd	0.25
Ethyl Ether	nd	nd	nd	nd	nd	nd	0.25
Ethylbenzene	nd	nd	nd	nd	nd	nd	0.25
Hexachlorobutadiene	nd	nd	nd	nd	nd	nd	0.25
Hexachloroethane	nd	nd	nd	nd	nd	nd	0.25
Iodomethane	nd	nd	nd	nd	nd	nd	0.25
Isopropylbenzene	nd	nd	nd	nd	nd	nd	0.25
m,p-Xylene	nd	nd	nd	nd	0.69	0.70	0.50
Methacrylonitrile	nd	nd	nd	nd	0.27	nd	0.25

**DRAFT**

	Trip Blank	EQ Blank	Field Blank	Trip Blank	Field Blank	Field Blank	RL
	10/6/2010	10/7/2010	10/5/2010	4/14/2011	4/18/2011	4/21/2011	
Methyl Acrylate	nd	nd	nd	nd	nd	nd	0.25
Methyl tert-Butyl Ether	nd	nd	nd	nd	nd	nd	0.25
Methylene chloride	nd	nd	nd	nd	nd	nd	0.25
Naphthalene	nd	nd	nd	nd	nd	nd	0.25
n-Butyl Benzene	nd	nd	nd	nd	nd	nd	0.25
n-Propyl Benzene	nd	nd	nd	nd	nd	nd	0.25
o-Xylene	nd	nd	nd	nd	nd	nd	0.25
p-Isopropyltoluene	nd	nd	nd	nd	nd	nd	0.25
sec-Butylbenzene	nd	nd	nd	nd	nd	nd	0.25
Styrene	nd	nd	nd	nd	nd	nd	0.25
tert-Butylbenzene	nd	nd	nd	nd	nd	nd	0.25
Tetrachloroethene	nd	nd	nd	nd	nd	nd	0.25
Toluene	0.54	0.16	0.16	nd	nd	nd	0.25
trans-1,2-Dichloroethene	nd	nd	nd	nd	nd	nd	0.25
trans-1,3-Dichloropropene	nd	nd	nd	nd	nd	nd	0.25
Trichloroethene	nd	nd	nd	nd	nd	nd	0.25
Trichlorofluoromethane	nd	nd	nd	nd	nd	nd	0.25
Vinyl chloride	nd	nd	nd	nd	nd	nd	0.25
Xylenes (total)	nd	nd	nd	nd	nd	nd	0.75

RL – Reporting Limit (µg/L). nd – not detected. ---- not measured.

**DRAFT**

**Table B10.** Blank results for Volatile Organic Compounds (µg/L) in Phase IV sampling (ORD laboratory, Ada, OK)

	Trip Blank	Field Blank	Field Blank	MDL	QL
	4/14/2011	4/18/2011	4/21/2011		
Vinyl chloride	nd	nd	nd	0.14	1.0
1,1-Dichloroethene	nd	nd	nd	0.07	0.5
Methylene Chloride	nd	nd	nd	0.19	0.5
trans-1,2-Dichloroethene	nd	nd	nd	0.05	0.5
cis-1,2-Dichloroethene	nd	nd	nd	0.15	0.5
Chloroform	nd	nd	nd	0.07	0.5
1,1,1-Trichloroethane	nd	nd	nd	0.03	0.5
Carbon Tetrachloride	nd	nd	nd	0.04	0.5
1,2-Dichloroethane	nd	nd	nd	0.03	0.5
Trichloroethene	nd	nd	nd	0.07	0.5
1,1,2-Trichloroethane	nd	nd	nd	0.03	0.5
Tetrachloroethene	nd	nd	nd	0.09	0.5
Chlorobenzene	nd	nd	nd	0.04	0.5
1,3-Dichlorobenzene	nd	nd	nd	0.06	0.5
1,4-Dichlorobenzene	nd	nd	nd	0.04	0.5
1,2-Dichlorobenzene	nd	nd	nd	0.03	0.5
Ethanol	nd	nd	nd	0.11	1.0
Isopropanol	nd	nd	nd	24.7	100
n-Propanol	nd	nd	nd	11.4	100
Isobutanol	nd	nd	nd	13.5	100
n-Butanol	nd	nd	nd	15.6	100
tert-Butyl Alcohol	nd	nd	nd	15.5	100
Methyl tert-Butyl Ether	nd	nd	nd	1.72	5.0
di-Isopropyl Ether	nd	nd	nd	0.11	0.5
Ethyl tert-Butyl Ether	nd	nd	nd	0.11	0.5
Benzene	nd	nd	nd	0.03	0.5
tert-Amyl Methyl Ether	nd	nd	nd	0.06	0.5
2,5-Dimethylfuran	nd	nd	nd	0.06	0.5
Toluene	BQL 0.228	nd	BQL 0.227	0.03	0.5
1,2-Dibromoethane	nd	nd	nd	0.03	0.5
Ethyl Benzene	nd	nd	nd	0.09	1.0
m+p Xylene	BQL 0.229	nd	BQL 0.133	0.03	0.5
o-Xylene	nd	nd	nd	0.08	0.5
1,3,5-Trimethylbenzene	nd	nd	nd	0.03	0.5
1,2,4-Trimethylbenzene	nd	nd	nd	0.04	1.0
1,2,3-Trimethylbenzene	nd	nd	nd	0.02	1.0
Naphthalene	nd	nd	nd	0.04	1.0

All results in µg/L. MDL – method detection level. QL – quantitation level. nd – not detected.

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**Table B11.** Blank results for Semi-Volatile Organic Compounds (µg/L) in Phase III and Phase IV sampling (Region 8 laboratory, Golden, CO)

	Trip Blank	EQ Blank	Field Blank	Trip Blank	Field Blank	Field Blank	RL
	10/6/2010	10/7/2010	10/5/2010	4/14/2011	4/18/2011	4/21/2011	
1,2,4-Trichlorobenzene	nd	nd	nd	nd	nd	nd	0.100
1,2-Dichlorobenzene	nd	nd	nd	nd	nd	nd	0.100
1,2-Dinitrobenzene	nd	nd	nd	nd	nd	nd	0.100
1,3-Dichlorobenzene	nd	nd	nd	nd	nd	nd	0.100
1,3-Dinitrobenzene	nd	nd	nd	nd	nd	nd	0.100
1,4-Dichlorobenzene	nd	nd	nd	nd	nd	nd	0.100
1,4-Dinitrobenzene	nd	nd	nd	nd	nd	nd	0.100
1-Methylnaphthalene	nd	nd	nd	nd	nd	nd	0.100
2,3,4,6-Tetrachlorophenol	nd	nd	nd	nd	nd	nd	0.250
2,3,5,6-Tetrachlorophenol	nd	nd	nd	nd	nd	nd	0.250
2,4,5-Trichlorophenol	nd	nd	nd	nd	nd	nd	0.100
2,4,6-Trichlorophenol	nd	nd	nd	nd	nd	nd	0.100
2,4-Dichlorophenol	nd	nd	nd	nd	nd	nd	0.100
2,4-Dimethylphenol	nd	nd	nd	nd	nd	nd	0.100
2,4-Dichlorophenol	nd	nd	nd	nd	nd	nd	0.100
2,4-Dimethylphenol	nd	nd	nd	nd	nd	nd	0.100
2,4-Dinitrophenol	nd	nd	nd	nd	nd	nd	1.00
2,4-Dinitrotoluene	nd	nd	nd	nd	nd	nd	1.00
2,6-Dinitrotoluene	nd	nd	nd	nd	nd	nd	0.100
2-Chloronaphthalene	nd	nd	nd	nd	nd	nd	0.100
2-Chlorophenol	nd	nd	nd	nd	nd	nd	0.100
2-Methylnaphthalene	nd	nd	nd	nd	nd	nd	0.100
2-Methylphenol	nd	nd	nd	nd	nd	nd	0.100
2-Nitroaniline	nd	nd	nd	nd	nd	nd	0.100
2-Nitrophenol	nd	nd	nd	nd	nd	nd	0.100
3 & 4-Methylphenol	nd	nd	nd	nd	nd	nd	0.200
3,3'-Dichlorobenzidine	nd	nd	nd	nd	nd	nd	0.500
3-Nitroaniline	nd	nd	nd	nd	nd	nd	0.100
4,6-Dinitro-2-methylphenol	nd	nd	nd	nd	nd	nd	0.500
4-Bromophenyl phenyl ether	nd	nd	nd	nd	nd	nd	0.100
4-Chloro-3-methylphenol	nd	nd	nd	nd	nd	nd	0.100
4-Chloroaniline	nd	nd	nd	nd	nd	nd	0.100
4-Chlorophenyl phenyl ether	nd	nd	nd	nd	nd	nd	0.100
4-Nitroaniline	nd	nd	nd	nd	nd	nd	0.500
4-Nitrophenol	nd	nd	nd	nd	nd	nd	1.00
Acenaphthene	nd	nd	nd	nd	nd	nd	0.100
Acenaphthylene	nd	nd	nd	nd	nd	nd	0.100
Aniline	nd	nd	nd	nd	nd	nd	0.100
Anthracene	nd	nd	nd	nd	nd	nd	0.100
Azobenzene	nd	nd	nd	nd	nd	nd	0.100
Benzo (a) anthracene	nd	nd	nd	nd	nd	nd	0.100
Benzo (a) pyrene	nd	nd	nd	nd	nd	nd	0.100
Benzo (g,h,i) perylene	nd	nd	nd	nd	nd	nd	0.100
Benzo (k) fluoranthene	nd	nd	nd	nd	nd	nd	0.100
Benzo(b)fluoranthene	nd	nd	nd	nd	nd	nd	0.100
Benzoic acid	0.83	0.78	nd	3.00	nd	nd	0.500
Benzyl alcohol	nd	0.40	0.63	nd	nd	nd	0.500
Bis(2-chloroethoxy)methane	nd	nd	nd	nd	nd	nd	0.100
Bis(2-chloroethyl)ether	nd	nd	nd	nd	nd	nd	0.100
Bis(2-chloroisopropyl)ether	nd	nd	nd	nd	nd	nd	0.100
Bis-(2-Ethylhexyl) Adipate	nd	nd	nd	nd	nd	nd	0.100
Bis(2-ethylhexyl)phthalate	nd	nd	nd	5.44	nd	nd	0.500
Butyl benzyl phthalate	nd	nd	nd	nd	nd	nd	0.100
Carbazole	nd	nd	nd	nd	nd	nd	0.100
Chrysene	nd	nd	nd	nd	nd	nd	0.100
Dibenz (a,h) anthracene	nd	nd	nd	nd	nd	nd	0.100



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	Trip Blank	EQ Blank	Field Blank	Trip Blank	Field Blank	Field Blank	RL
	10/6/2010	10/7/2010	10/5/2010	4/14/2011	4/18/2011	4/21/2011	
Dibenzofuran	nd	nd	nd	nd	nd	nd	0.100
Diethyl phthalate	nd	nd	nd	nd	nd	nd	0.100
Dimethyl phthalate	nd	nd	nd	nd	nd	nd	0.100
Di-n-butyl phthalate	nd	nd	nd	nd	nd	nd	0.100
Di-n-octyl phthalate	nd	nd	nd	nd	nd	nd	0.100
Diphenylamine	nd	nd	nd	nd	nd	nd	0.100
Fluoranthene	nd	nd	nd	nd	nd	nd	0.100
Fluorene	nd	nd	nd	nd	nd	nd	0.100
Hexachlorobenzene	nd	nd	nd	nd	nd	nd	0.100
Hexachlorobutadiene	nd	nd	nd	nd	nd	nd	0.100
Hexachlorocyclopentadiene	nd	nd	nd	nd	nd	nd	0.100
Hexachloroethane	nd	nd	nd	nd	nd	nd	0.100
Indeno (1,2,3-cd) pyrene	nd	nd	nd	nd	nd	nd	0.100
Isophorone	nd	nd	nd	nd	nd	nd	0.100
Naphthalene	nd	nd	nd	nd	nd	nd	0.100
Nitrobenzene	nd	nd	nd	nd	nd	nd	0.100
N-Nitrosodi-n-propylamine	nd	nd	nd	nd	nd	nd	0.100
Pentachlorophenol	nd	nd	nd	nd	nd	nd	0.500
Phenanthrene	nd	nd	nd	nd	nd	nd	0.100
Phenol	nd	nd	nd	nd	nd	nd	0.100
Pyrene	nd	nd	nd	nd	nd	nd	0.100
Limonene	nd	nd	nd	nd	nd	nd	0.100
1,3-Dimethyl adamantane	nd	nd	nd	nd	nd	nd	0.100
2-Butoxyethanol	nd	nd	nd	nd	nd	nd	0.100
Adamantane	nd	0.32	nd	nd	nd	nd	0.100
Squalene	0.36	0.49	0.23	nd	nd	nd	1.00
Terpinol	nd	nd	nd	nd	nd	nd	0.100
Tri(2-butoxyethyl) Phosphate	nd	2.53	nd	nd	nd	nd	0.500

RL – Reporting Limit (µg/L). nd – not detected. ----- not measured.

**Table B12.** Blank results for GRO and DRO analyses for Phase III and Phase IV sampling (Region 8 laboratory, Golden, CO) and blank results for glycol ethers in Phase IV sampling (Region 3 laboratory, Fort Meade, MD)

	Trip Blank	EQ Blank	Field Blank	Trip Blank	Field Blank	Field Blank	RL
	10/6/2010	10/7/2010	10/5/2010	4/14/2011	4/18/2011	4/21/2011	
Gasoline Range Organics	nd	nd	nd	nd	21.3	nd	20
Diesel Range Organics	nd	nd	nd	nd	nd	135	22
2-Butoxyethanol	-----	-----	-----	nd	nd	nd	10
Diethylene Glycol	-----	-----	-----	nd	nd	nd	50
Triethylene Glycol	-----	-----	-----	nd	nd	nd	10
Tetraethylene Glycol	-----	-----	-----	3.6	3.1	3.4	10

RL – Reporting Limit (µg/L). nd – not detected. ----- not measured.

**Table B13.** Duplicate data for selected major ions, DOC, and DIC in ground water samples collected during Phase III and Phase IV sampling activities

Sample	Date	Na ppm	K ppm	Ca ppm	Mg ppm	Ba ppm	Sr ppm	Si ppm	Cl ppm	SO4 ppm	F ppm	NO3 ppm	DOC ppm	DIC ppm
LD01	10/6/2010	562	1.05	71.9	8.12	0.0096	1.08	5.82	33.0	1320	0.90	0.354	0.568	17.8
LD01 dup	10/6/2010	565	0.97	71.9	8.14	0.0096	1.08	5.81	32.9	1320	0.99	0.337	0.558	17.2
RPD		0.53	7.92	0.00	0.25	0.00	0.00	0.17	0.30	0.00	9.52	4.92	1.78	3.48
PGDW32	4/18/2011	198	0.09	7.19	0.028	0.010	0.090	6.74	18.8	361	1.95	ND	0.41	7.70
PGDW32 dup	4/18/2011	198	0.27	7.28	0.026	0.009	0.090	6.80	19.1	349	2.02	ND	0.37	7.73
RPD		0.00	100	1.24	7.41	10.53	0.00	0.89	1.58	3.38	3.53	NC	10.26	0.39
EPAMW02	4/19/2011	448	43.6	60.5	0.032	0.093	1.78	2.94	457	62.6	1.54	ND	19.7	1.40
EPAMW02 dup	4/19/2011	449	44.0	60.5	0.019	0.093	1.79	2.93	456	62.5	1.49	ND	19.7	1.39
RPD		0.22	0.91	0.00	50.98	0.00	0.56	0.34	0.22	0.16	3.30	NC	0.00	0.72

RPD is the calculated relative percent difference:  $RPD = \frac{|(sample1-sample2)|}{((sample1+sample2)/2)} * 100$ . ND -- not detected. ----- not measured. NC -- not calculated.

**Table B14.** Duplicate data for methane and selected dissolved organic compounds in ground water samples collected during Phase III and Phase IV sampling activities

Sample	Date	Methane	Benzene	Toluene	m,p-Xylenes	Isopropyl alcohol	Tert-butyl alcohol	Phenol	Diethylene Glycol	Triethylene Glycol	Acetone
LD01	10/6/2010	ppm 0.189	ppb <0.25	ppb <0.25	ppb <0.25	ppb -----	ppb -----	ppb <0.1	ppb -----	ppb -----	ppb -----
LD01 dup	10/6/2010	0.168	<0.25	<0.25	<0.25	-----	-----	<0.1	-----	-----	-----
RPD		11.76	NC	NC	NC	NC	NC	NC	NC	NC	NC
PGDW32	4/18/2011	0.07	<0.25	<0.25	<0.25	<11.4	<1.7	<0.5	<50	<10	<1.00
PGDW32 dup	4/18/2011	0.06	<0.25	<0.25	<0.25	<11.4	<1.7	<0.5	<50	<10	<1.00
RPD		15.38	NC	NC	NC	NC	NC	NC	NC	NC	NC
EPAMW02	4/19/2011	18.82	139	336	280	581	4470	14.5	1570	314	641
EPAMW02 dup	4/19/2011	22.62	164	424	354	553	4580	29.2	1610	293	616
RPD		18.34	16.50	23.16	23.34	4.94	2.43	67.28	2.52	6.92	3.98

RPD is the calculated relative percent difference:  $RPD = \frac{|(\text{sample 1} - \text{sample 2})|}{(\text{sample 1} + \text{sample 2})/2} \times 100\%$ . ND – not detected. ----- not measured. NC – not calculated.

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**Table B15. QA/QC requirements for analysis of  $\delta^{13}\text{C}$  of DIC**

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

Working standards were calibrated against IAEA (International Atomic Energy Agency) standard LSVEC and NBS-19; referenced to  $\delta^{13}\text{C}$  of the PeeDee belemnite (NIST material).

