EPAPAV0037744

DRAFT

DRAFT

Investigation of Ground Water Contamination near Pavillion, Wyoming

Dominic C. DiGiulio
Richard T. Wilkin
Carlyle Miller
U.S. Environmental Protection Agency
Office of Research and Development
National Risk Management Research Laboratory
919 Kerr Research Drive
Ada, OK 74820

Gregory Oberley
U.S. Environmental Protection Agency
Region 8
1595 Wynkoop Street
Denver, CO 80202

Office of Research and Development
National Risk Management Research Laboratory, Ada, Oklahoma 74820

EPAPAV0037746

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.

EPAPAV0037747

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.

EPAPAV0037748

Acknowledgements

The authors would to like to acknowledge valuable comments from 1 internal and 3 external reviewers used to improve this manuscript. We would also like to acknowledge Dr. Randall Ross, Dr. Junqi Huang, Dr. Doug Beak, Mr. Steve Acree, Mr. Tony Lee, Mr. Ken Jewell, Mr. Tim Lankford, Mr. Russell Neil, and Ms. Kristie Hargrove from ORD/NRMRL/Ada and Mr. Christopher Ruybal and Ms. Alexandra Kirkpatrick (student contractors) for their assistance in collecting ground water and gas samples. We would like to acknowledge Dr. Jennifer Gundersen of EPA's Region 3 Laboratory for conducting analysis water samples for glycols and 2-butoxyethanol and Dr. William Batschelet of EPA's Region 8 Laboratory for conducting and arranging the analysis of water samples for a number of classes of compounds. We also thank Mr. John Cox, Mr. Steve Markham, Ms. Tracy Pardue, Dr. Feng Lu, Mr. Joseph Karikari, Ms. Lisa Hudson, Dr. Sujith Kumar, Mr. Joe Tyburski, Mr. David Kessler, Mr. Jim Wilson (Shaw Environmental and Infrastructure), Mr. Mark White, Ms. Lynda Callaway, and Mr. Dennis Miller (ORD/NRMRL/Ada) for analytical support. We would like to thank Mr. Nathan Wiser, Mr. Robert Parker, and Ms. Johanna Miller of EPA Region 8 and Mr. Ron Mellor (SEE employee) for assistance in interpreting data and numerous helpful comments. We would like to acknowledge Mr. Steve Vandegrift of ORD/NRMRL/Ada for providing helpful comments in improving QA/QC aspects of this investigation and overseeing development of the QAPP and ADQs. We would like to acknowledge Dr. John Wilson for assistance in interpretation of data. We are grateful to Ms. Ayn Schmit of EPA Region 8 and Dr. David Jewett of ORD/NRMRL/Ada for ongoing support in their respective management roles and ability to effectively communicate technical details in this manuscript to others. We would like to express our appreciation to Mr. Jeff Locker and Ms. ZoeAnn Randall for access to their property for monitoring well installation and to Mr. Louis Meeks for access to his property for domestic well sampling. We are grateful to Mr. John Fenton for access to his property for domestic well sampling and facilitating contact with domestic well owners in the area. We are grateful to Ms. Kathy Tynsky of SRA for assistance in developing graphics in this document.

EPAPAV0037749

DRAFT

Contents

Notice ii

Foreword iii

Acknowledgements iv

Figures vi

Tables ix

Extended Abstract xi

1.0 Site Background 1

2.0 Methods 5

Sampling Chronology 5

Deep Monitoring Well Installation 5

Ground Water Sampling of Deep Monitoring Wells in Phase III and IV 11

Gas Sampling from Casing of Deep Monitoring Wells in Phase III and IV 15

Domestic Well Sampling for Methane Using a Closed System in Phase IV 15

Review of Borehole Geophysical Logs 15

Review of Cement Bond/Variable Density Logs 16

3.0 Results and Discussion 17

Ground Water and Soil Sample Results near Three Pits 17

Inorganic Geochemistry 17

Organic Geochemistry 23

Natural Gas Migration 27

Evaluation of Cement Bond/Variable Density Logs Along Transect 29

Potential Migration Pathways 32

4.0 Conclusions 33

5.0 References 40

Appendices A1

Appendix A – Summary of Analytical Results A1

Appendix B