\*If < 5 samples were submitted, a duplicate was run regardless of total number.

Corrective Actions: If re-analysis was not possible (such as lack of sample volume), the data was qualified with a determination about the impact on the sample data.

**Table B16. QA/QC requirements for analysis for  $\delta^{13}\text{C}$  and  $\delta\text{D}$  of light hydrocarbons for aqueous and gas samples**

QC Type	Performance Criteria	Frequency
Mass Spec Calibration Check	Difference of calibrated/true $\leq 0.5\text{‰}$ for $\delta^{13}\text{C}$ and $\leq 3\text{‰}$ for $\delta\text{D}$ +/- 1 pMC for $^{14}\text{C}$	One at beginning of day and after samples are analyzed for $\delta^{13}\text{C}$ *; one at beginning of day and every tenth sample for $\delta\text{D}$ **
Mass Spec Zero Enrichment Check	0 +/- 0.1 ‰ for $\delta^{13}\text{C}$ and 0 +/- 1 ‰ for $\delta\text{D}$	Once a day for $\delta^{13}\text{C}$ and every tenth sample for $\delta\text{D}$
Lab Duplicates	$\leq 1\text{‰}$ for $\delta^{13}\text{C}$ and $\leq 3\text{‰}$ for $\delta\text{D}$ +/- 1 pMC for $^{14}\text{C}$	1 per every 10 samples for $\delta^{13}\text{C}$ and $\delta\text{D}$ ***
Preparation System Check/Reference Standards	$\leq 1\text{‰}$ for $\delta^{13}\text{C}$ and $\leq 3\text{‰}$ for $\delta\text{D}$ +/- 1 pMC	One per every 10 samples for $\delta^{13}\text{C}$ and $\delta\text{D}$

\*Working standards calibrated against IAEA (International Atomic Energy Agency) standard LSVEC and NBS-19; referenced to  $\delta^{13}\text{C}$  of the PeeDee belemnite (NIST material).

\*\*Working standards calibrated against VSMOW, SLAP, and GISP; referenced to VSMOW.

\*\*\*If < 10 samples were submitted, duplicate run regardless of total number.

Corrective Actions: If re-analysis is not possible (such as lack of sample volume), the data will be qualified with a determination about the impact on the sample data

**Table B17. QA/QC requirements for analysis of fixed gases and light hydrocarbons for aqueous and gas samples**

Measurement	Analysis Method	Blanks (Frequency)	Calibration Checks (Frequency)	Second Source (Frequency)	Duplicates (Frequency)	Matrix Spikes (Frequency)
Ar, He, H <sub>2</sub> , O <sub>2</sub> , N <sub>2</sub> , CO <sub>2</sub> , CH <sub>4</sub> , C <sub>2</sub> H <sub>6</sub> , C <sub>2</sub> H <sub>4</sub> , C <sub>3</sub> H <sub>6</sub> , C <sub>3</sub> H <sub>8</sub> , iC <sub>4</sub> H <sub>10</sub> , nC <sub>4</sub> H <sub>10</sub> , iC <sub>5</sub> H <sub>12</sub> , nC <sub>5</sub> H <sub>12</sub> , C <sub>6</sub> H <sub>6</sub>	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

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**Table B18. Summary of quality control samples, purpose, method, and frequency to support gas analysis**

QC Sample	Purpose	Method	Frequency	Acceptance Criteria
<b>Equipment Blanks</b>	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 <sub>2</sub> gas via the sample train.	One sample per day	< Detection limit
<b>Travel Blanks</b>	Ensure that cross-contamination does not occur during sampling or transport to the laboratory	Fill sample bags with ultrapure N <sub>2</sub> gas and place in shipping container with other samples.	One sample per shipment	< Detection limit
<b>Duplicates</b>	Check precision of sampling method and analysis	Use a tee to collect two samples simultaneously.	One sample every 10 samples	RPD < 20%

**Table B19. Summary of analytes, instruments, calibration, and check standards for portable gas analyzers**

Analyte	Instrument (Detector)	Method	Range	Calibration	Check Standard	Accuracy
O <sub>2</sub>	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 <sub>4</sub>	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 <sub>2</sub>	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%)
VOCs	Thermo Scientific TVA-1000B (FID)	RSKSOP-320v1	1.0 – 10,000 ppmv	0.0, 10, 100, 1000, 9000 ppmv CH <sub>4</sub>	10, 100, 1000, 9000 ppmv CH <sub>4</sub>	±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.

**Table B20. QA/QC Requirements for portable gas analyzers**

Measurement	Analysis Method	Blanks** (Frequency)	Calibration Check Standards (Frequency)	Second Source Standards (Frequency)
O <sub>2</sub> , CO <sub>2</sub> , CH <sub>4</sub>	RSKSOP-314v1	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)
Hydrocarbons	RSKSOP-320v1	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

Corrective actions are detailed in the SOPs.

\*Duplicate sample not appropriate for measurements from a sample train.

\*\*Meter reading

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## Appendix C

# Photographic Log of Deep Monitoring Well Construction

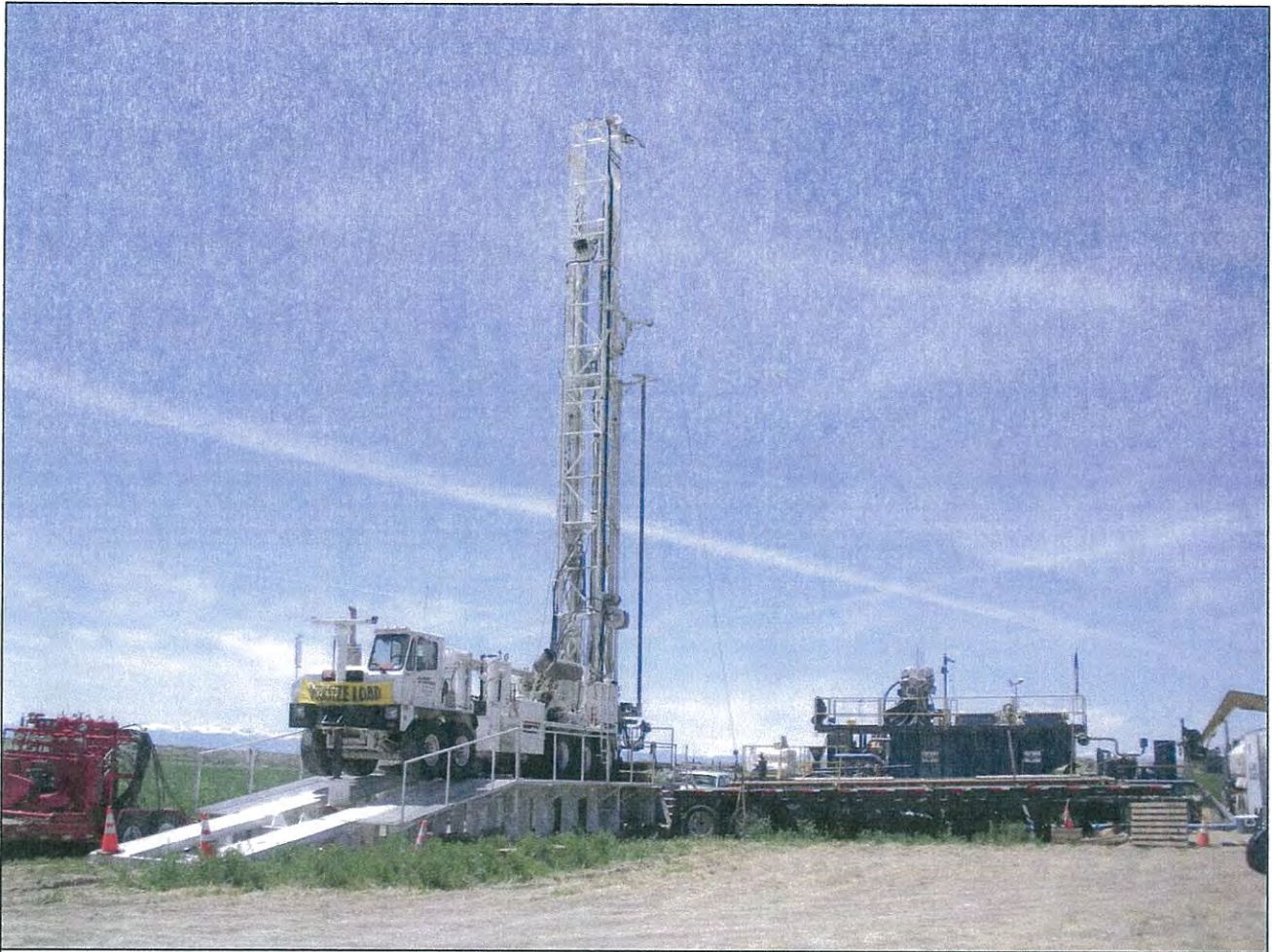


Figure C1. Photograph of drilling rig on platform with shakers for mud recirculation at MW02.



Figure C2. Photograph of blowout prevention (BOP) for annular space at base of drilling rig platform at MW02.



Figure C3. Photograph of blowout preventer for drillstem.



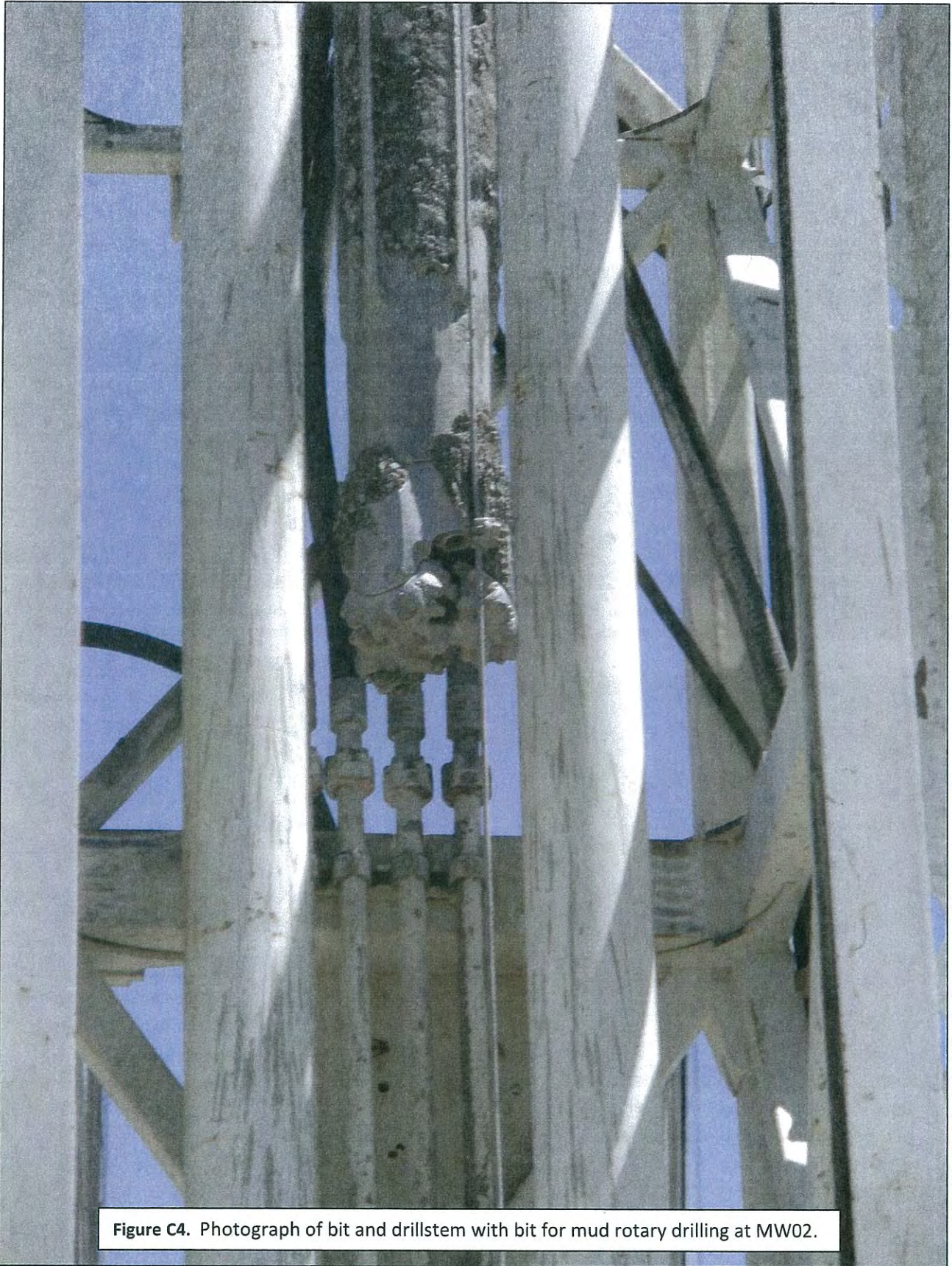


Figure C4. Photograph of bit and drillstem with bit for mud rotary drilling at MW02.

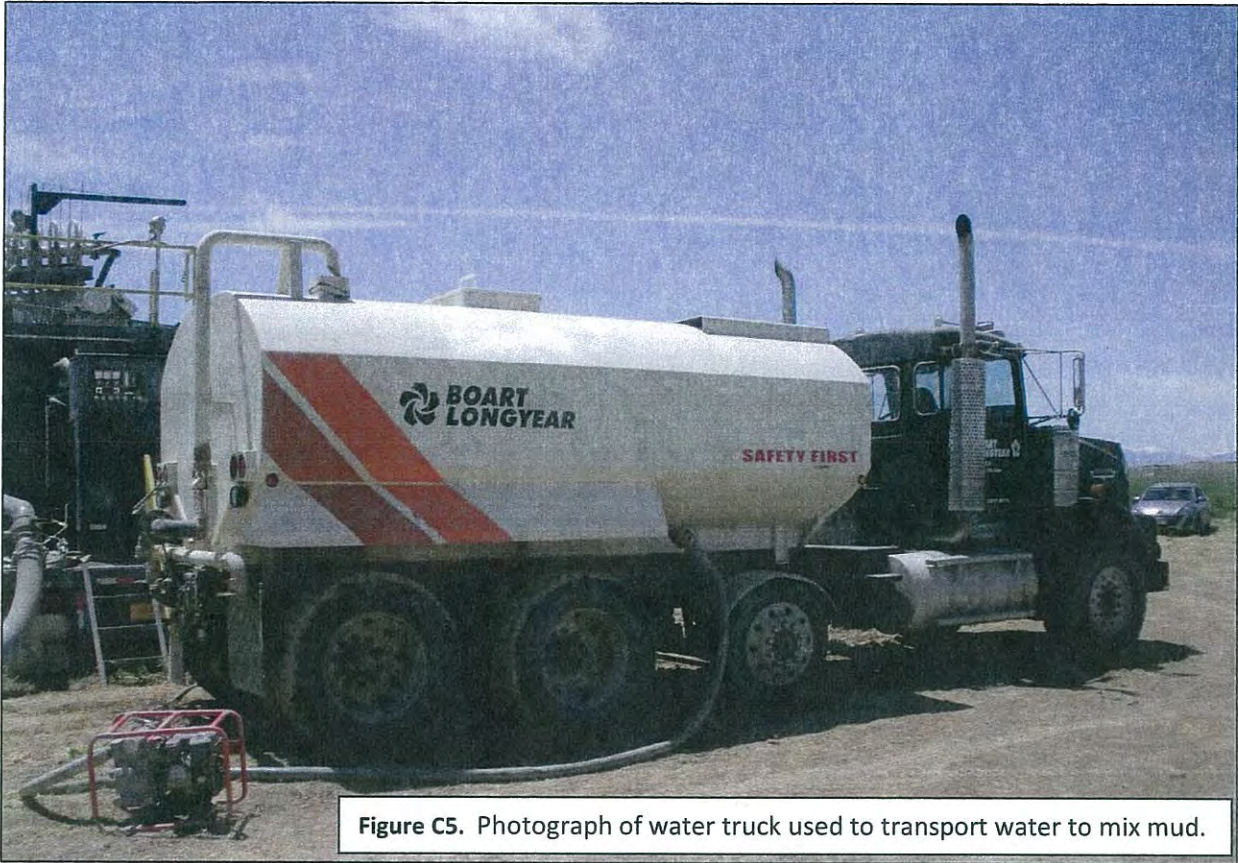


Figure C5. Photograph of water truck used to transport water to mix mud.

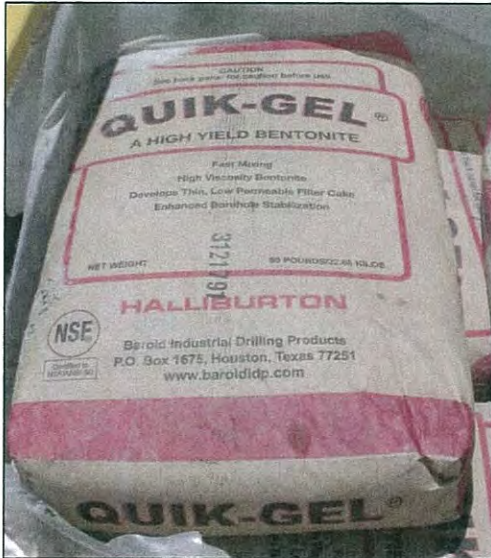


Figure C6. Photograph of Quik-Gel bentonite (Halliburton) used to create mud for drilling.



Figure C7. Photograph of mud additives EZ Mud Gold (Halliburton) and Dense Soda Ash.



Figure C8. Photograph of mud additive Penetrol (Halliburton).

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Figure C9. Photograph of flow of mud and cuttings from borehole at MW02.

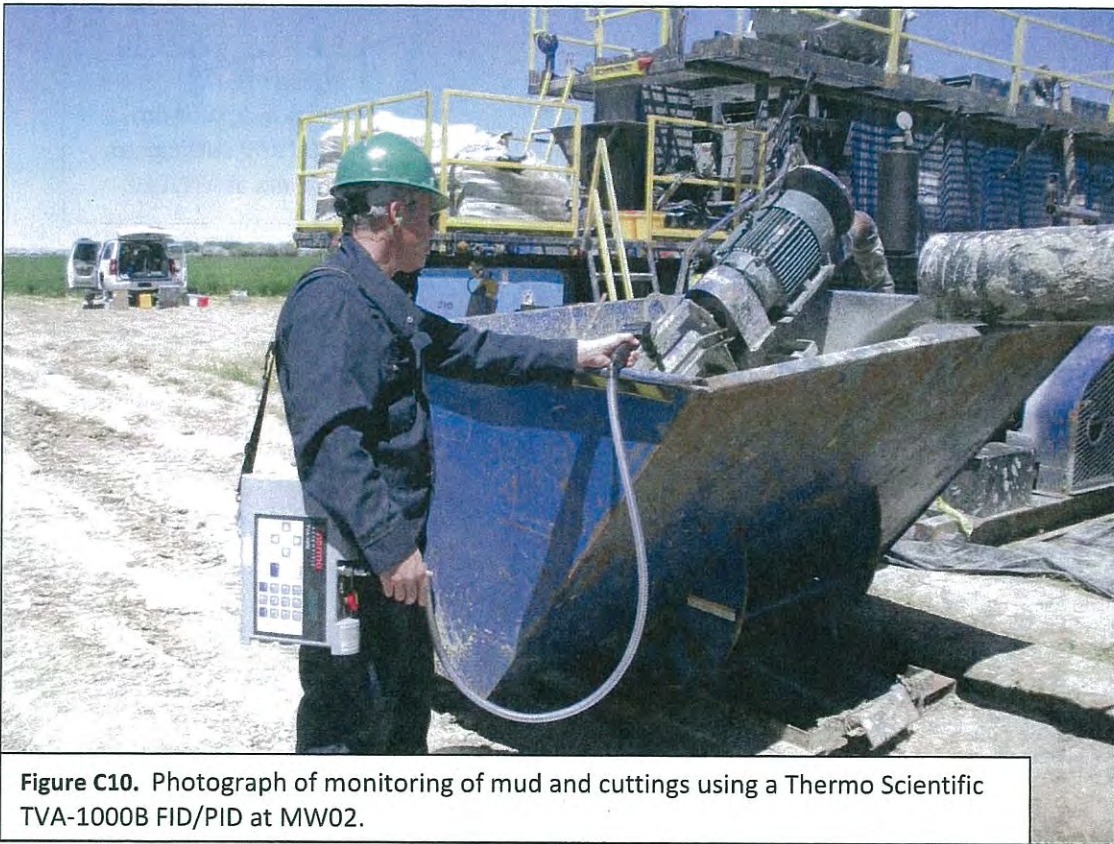
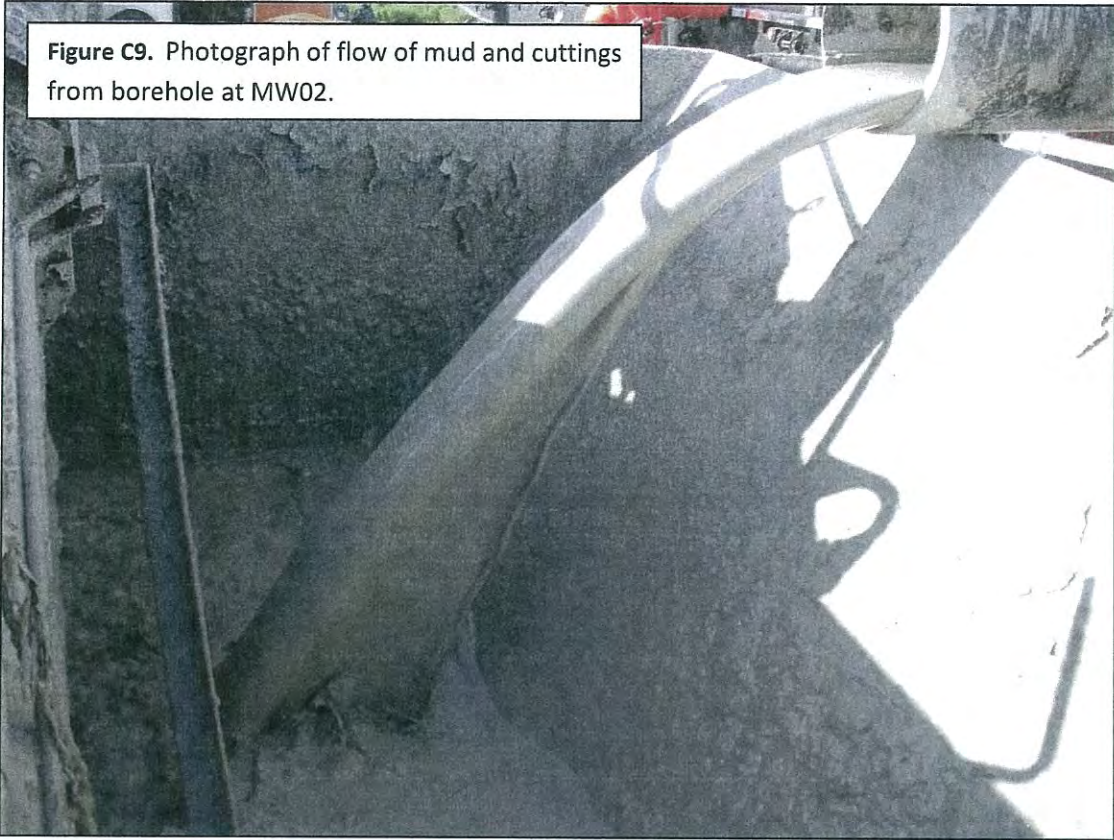


Figure C10. Photograph of monitoring of mud and cuttings using a Thermo Scientific TVA-1000B FID/PID at MW02.

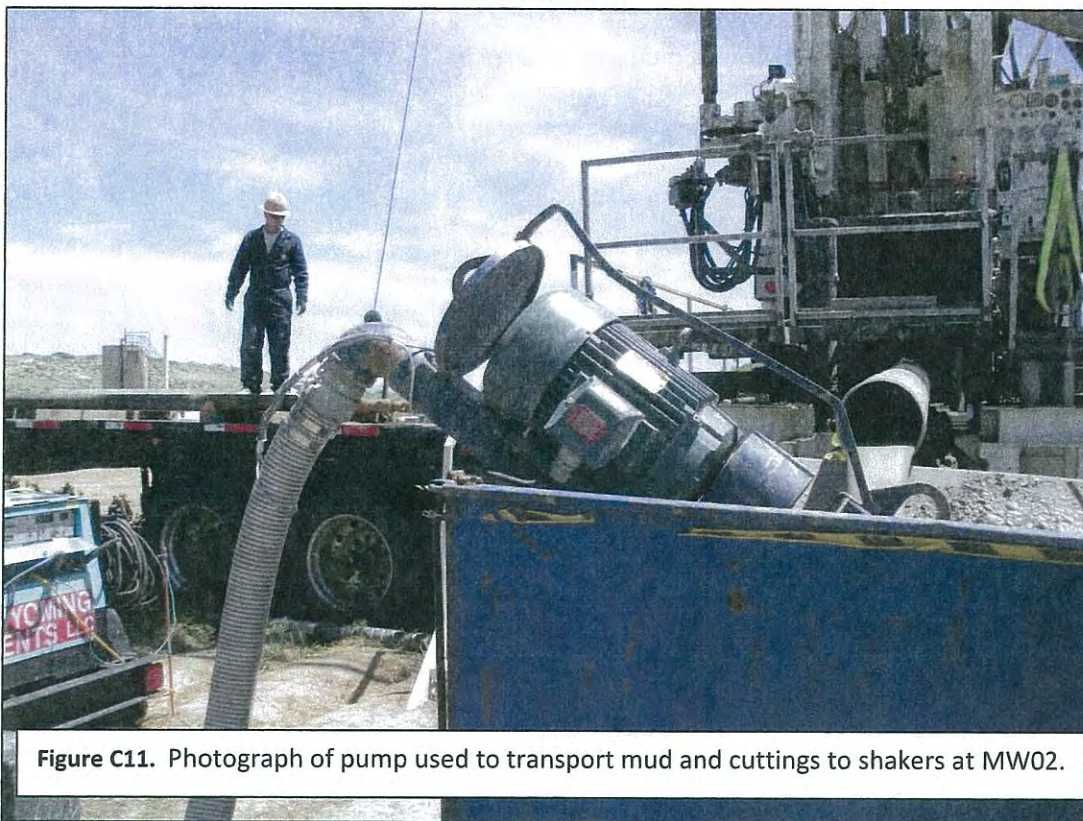


Figure C11. Photograph of pump used to transport mud and cuttings to shakers at MW02.



Figure C12. Photograph of flow of mud and cuttings to shakers at MW02.

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Figure C13. Photograph of shakers separating mud from cuttings at MW02.

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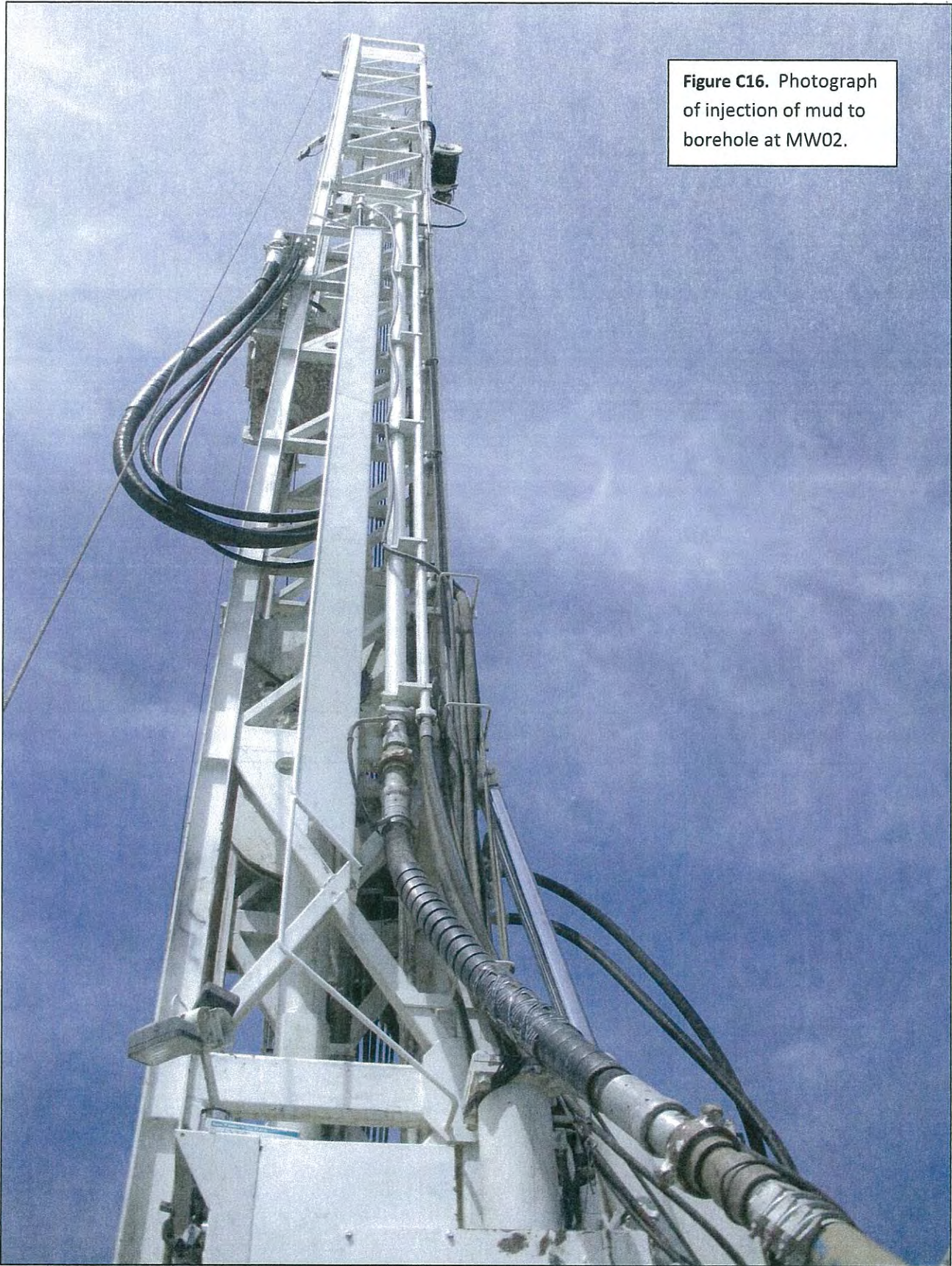
Figure C14. Photograph of cuttings transported to disposal bins at MW02.

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Figure C15. Photograph of pumping of mud back to borehole at MW02.

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**Figure C16.** Photograph of injection of mud to borehole at MW02.





Figure C17. Photograph of collection of cuttings for lithologic characterization at MW02.



Figure C18. Photograph of removal of mud from cuttings at MW02.



Figure C19. Photograph of white coarse-grained sand targeted by local well drillers and media in which screens are set in for both deep monitoring wells.

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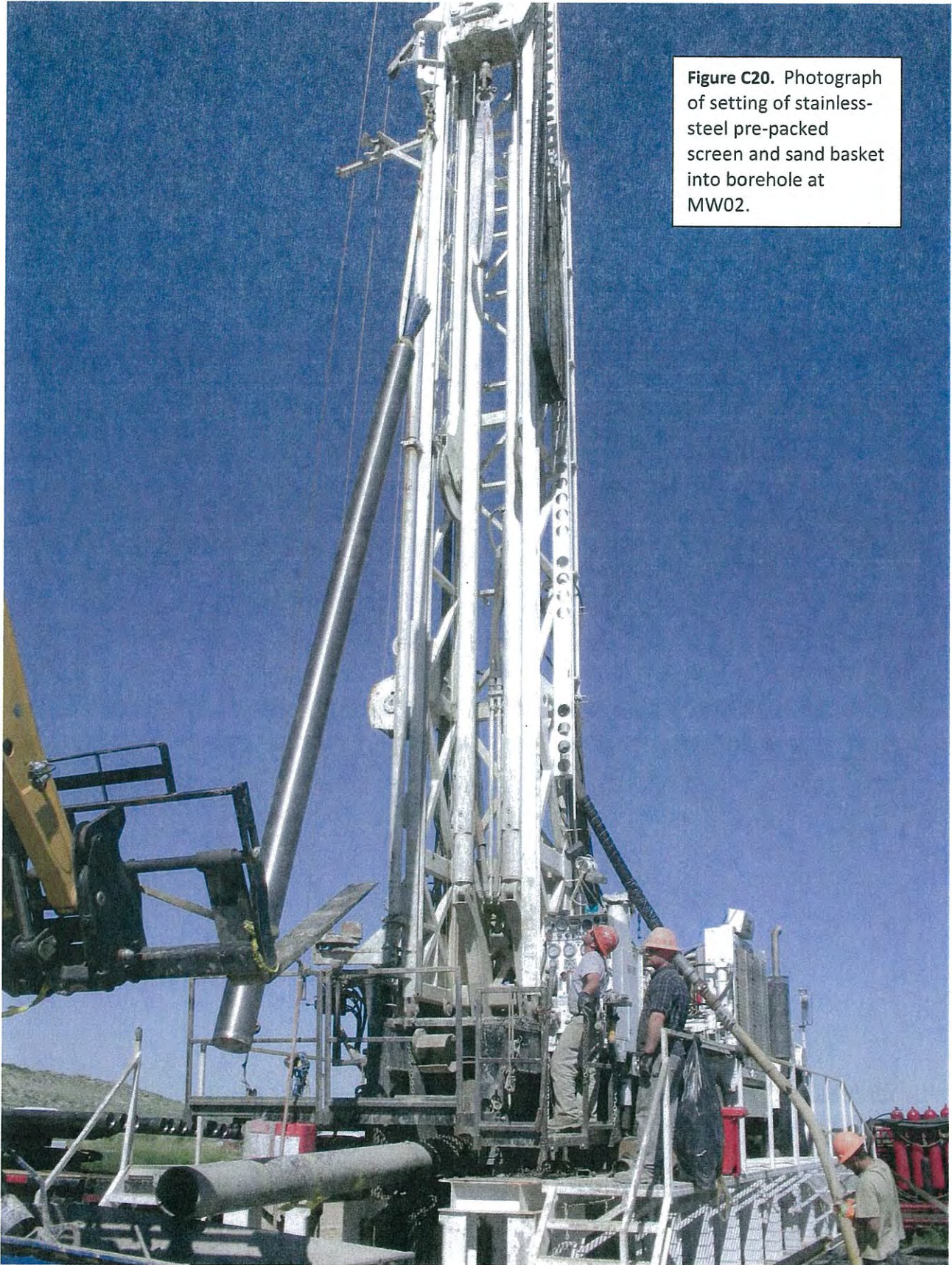


Figure C20. Photograph of setting of stainless-steel pre-packed screen and sand basket into borehole at MW02.



**Figure C21.** Photograph of securing sand basket and casing above screen.



**Figure C22.** Photograph of placement of sand in sandbasket.

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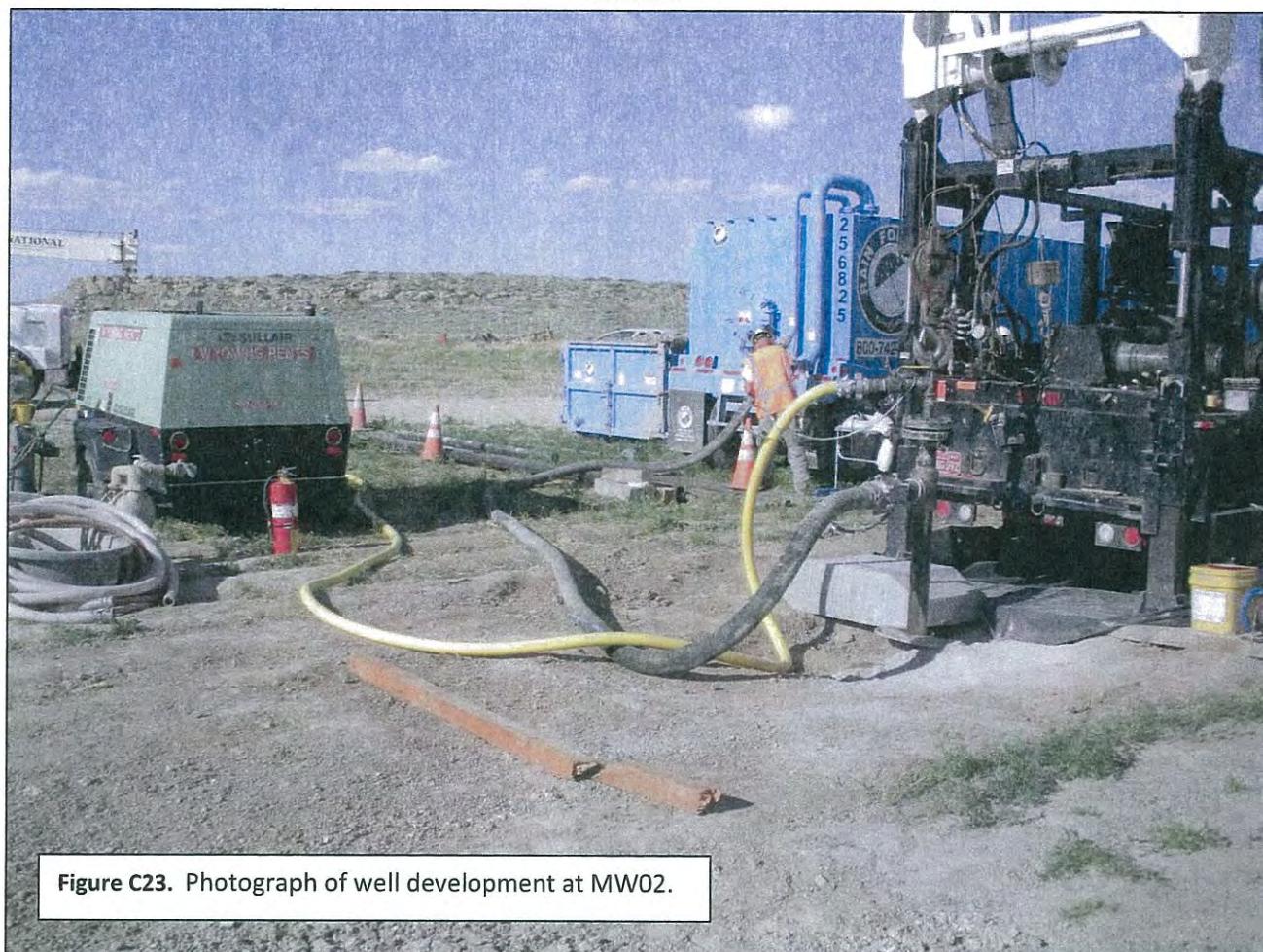


Figure C23. Photograph of well development at MW02.

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# **Appendix D**

## Photographic Log of Ground Water Sampling

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Figure D1. Photograph of flow from submersible pump through flowmeter at MW02.

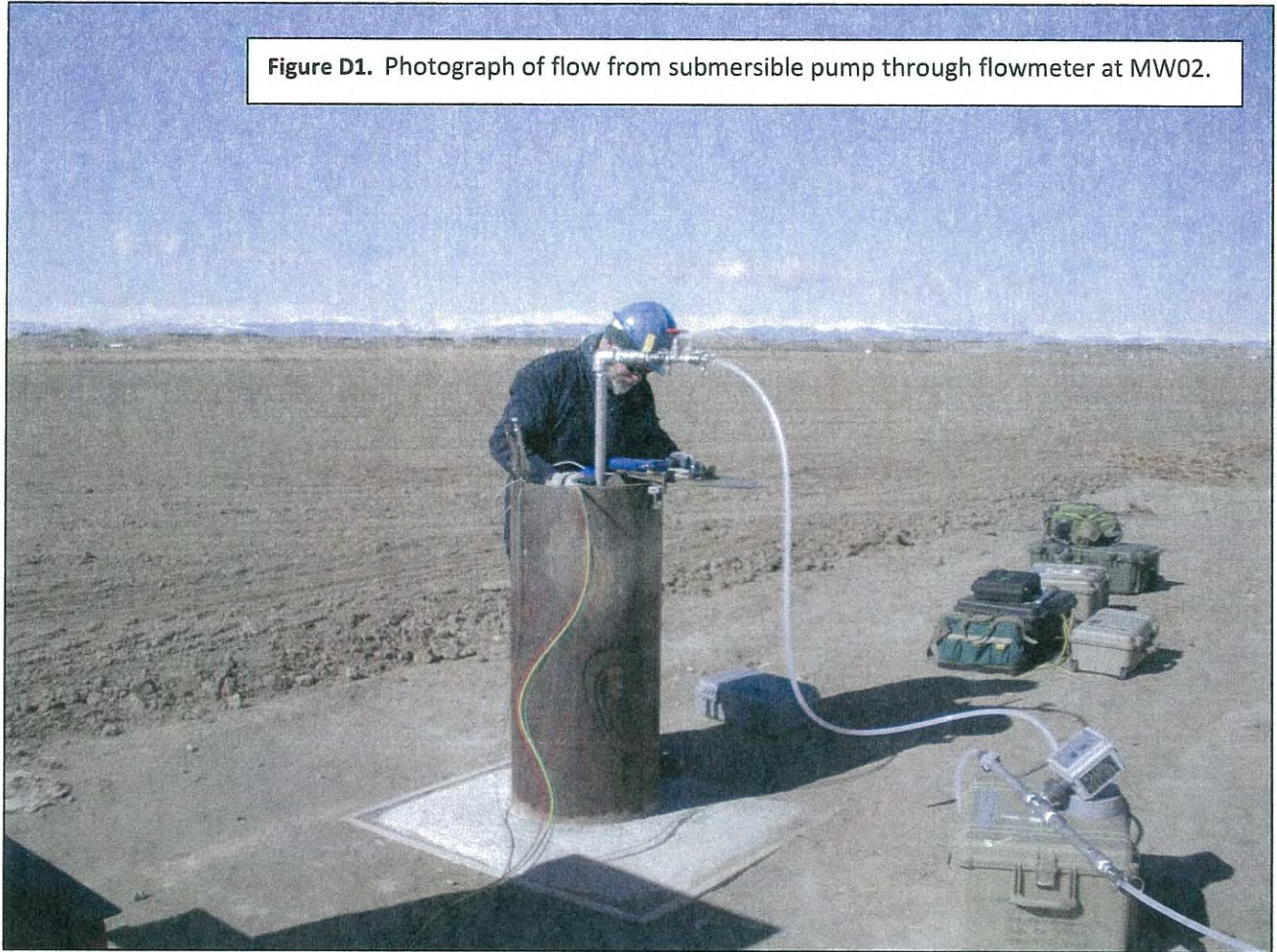


Figure D2. Photograph of flow of water to purge water disposal tank at MW02.



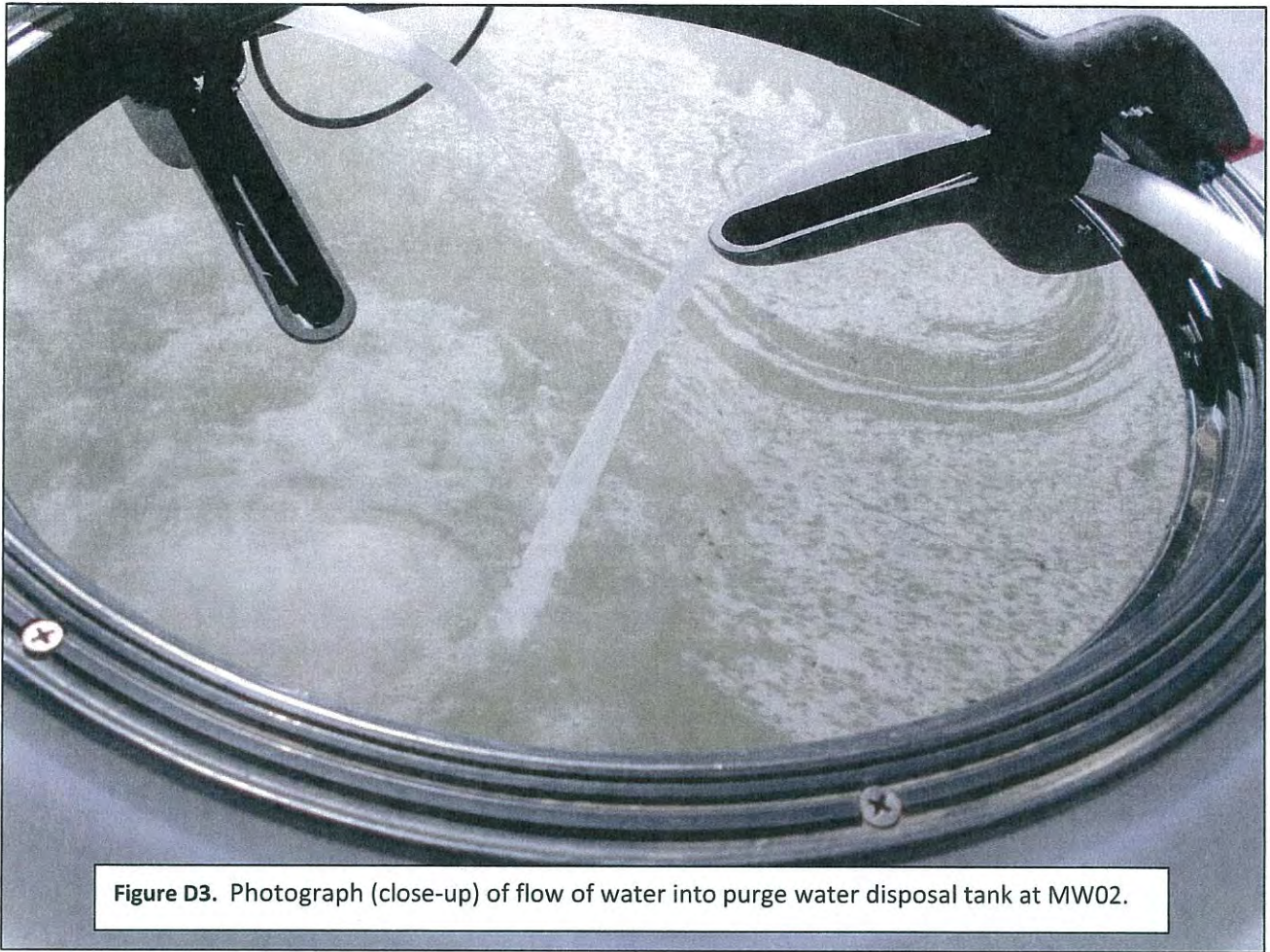


Figure D3. Photograph (close-up) of flow of water into purge water disposal tank at MW02.

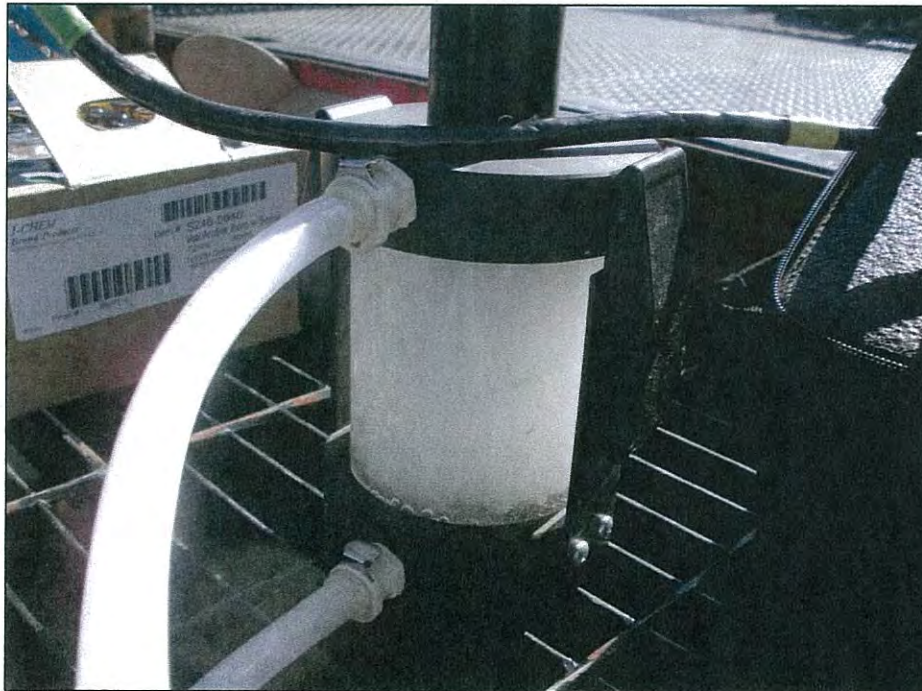


Figure D4. Photograph of water (foaming) flowing into YSI flow cell at MW02.

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Figure D5. Photograph of sampling at MW02. The sample train was split prior to entry into purge water disposal container.



Figure D6. Photograph of field filtering samples for metals analysis at MW02.



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Figure D7. Photograph of sample collection at PGDW14.

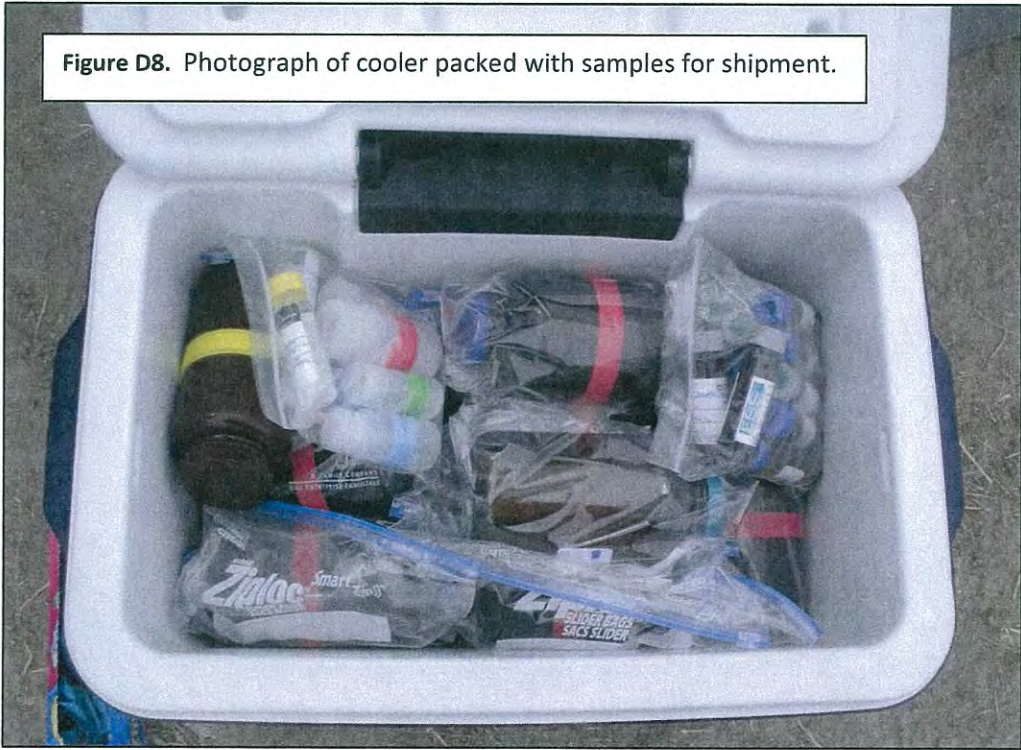


Figure D8. Photograph of cooler packed with samples for shipment.

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# Appendix E

## Examples of Cement Bond/Variable Density Log Interpretation

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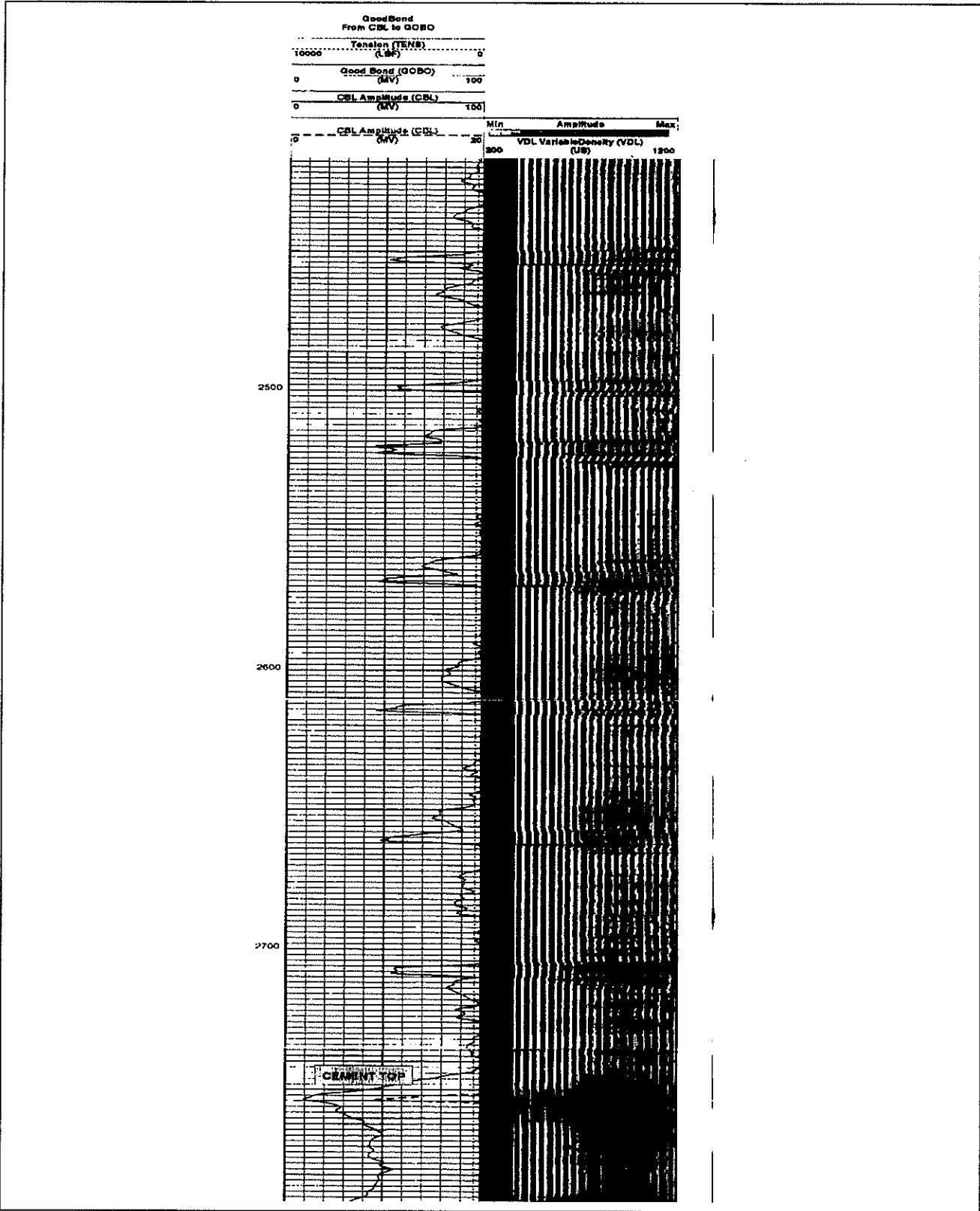


Figure E1. Example of CBL/VDL indicating "no cement" at Pavillion Fee 34-03B. The CBL/VDL indicates no cement 2750 feet below ground surface at the time of logging.

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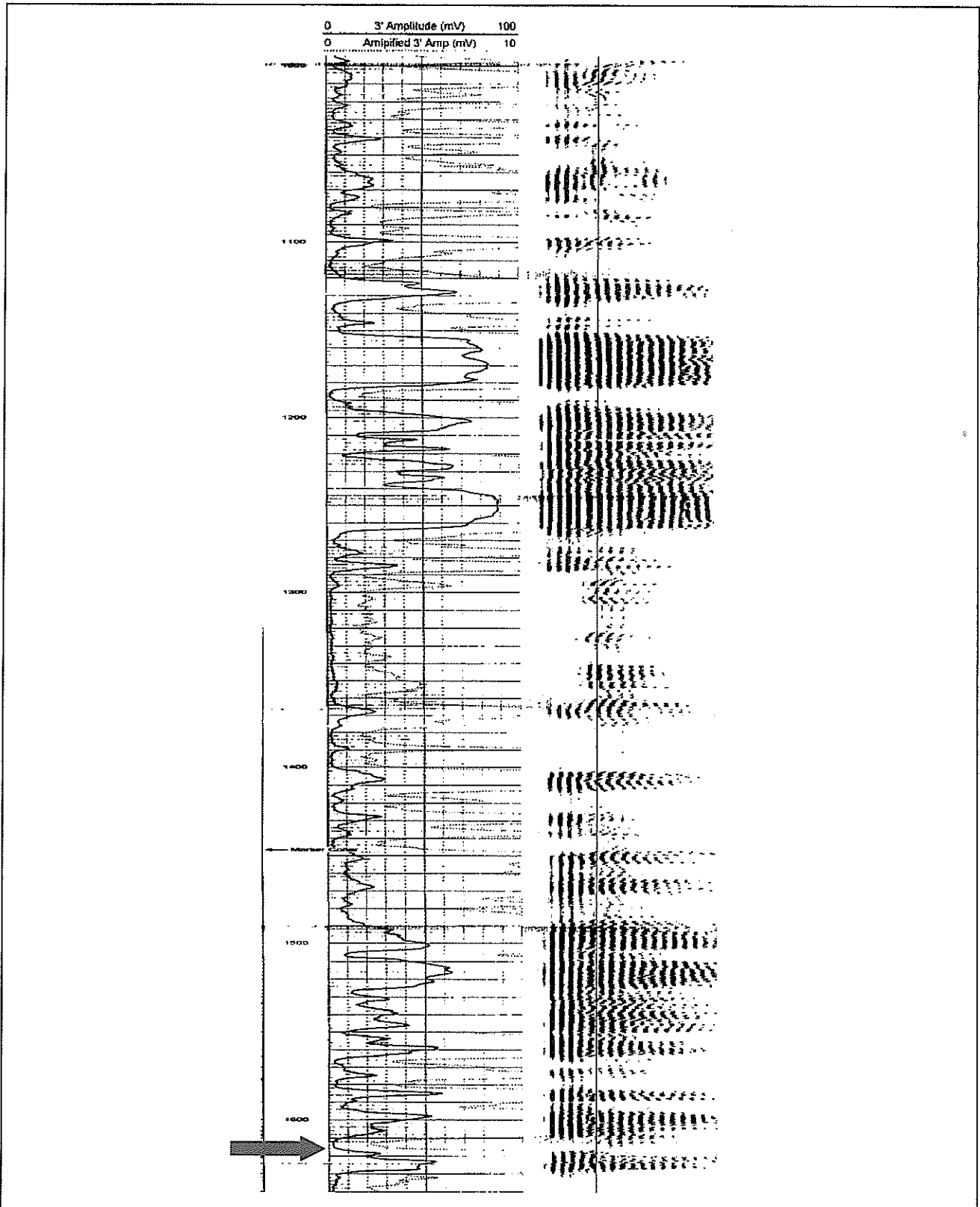


Figure E2. Example of "sporadic bonding" at Pavillion Fee 41-10 from 1000 to 1640 ft bgs. Hydraulic fracturing occurred at 1618 feet below ground surface. Arrow denotes interval of hydraulic fracturing.

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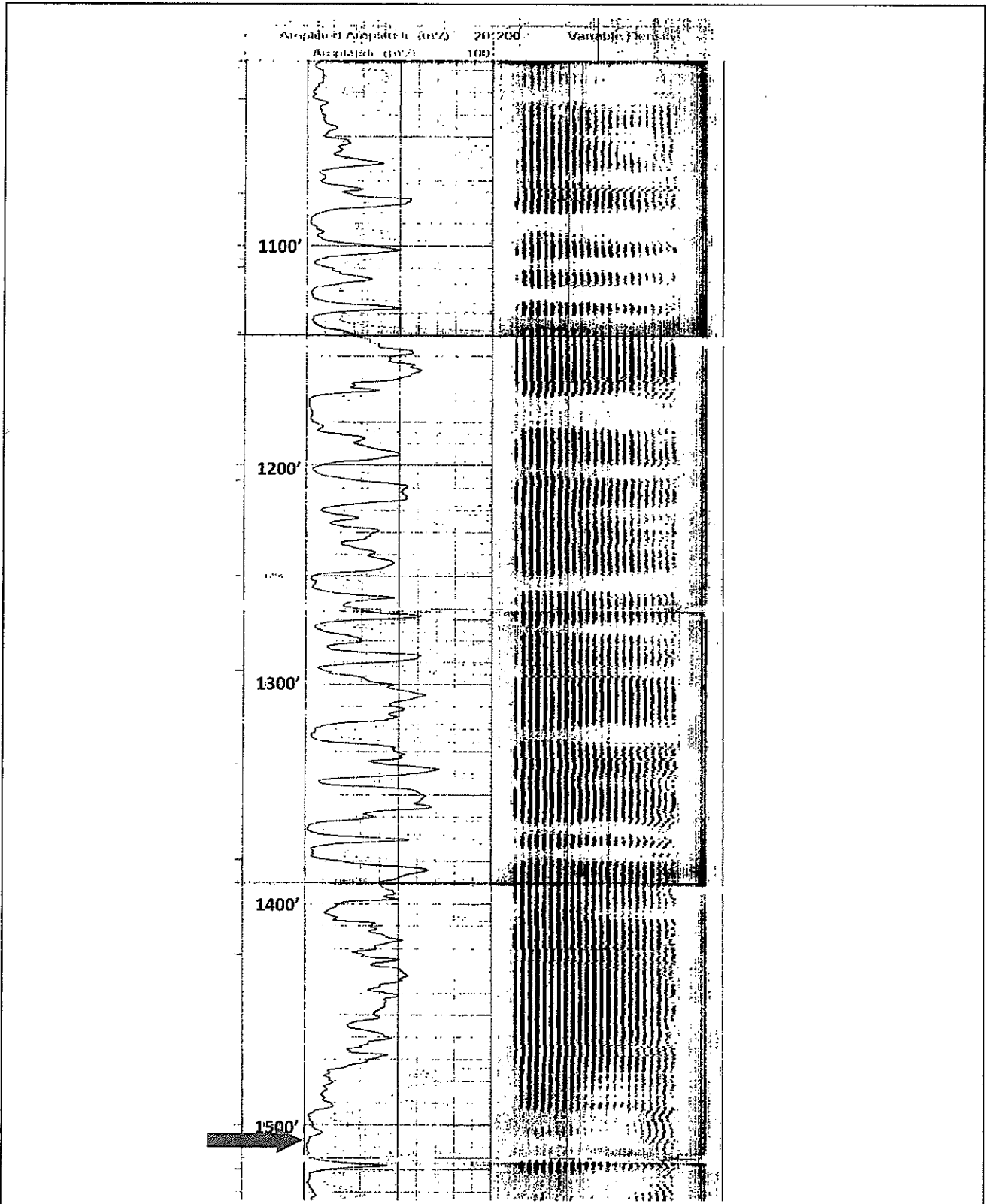


Figure E3a. Example of "sporadic bonding" at Pavillion Fee 11-11B. Hydraulic fracturing occurred at 1516 feet below ground surface. Arrow denotes interval of hydraulic fracturing. Depths on CBL/VDL difficult to read and inserted on left margin.

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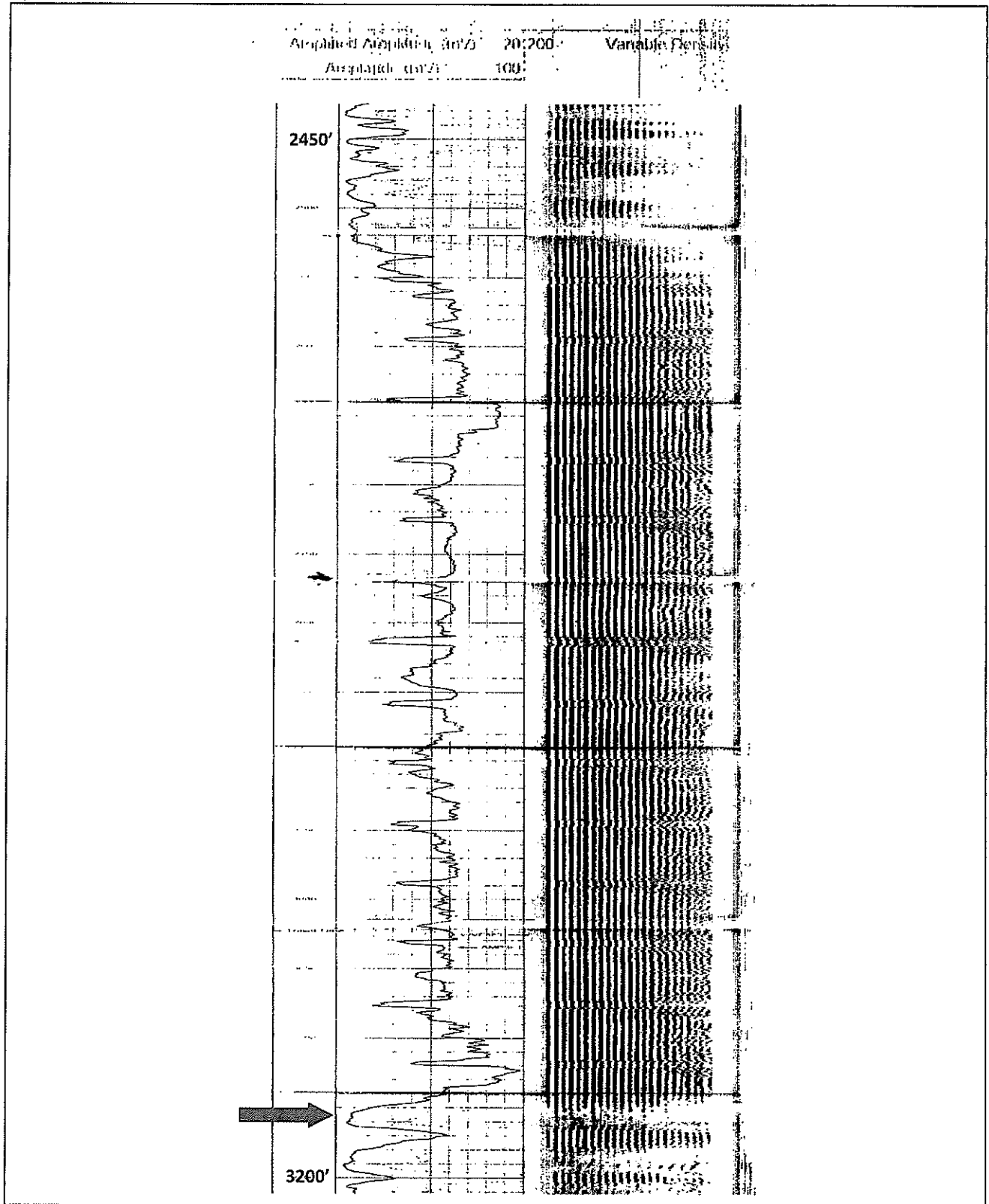


Figure E3b. Example of "sporadic bonding" Pavillion Fee 11-11B between 2350-3200 feet below ground surface. Hydraulic fracturing occurred at 3165 feet below ground surface. Arrow denotes interval of hydraulic fracturing. Depths on CBL/VDL difficult to read and inserted on left margin.

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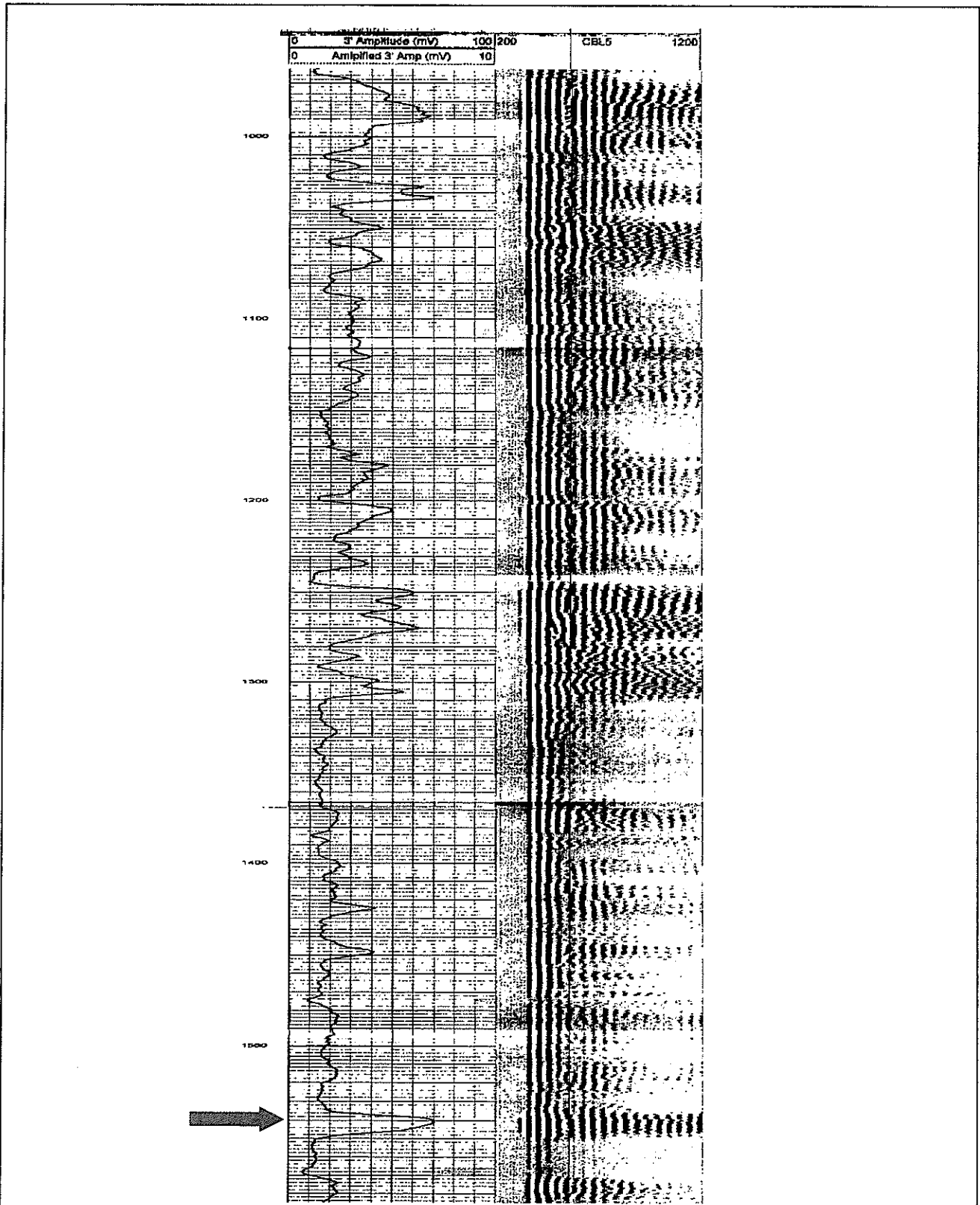


Figure E4. Example of "Sporadic Bonding" at Tribal Pavillion 24-02. Hydraulic fracturing occurred at 1538 feet bgs. Arrow denotes interval of hydraulic fracturing.



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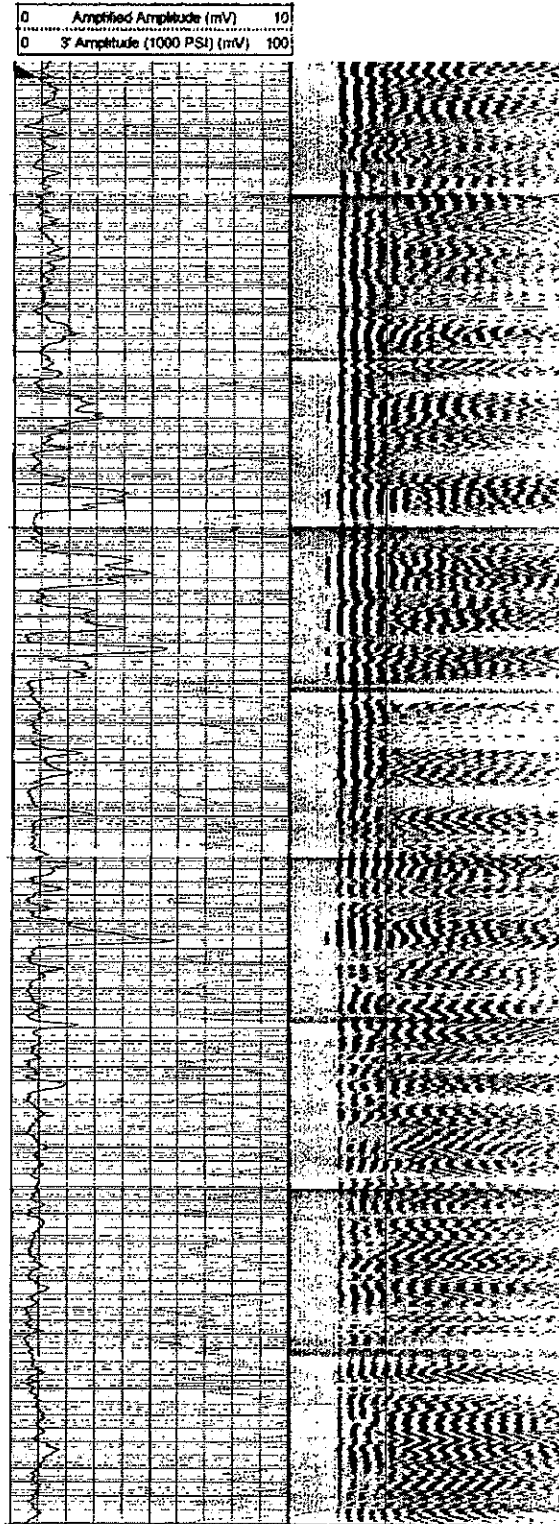


Figure E5. Example of "Good Bonding" (from surface casing at 645 ft bgs to 820 ft bgs) followed by "Sporadic Bonding" (from 820 ft bgs 1310 ft bgs) to "Good Bonding" at 1310 to target depth at Pavillion Fee 41-10B.

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## Hazard Assessment Articles

### Natural Gas Operations from a Public Health Perspective

Theo Colborn, Carol Kwiatkowski, Kim Schultz, and Mary Bachran  
TEDX, The Endocrine Disruption Exchange, Paonia, CO, USA

#### ABSTRACT

The technology to recover natural gas depends on undisclosed types and amounts of toxic chemicals. A list of 944 products containing 632 chemicals used during natural gas operations was compiled. Literature searches were conducted to determine potential health effects of the 353 chemicals identified by Chemical Abstract Service (CAS) numbers. More than 75% of the chemicals could affect the skin, eyes, and other sensory organs, and the respiratory and gastrointestinal systems. Approximately 40–50% could affect the brain/nervous system, immune and cardiovascular systems, and the kidneys; 37% could affect the endocrine system; and 25% could cause cancer and mutations. These results indicate that many chemicals used during the fracturing and drilling stages of gas operations may have long-term health effects that are not immediately expressed. In addition, an example was provided of waste evaporation pit residuals that contained numerous chemicals on the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) and Emergency Planning and Community Right-to-Know Act (EPCRA) lists of hazardous substances. The discussion highlights the difficulty of developing effective water quality monitoring programs. To protect public health we recommend full disclosure of the contents of all products, extensive air and water monitoring, coordinated environmental/human health studies, and regulation of fracturing under the U.S. Safe Drinking Water Act.

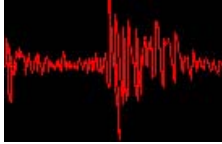
**Key Words:** drilling, health, hydraulic fracturing, natural gas, ozone, pollution.

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Received 8 June 2010; revised manuscript accepted 4 September 2010.

USEPA makes no claims regarding the accuracy or completeness of the information in this article. Competing interest declaration: The authors have no conflicts of interest.

Address correspondence to Theo Colborn, TEDX, P.O. Box 1407, Paonia, CO 81428, USA.  
E-mail: Colborn@tds.net



## Earthquakes Triggered by Humans in Colorado — a background paper by the Colorado Geological Survey



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### Natural Earthquakes and Earthquakes Triggered by Humans in Colorado

Colorado has experienced numerous natural earthquakes, including a magnitude 6.6 earthquake in 1882. However, the state is world famous for its triggered (induced) earthquakes. A variety of human activities in Colorado have triggered earthquakes during the past half century:

- During the 1960s, the triggering of earthquakes from injection of waste fluids at the Rocky Mountain Arsenal near Denver made news around the world.
- In the 1970s, an experiment involving a waterflood at the Rangely oil field in northwest Colorado was the first time in human history that earthquakes were intentionally turned off and on, by varying the injection pressures of water underground.
- Two earthquakes greater than magnitude 5.0 were created in 1969 and 1973 by underground nuclear explosions that were part of an experiment to increase extraction of natural gas.
- A seven-fold increase in earthquakes was recorded during filling of the Ridgeway reservoir in 1986.
- Beginning in the 1990s, injection of brine water beneath the Paradox Valley of western Colorado triggered thousands of earthquakes that increased in magnitude up to 4.2, but decreased in magnitude after the injection protocol was modified.
- Nearly 200 earthquakes with magnitude 2.8 to 3.4 were recorded in a two-year period (2007-2009) in the Paonia area, and are attributed to underground coal mining activity.

With this background in human-caused seismicity in Colorado, it is normal to ask whether any new earthquake activity occurring in the state is triggered by some human activity. It is important in this discussion to remember that Colorado is an active tectonic province that is essentially being pulled apart where the Rio Grande Rift cuts north/south across the mountainous, central part of the state. The high

mountains in the state are a result of uplift on faults (with associated earthquakes) that are part of the rift system.

Three faults in the state have received sufficient study to be included in the USGS National Seismic (Earthquake) Hazard Map, and are listed as being capable of generating earthquakes of 7.0 magnitude, or greater. There are many more faults in the state that could probably generate significant earthquakes, but have not received sufficient study, or documentation, to be included in the hazard map. With our current state of knowledge, it is not possible to predict when or where, the next large earthquake might occur in Colorado.

#### Hydraulic Fracturing (Hydro-fracs) and Earthquakes

Using water to artificially fracture rock layers below ground in order to increase oil and gas production has been conducted in the United States since 1947. Before that, nitro glycerin was used to artificially fracture the rock. Nearly all of the oil and gas wells drilled in Colorado today require hydro-fracing in order to produce economic quantities of oil and gas.

There are only two instances in the world where hydro-fracing near faults has been interpreted to cause earthquakes, one in Oklahoma and one in Great Britain. Both of these were less than magnitude 3.0, which causes a shaking intensity that most people would not notice. The USGS states, "Fracking causes small earthquakes, but they are almost always too small to be a safety concern." Scientists at both the state and federal level have been frustrated by the widespread misrepresentation in the media that "fracking causes earthquakes".

#### Waste Fluid Disposal from Oil & Gas Operations and Earthquakes

Oil and natural gas operations commonly produce water that must be handled within strict state and federal regulations.

- Small amounts of water are produced with normal, natural-gas wells and oil wells.
- Larger amounts of water can be produced from coalbed methane wells, from water-flooding of an oil field, and from very old oil wells.
- After a well is hydro-frac'ced, not all of the water stays in the formation, but some of the water is recovered and flows back to the surface (~ 9% of all oil & gas waste fluids in Colorado).

Any water brought to the surface during oil and gas operations, must be disposed of properly. There are several common ways to deal with the water depending on its chemical properties.

- Putting it into lined ponds and evaporating the water,
- Disposing of it directly into streams or applying it to the surface (must meet water-quality standards),
- Treating it to water-quality standards before putting into streams or rivers,

- Re-injecting it into the ground in a Class II UIC well under guidelines promulgated by the US EPA and administered by the Colorado Oil and Gas Conservation Commission (COGCC). There are approximately 145,000 of these wells in the U.S., and 309 in Colorado.

Several recent earthquake swarms across the U.S. have generated questions as to whether they were triggered by oil and gas operations. Indeed, the USGS created a recent flurry of publicity and controversy by claiming that an increase in earthquake activity throughout the midcontinent (including Colorado), is “almost certainly manmade”. The directors of the Oklahoma and Colorado Geological Surveys independently characterized these conclusions for their states as premature.

A number of earthquakes in several states are currently being investigated in order to determine whether it is plausible that water injection may have triggered them.

- The Center for Earthquake Research at the University of Memphis and the Arkansas Geological Survey jointly concluded that water disposal from oil and gas operations was the most probable cause of more than 1200 micro-earthquakes on a fault near Guy, Arkansas.
- The Youngstown, Ohio area experienced several small earthquakes, culminating in a 4.0 magnitude event on January 1<sup>st</sup>, 2012. Current evidence suggests these events were triggered by a nearby brine injection well. Scientists continue to gather data and investigate the connection between the quakes and well.
- Oklahoma experienced a 5.6 magnitude earthquake near some injection wells. Scientists are investigating whether there is a causal link between the two.
- Earthquakes in the Raton Basin of Colorado and New Mexico are currently being re-studied to evaluate whether there is a link between injection of water from coalbed methane production and earthquakes in that area.

### The Trinidad Earthquakes

The Raton Basin of Colorado and New Mexico has more than 3,000 wells producing natural gas from coal beds (coalbed methane or CBM). Trinidad, Colorado is located near the eastern apex of the basin. The earthquakes occurring in the basin are commonly referred to as the “Trinidad earthquakes”; although the earthquakes extend out more than 30 miles to the southwest, west, northeast, and northwest from Trinidad. The Colorado portion of the Raton Basin has 22 Class II UIC wells disposing of produced water. Most of these wells are not using pressure to inject the water, but are simply flowing into the underground layers 4,000 to 5,000 feet deep under gravity. Other produced water in the basin is disposed of on the surface.

The Trinidad area has a history of natural earthquakes:

- In 1966, a 4.5 magnitude earthquake was reported northeast of Trinidad.
- In 1973, a swarm of four earthquakes  $\leq 4.2$  magnitude was reported west of Trinidad, decades before water injection began.
- In 1983, a magnitude 3.2 earthquake was reported northeast of Trinidad.
- In 1996, a series of three earthquakes  $\geq 3.2$  magnitude hit northeast of Trinidad.



- During this era, detection and location of earthquakes in Colorado was significantly inadequate.

In 2001, a swarm of earthquakes culminating in a magnitude 4.6 occurred west of Trinidad.

- Initial location of the earthquakes showed the epicenters scattered over 75 square miles with a random pattern.
- USGS deployed 12 portable seismometers.
- Several lines of data and studies demonstrated that the earthquakes were actually occurring along a previously unrecognized, normal fault that trends northeast-southwest, and is inclined ~75 degrees toward the southeast.
- Two water-disposal wells are located within 7,400 feet of the fault.
- Separate, and different, analyses conducted by CGS and USGS both concluded the data was equivocal as to whether the earthquakes were triggered by fluid injection.
- The earthquakes on the fault mapped in 2001 stopped, even though injection in the wells continued at the same rate.

For the next decade, no earthquakes were reported on the fault by the National Earthquake Information Center (NEIC). However, small earthquakes (most too small to feel) occurred fairly regularly throughout the rest of the Raton Basin. These earthquakes appeared to follow no pattern, but seemed fairly random. It should be remembered that seismograph coverage in Colorado was inadequate to pinpoint the epicenters of earthquakes. Errors of plus or minus ten miles, or more, could be experienced.

During this decade, the Earthscope Transportable Array moved across Colorado providing better data for locating earthquakes during the two years that those seismographs were in place. The Earthscope data showed several clusters of earthquakes (rather than the random patterns seen before), with the largest cluster in the New Mexico portion of the basin. CGS purchased one of those stations east of Trinidad in an effort to improve the accuracy of locating earthquakes. Researchers have recently studied the Earthscope data and attempted to retroactively improve the NEIC locations.

A damaging, magnitude 5.3 earthquake struck the Trinidad area in August 2011. This event renewed interest in whether the earthquakes were triggered by underground disposal of produced water. Several seismographs were deployed by the USGS in the area immediately after the 5.3 M earthquake. In December, the oil and gas industry deployed additional seismographs deep underground to complement the USGS instruments. Excellent data is now being obtained on the location, number, and size of the earthquakes; most of which are too small to feel. This new data will provide researchers with information to perhaps finally understand the cause(s) of the earthquakes in the Raton Basin.

#### The Colorado Oil and Gas Conservation Commission (COGCC) and the Potential for Triggering Earthquakes

In 2011, the COGCC took a proactive stance toward the possibility of injection wells causing earthquakes and asked the Colorado Geological Survey (CGS) to review all new permit applications for water disposal wells. CGS has been reviewing those applications since October 2011 and is making recommendations to COGCC. CGS is also working with COGCC to understand the origin of the Trinidad earthquakes.

## Resources on Colorado Earthquakes

### [Earthquake Reference Collection](#)

This CGS collection consists of more than 500 publications relevant to Colorado earthquakes, including many that are hard to find. A large number of these are available online as PDFs.

### [Earthquake and Fault Map Server](#)

This CGS online resource shows earthquakes and young faults in Colorado. Mousing over an earthquake will show the date and magnitude/intensity. Double-clicking on an earthquake will bring up an information sheet on the event.

Mousing over a fault will show the name of the fault. Double-clicking on a fault will bring up an information sheet on the event. The sheet will include a variety of information including applicable literature references.

### [Induced Earthquake Bibliography](#)

This is an excellent online resource for publications relevant to the triggering of earthquakes by a variety of means.

### [We Don't Have Earthquakes in Colorado, Do We?](#)

This 2002 RockTalk publication by CGS is a primer on earthquakes in Colorado. It also has a summary of the USGS and CGS investigations of the 2001 Trinidad earthquake swarm.

### [Earthquake Hazards Brochure](#)

This map and information brochure contains locations of earthquakes and Quaternary faults in Colorado. It was produced by the Colorado Earthquake Hazard Mitigation Council in 2008. You can obtain free hard copies from the Colorado Geological Survey, or view it online.

**ATTACHMENT F**  
**PRESENTATIONS BY PANELISTS**

**DR. KENNETH H. CARLSON**

Ken Carlson is an Associate Professor in Civil and Environmental Engineering at Colorado State University

Pages 2-6

**TISHA CONOLY SCHULLER**

Ms. Tisha Conoly Schuller serves as President and Chief Executive Officer of the Colorado Oil & Gas Association (COGA)

Page 7

**SHANE DAVIS**

Shane Davis currently chairs the Poudre Canyon Group of the Rocky Mountain Chapter of the Sierra Club, and serves as the Group's Conservation Chair

Page 8

**THOM KERR**

Thom Kerr is the Acting Director at the Colorado Oil and Gas Conservation Commission (COGCC)

Page 9

**KENT KUSTER**

Kent Kuster is the Oil and Gas Liaison from the Colorado Department of Public Health and Environment (CDPHE)

Pages 10-17

**RANDY MIROWSKI**

Randy Mirowski is the Fire Chief for Loveland Fire Rescue Authority (LFRA).


Pages 18-25

Colorado State University

# The Natural Gas Initiative

## Colorado State University


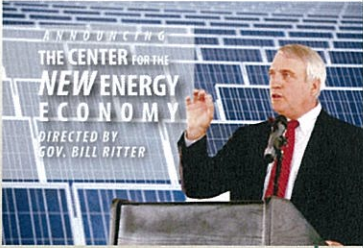
**Ken Carlson**  
Associate Professor  
Civil and Environmental Engineering



Colorado State University

# Center for the New Energy Economy

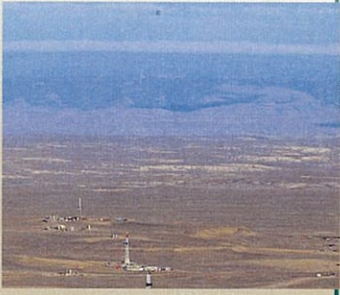
- Established Jan 2011
- Directed by former Colorado governor **Bill Ritter**
- Source of science-based information
- Will convene statewide, national, and international discussions among policymakers, scientists, business, environmental organizations, and others
- Significant focus on energy policy



Colorado State University

## Air Quality


- Recognized program in Atmospheric Chemistry
- Strong presence in Mechanical Engineering
- Air quality studies
  - ✓ NOX, SOX, VOCs
- West slope (Garfield County) study beginning in 2012
  - ✓ \$1.8 MM
  - ✓ CDPHE, industry, county
  - ✓ Primary focus air toxics secondary, ozone precursors



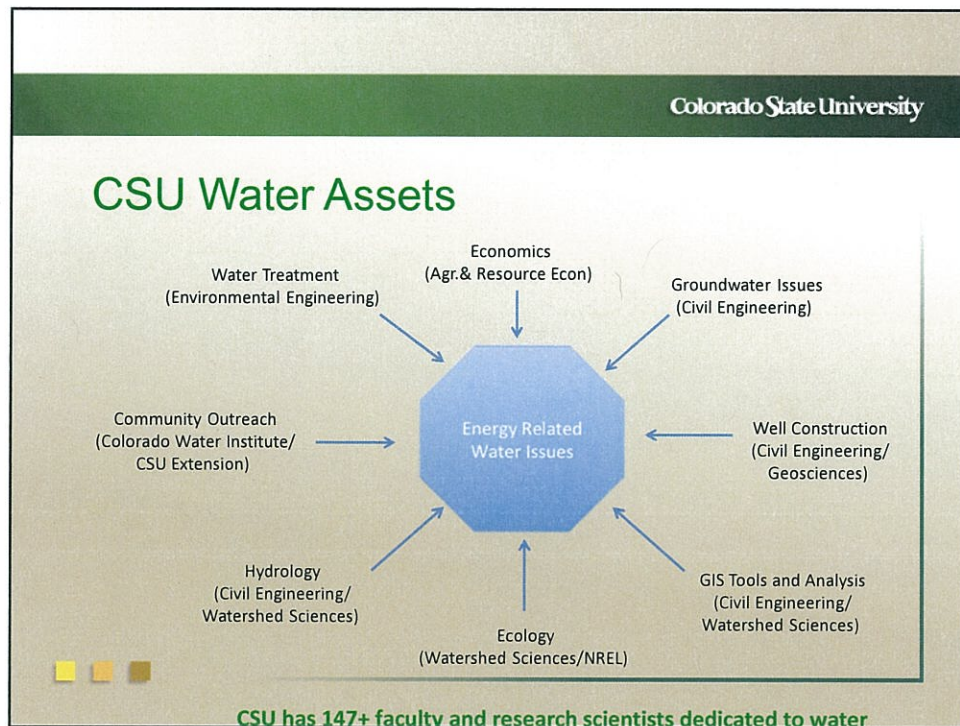
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Colorado State University

## What About Water?



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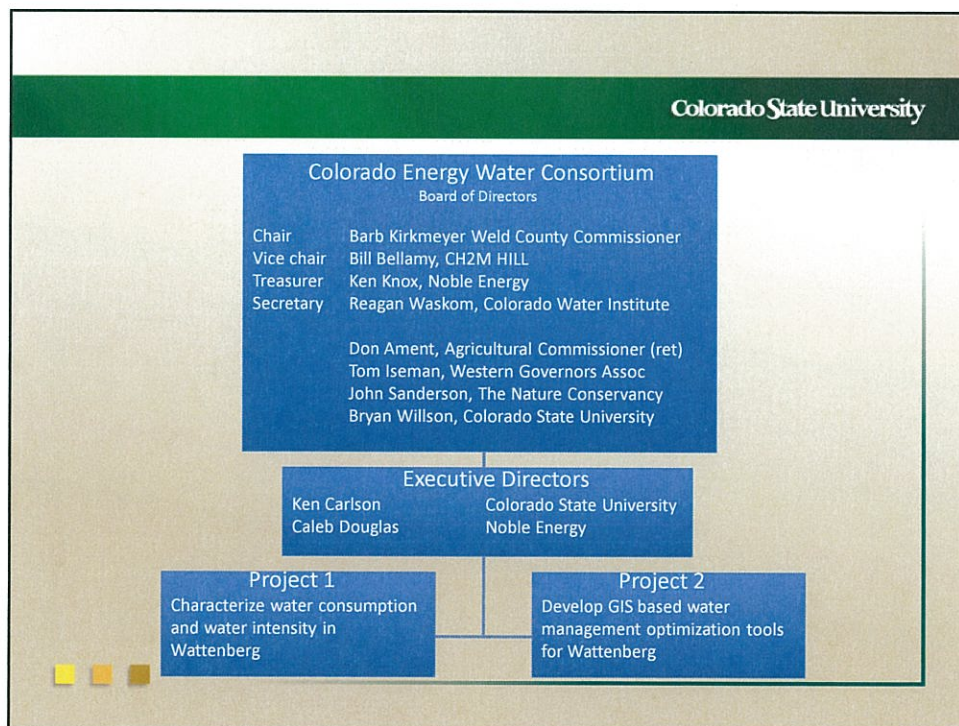
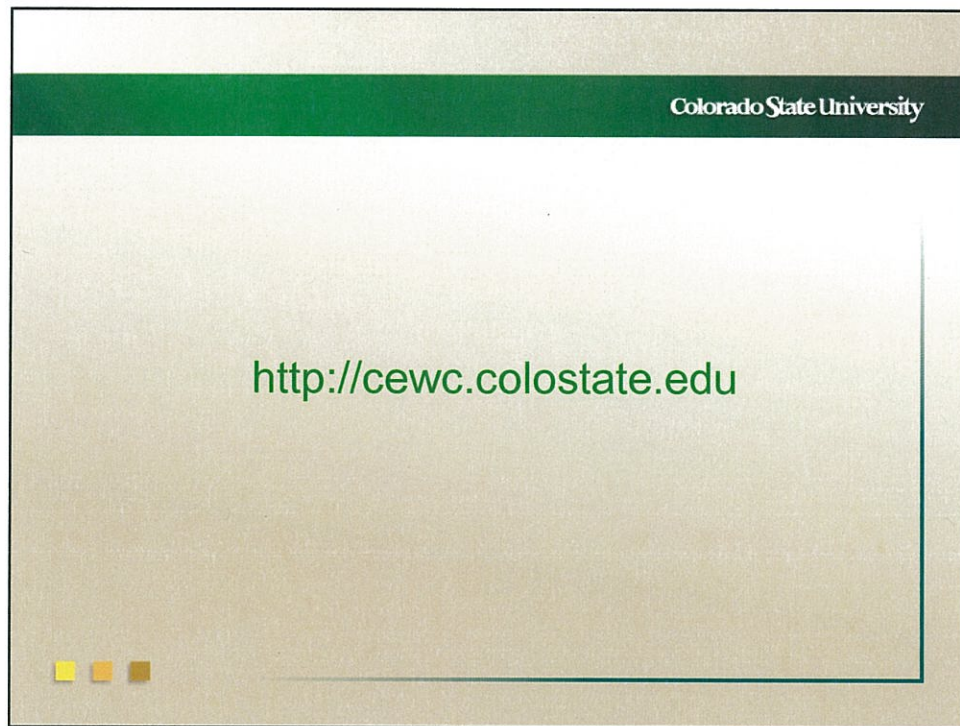


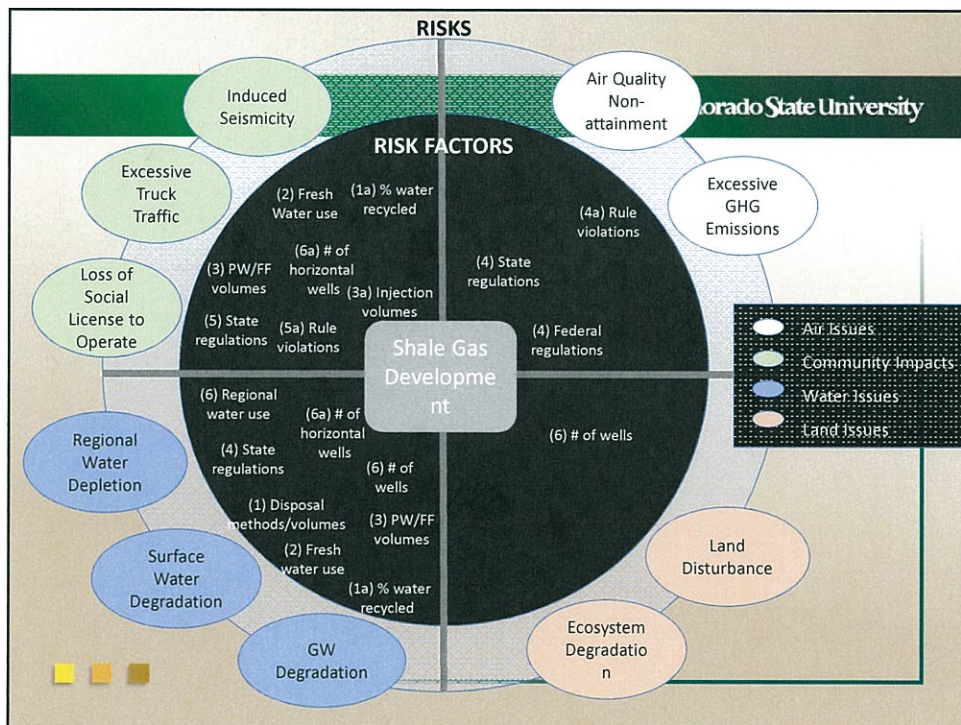
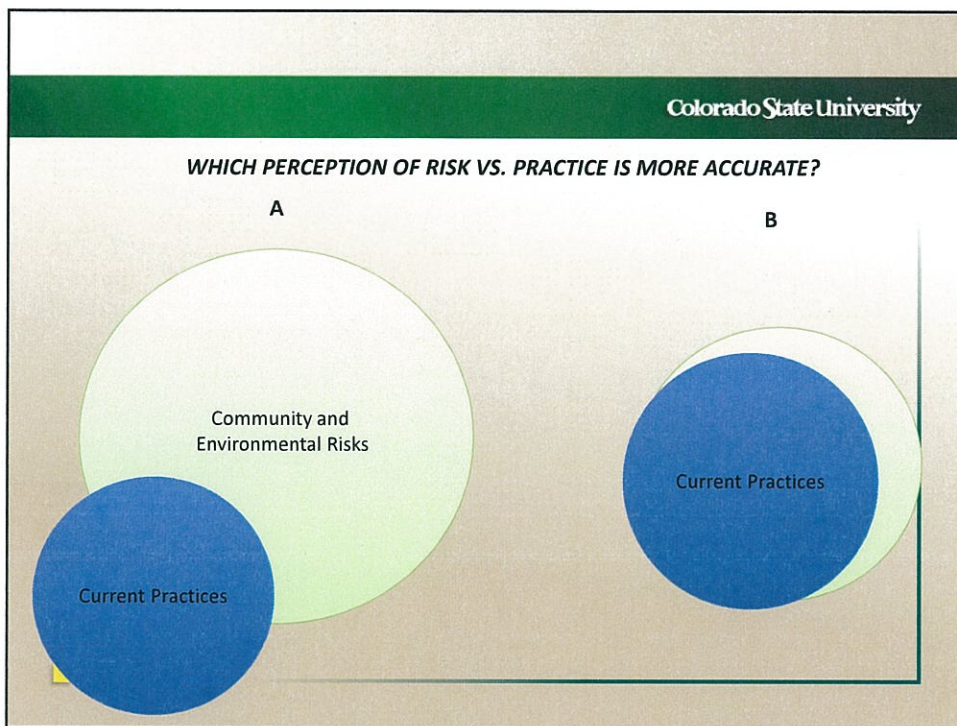
Colorado State University

## Colorado Energy Water Consortium Objectives

- Industry/university research center focused on natural gas/oil water issues.
- Collaborative industry/CSU research.
- Communicate natural gas related water issues and solutions to public, industry and others.
- Enhance curricula and programs within CSU to respond to an evolving job market in the energy-water resources field.

3







**TISHA CONOLY SCHULLER**

Ms. Tisha Conoly Schuller serves as President and Chief Executive Officer of the Colorado Oil & Gas Association (COGA).

Oil and gas development has been occurring safely in Colorado for over 100 years. With operations moving into communities new to oil and gas production, there is heightened public interest and concern. This presentation will briefly address common misconceptions about oil and gas development and will cover water protection, spill prevention, water use, drilling locations, property values, air quality protection, and disclosure of hydraulic fracturing fluids.

**SHANE DAVIS**

Shane Davis currently chairs the Poudre Canyon Group of the Rocky Mountain Chapter of the Sierra Club, and serves as the Group's Conservation Chair. He serves as an At-Large Member of the Chapter Executive Committee and as the Information and Research Manager - Oil & Gas Mining.

"The Hidden Impacts of Fracking in Colorado"

This presentation uses genuine COGCC data to arrive at analyses that demonstrate temporal trends of impacts caused by mining that uses hydraulic fracturing methods. The presentation is a visual journey of Colorado specific oil and gas incidents that have caused adverse impacts to the environment and human health. I use statistics, actual reported cases, reclamation issues, failures, Notice of alleged violations, API information, methods of improvements, satellite imagery, and various other data collected and compiled from Colorado Oil and Gas Conservation Commission's database(s).

**THOM KERR**

Thom Kerr is the Acting Director at the Colorado Oil and Gas Conservation Commission (COGCC).

His presentation will include:

1. A recap of the activity in the Loveland area.
2. A review of COGCC rules and regulations that directly address the concerns about environmental impacts from hydraulic fracturing.

## The Colorado Department of Public Health and Environment

Loveland City Council Study Session  
June 12, 2012

### APCD's Regulation of Oil and Gas

- The Air Pollution Control Division (APCD) is responsible for oversight and permitting of Federal and State Air Quality Rules.
  - **State Air Quality Rules**
    - AQCC Rule 1 - Opacity (e.g. smoke and fugitive dust)
    - AQCC Regulation 2 - Odor
    - AQCC Regulation 3 - State permitting Requirements
    - AQCC Regulation 6 – New Source Performance Standards
    - AQCC Regulation 7 – Ozone Precursor Control
    - AQCC Regulation 8 – Maximum Achievable Control Technology (MACT) Standards

## APCD's Regulation of Oil and Gas

### Federal Rules

#### New Source Performance Standards (NSPS) 40 CFR Part 60

- NSPS Kb – Storage tanks
- NSPS GG – Gas turbines
- NSPS KKK – Fugitive Volatile Organic Compound emissions) (under revision)
- NSPS LLL – Amine and sulfur recovery units) (under revision)
- NSPS IIII – Compression ignition engines
- NSPS JJJJ – Spark ignition engines
- NSPS KKKK – Combustion turbines
- NSPS OOOO – Oil and Gas (proposed)
- NSPS Dc – Small boilers

#### Maximum Achievable Control Technology (MACT) 40 CFR Part 63

- MACT HH – Oil and natural gas production facilities (tanks, compressors, and ancillary equipment) (under revision)
- MACT HHH – Natural gas transmission and storage facilities (dehydrators) ) (under revision)
- MACT YYYY – Combustion turbines
- MACT ZZZZ – Reciprocating engines
- MACT DDDDD – Boilers and process heaters
- MACT GGGGG – Site remediation requirements

## APCD Permit

A permit is required for facilities that have the potential to emit 2 tpy VOCs in Larimer County.

- Defines what pollutants can be emitted and at what levels
- Identifies what steps a facility must take to reduce emissions
- Specifies how emissions must be measured and reported

## How much is 2 tons per year?

- Based on State default emission factor for Larimer County two tons of VOCs = ~ 292 bbls\* of throughput for condensate tanks
- Thus, about two tanks are enough to trigger APCD permitting (2 tpy) and about one tank would trigger reporting requirements (1 tpy).

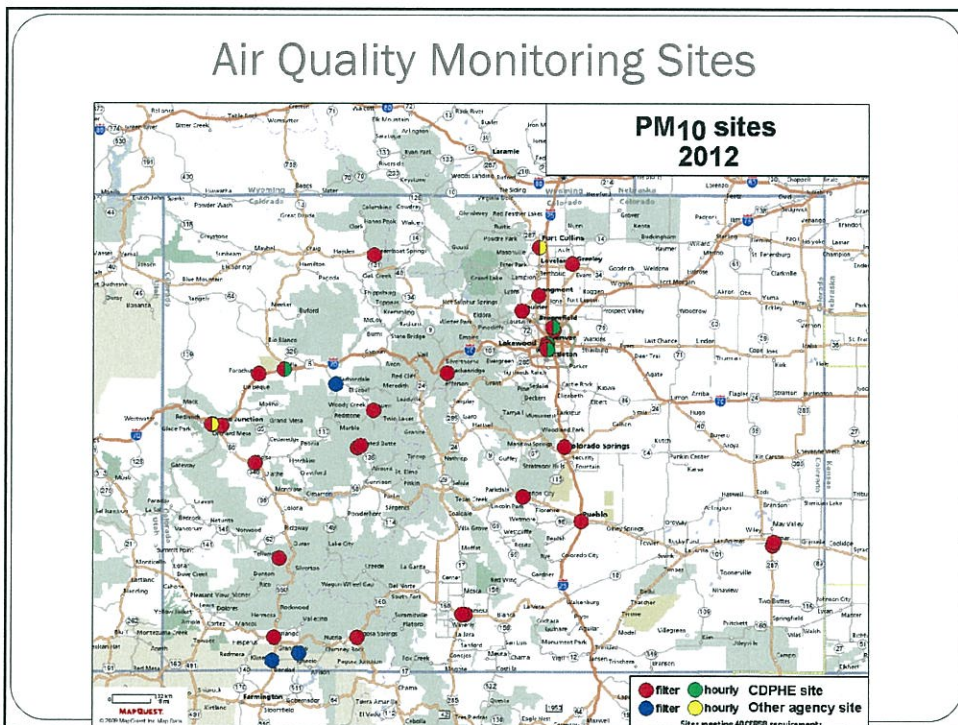
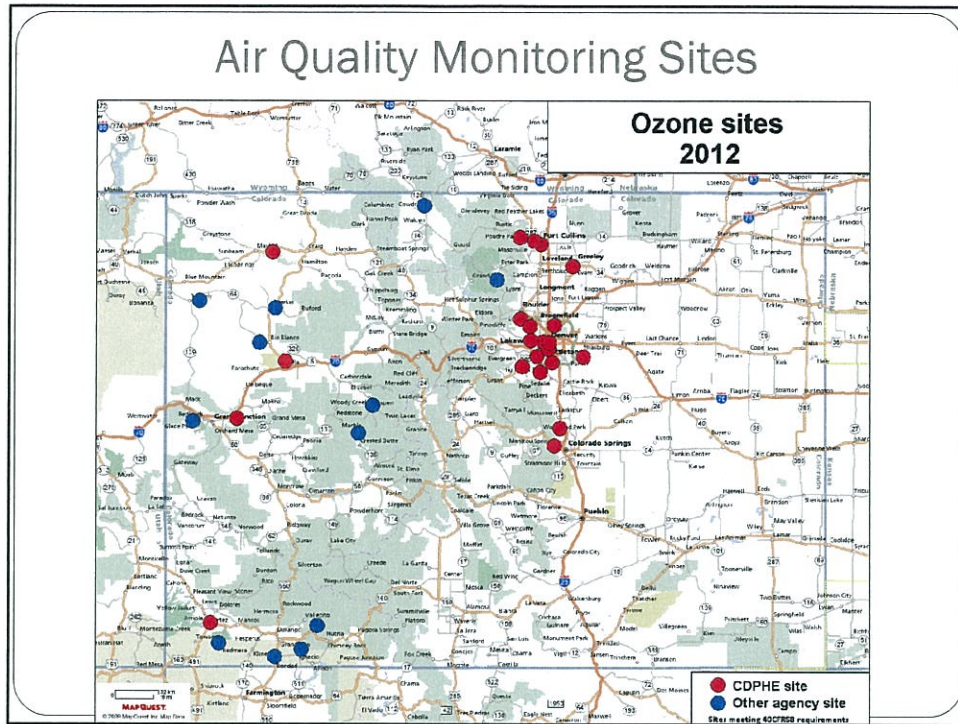
\*13.7 lb/barrel emission factor or site-specific sampling.

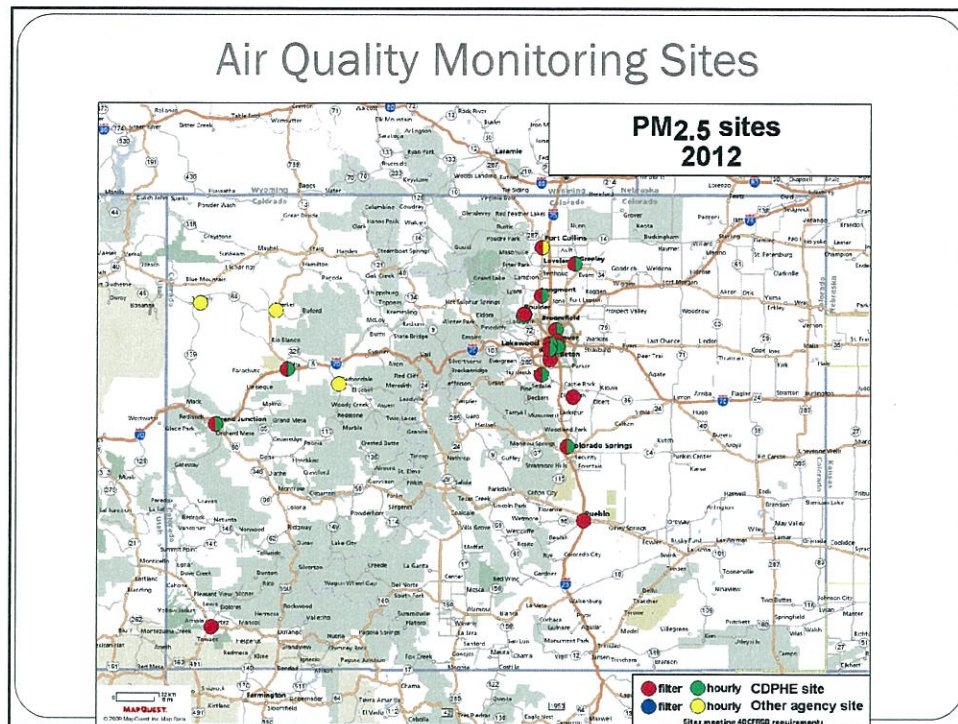


Each tank pictured is  $\approx$  300bbl

## Air Monitoring Overview

- EPA has 6 “Criteria” pollutants for National Ambient Air Quality Standards (NAAQS) – primary focus for CDPHE/APCD
  - CO, O<sub>3</sub>, NO<sub>2</sub>, SO<sub>2</sub>, PM (PM<sub>10</sub> & PM<sub>2.5</sub>), Pb
- Designed to protect public health
- Performed across State of Colorado
  - APCD has approximately 60 sites (other agencies also have monitors)
  - Sites added or removed based on needs and concentrations recorded
- Mainly in population centers
- Different types
  - “Continuous” provides hourly values
    - CO, O<sub>3</sub>, NO<sub>x</sub>/NO<sub>y</sub>, SO<sub>2</sub>, PM<sub>10</sub>, PM<sub>2.5</sub>, meteorology
  - “Daily” provides 24-hour values
    - PM<sub>10</sub>, PM<sub>2.5</sub>, air toxics





- ### Monitoring Site Costs
- Cost for a monitoring site:
    - Shelter = \$15,000 - \$35,000
    - Analyzer = \$9,000 - \$32,000
    - Meteorological = \$5,000 - \$10,000
    - On-site QA equipment = \$2,000 - \$25,000
    - Data logging/communications = \$10,000
    - Installation = \$1,000 - \$20,000
  - Multi-pollutant site can cost \$250,000 or more
  - Operational:
    - Utilities = \$1,000 - \$3,000 /year
    - Filters/consumables/repairs = \$300 - \$2,000 /year
    - Laboratory analyses = \$1,200 - \$36,000 /year
    - Data processing/QA/QC = \$2,000 - \$30,000 /year



## APCD Data Availability

- “Continuous” data posted hourly on APCD Technical Services website and uploaded to EPA’s AIRNow website
  - <http://www.colorado.gov/airquality/>
  - <http://airnow.gov/>
- Forecasting performed daily and posted on APCD Technical Services website
- Annual Data Report published and on APCD website

## What we know about Public Health Impacts from Oil and Gas Development

- Air quality and health risk assessment studies conducted or reviewed by the department have major uncertainties due to a lack of critical information. Thus cannot be used to draw any definitive conclusions regarding health impacts.
- For example,
  - In the recent CSPH study, it is unknown whether data collected adjacent to well pads (130-500 ft from the well pads) can appropriately represent actual exposures for individuals living  $\leq 1/2$  mile (up to 2640 ft) from the well pad that is undergoing completion activities.
  - Air dispersion can rapidly dilute pollutants, so exposures beyond the 130-500 ft measurement distances may not relate to the data collected adjacent to the well pads.
  - The CSPH study concluded that “preliminary results indicate that health effects resulting from air emissions during development of unconventional natural gas resources are most likely to occur in residents living nearest to the well pads and warrant further study”.

## What we know about Public Health Impacts from Oil and Gas Development

- Currently, insufficient data exists at the local, State or Federal level to draw any definitive conclusions about public health impacts from oil and gas development.

The limited available information suggests a low potential for public health impacts

## What we are doing to learn more about Public Health Impacts

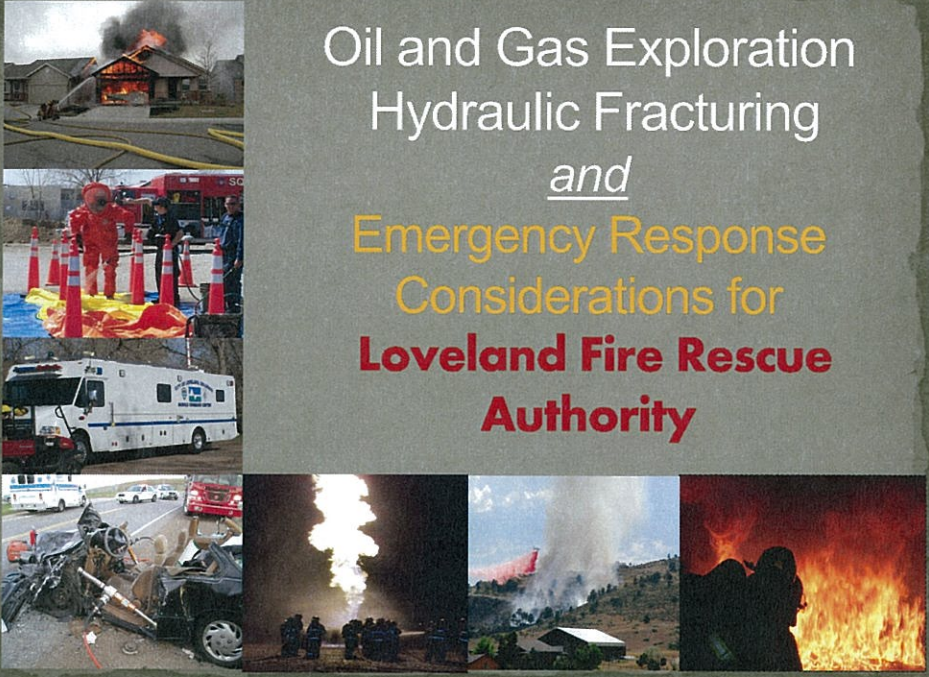
- CDPHE is participating on the Technical Advisory Committee at CSU for the research being done into air quality emissions from oil and gas activities in Garfield County.
- The study will provide data on emissions from oil and gas sites at various distances from the well pad. We hope to learn how quickly emissions disperse in the air and discover how different seasons affect these emissions.

## What we are doing to regulate emissions from Oil and Gas Development

- The Department provides thorough environmental permitting, enforcement and compliance assistance for oil and gas operations in Colorado.

## BMPs for a High Density Location

- Meet with nearby residents to explain the project and discuss their concerns.
- Designate a primary traffic route for all construction traffic and deliveries.
- Post signage notifying contractors of the designated access route.
- Minimize traffic during hours when School Buses are in operation.
- Require a gravel apron at the property line to prevent mud from being tracked from the site onto residential streets.
- To the extent possible, orient the drilling equipment away from the residential housing.
- Equip the drilling equipment with special noise reducing mufflers (Hospital Grade).
- Utilize a sound absorbing tarp around the drilling floor and draw works to muffle noise from the drilling operations.
- Place trailers and tanks on the well pad between the residential housing and the drilling site to reduce noise.
- Control access to the site. (use fencing to keep children away from the drilling site)
- Direct lighting away from the residential area as possible while still maintaining a safe working environment.
- Utilize emission control devices on tanks and pits to reduce odor from the well pad.
- Employ practices to minimize fugitive dust from the well pad and roads.



Oil and Gas Exploration  
Hydraulic Fracturing  
*and*  
Emergency Response  
Considerations for  
**Loveland Fire Rescue  
Authority**

#### INTRODUCTION

In this evening's presentation we will address many of the concerns raised by citizens and council members related to emergency response, oil & gas exploration and hydraulic fracturing ("fracking"). This presentation will be focused on the following 4 areas for emergency response:


1. Command and Control systems currently in place
2. Resources locally and regionally that can be deployed
3. The role of Emergency Management
4. Future needs and inquiry specific to hydraulic fracturing

*The seminal question for this presentation is:*

***Are emergency responders in Loveland prepared for a fracking emergency?***

COMMAND and CONTROL

### 1. Command and Control systems in place :



- Use of the NIMS Incident Command System
- The application of the Incident Priorities
- The development of an Incident Action Plan (IAP)

*We will briefly look at how we put this all together to make it work effectively with an emphasis on citizen and firefighter safety...*



We opened with this slide, it shows seven different incidents where a command system would be used: Our command system (NIMS) is an "All Risk" system...

- LFRA personnel are all trained, certified and qualified in NIMS and other compatible command systems
- We practice and train on these skills

*A fracking incident fits into the "All Risk"*

COMMAND and CONTROL

### The application of the Incident Priorities

- One of the basic tenets of the command system is the 3 incident Priorities:
  - 1. Life Safety**
  - 2. Incident Stabilization**
  - 3. Property Conservation**

In Training and in every day Operations, we focus on these 3

*The order of these priorities never change, they are a constant; tactical and task level operations fit around these three priorities...*

*This would apply to an emergency involving a fracking operation as well...*

COMMAND and CONTROL

### Development of the Incident Action Plan (IAP)

- The IAP begins with the first arriving officer or member and is refined and upgraded as needed; so too is the command system. The basic premise of the IAP is:

**Standard Conditions → Standard Actions →**  
**→ Standard Outcomes...**

*\*Fracking operations present a unique challenge because of our specific lack of experience and training*

*Initial size-up operations would determine:*

- 1. Life Safety concerns or Evacuation needs**
- 2. Fire Attack/Control or Haz-mat Operations**
- 3. Shut-off, shut down and containment**
- 4. Specialized resources needed**

COMMAND and CONTROL

**Putting this all together...**

*In a fracking emergency some task level operations would be different, however, most of the strategic and tactical levels would be consistent with other emergency operations handled by LFRA-*



*What may also be different in these incidents is the specialized resource needs...*

DEPLOYABLE RESOURCES

**2. Deployable Resources locally/ regionally :**



- Loveland Resources (LFRA)
- Automatic & Mutual Aid
- Other Emergency Response

*Resource needs for a fracking emergency are likely to be significant for both the incident and overall systems needs- however, we do encounter similar situations with other types of emergency operations...*

DEPLOYABLE RESOURCES

2. Deployable Resources locally/ regionally (cont.):

*Resource needs for this type of an incident may involve:*

- *A full first alarm assignment (4-6 companies)*
- *Special Operations Team (Haz-Mat response)*
- *2<sup>nd</sup>-3<sup>rd</sup> Alarms (auto-aid and mutual aid)*
- *Specialized Response (Haz-Mat) from region*

*The important part about this is that we have worked diligently over the past several years improving our regional relationships (surrounding departments) and beyond (FRFC) to enhance the number of resources...*

*This applies for all hazards including fracking...*

DEPLOYABLE RESOURCES

2. Deployable Resources locally/ regionally (cont.):

*The need for other resources and tools will be a vital part of the response to serious fracking incidents...*

*Law Enforcement, EMS, Public Works, Water & Power and other city services will likely be needed...*

*Citizen notification and the use of Everbridge as well...*

*These are all systems that are in place and used for other responses*





EMERGENCY MANAGEMENT

### 3. Emergency Management :



- **Community Safety and Emergency Management-**
  - Managed within LFRA
  - Community Safety Division- by Chief Green and Lieutenant Mialy

*We have developed strong working relationships with regional, county and state emergency management offices. We also have shared regional mitigation plans...*

*This type of emergency and operational planning would apply to any emergency including those involving a fracking operation ...*

EMERGENCY MANAGEMENT

- **Incident Stabilization and Recovery-**



*A primary initial goal for Emergency Management will be community stabilization and the initiation of a community recovery plan*

*Restoring Normalcy is the Ultimate Goal...*

*It would be the same thing in a major fracking emergency...*



CURRENT and FUTURE NEEDS

#### 4. Current, Future Needs and Inquiry :



*So, what is different about fracking operations and emergency response?*

*We will end by looking at what we are currently working on and what needs to be done in the future...*

CURRENT and FUTURE NEEDS

- **Current Operations and Discovery-**

Since this issue surfaced, we have put a work group together within LFRA responsible for gathering information and inquiry into fracking operations. We have:

1. *Evaluated our own system and needs*
2. *Contacted fire departments for information*
3. *Specifically looking for operational plans*
4. *Contacting oil and gas industry officials*

*\*This last area will be vitally important as we move forward with developing solid operational plans for responding to fracking emergencies...*

CURRENT and FUTURE NEEDS

- **Building working relationships with SME's**



*We will need to build strong working relationships with those in the industry that have the knowledge and expertise for these kinds operations...*

- Those in the oil and gas industry (state regulators)
- Specific companies working/ operating in Loveland
- Learning more about their available resources
- Learning more about process/ operational regulations

CURRENT and FUTURE NEEDS

- **LFRA Future Actions and Needs-**

During the time of the moratorium we will be:

1. *Developing LFRA's standard operational guidelines specific to fracking operations*
2. *Developing training plans and site visits*
3. *Delivering overall department training*
4. *Planning for technician level training*
5. *Implementing a tiered response (ops/ technician)*
6. *Planning for continuous improvement in our KSA's*

*\* Planning for and responding to fracking emergencies will create some unique challenges for LFRA, but we have done this before in other types of emergencies...*

Questions???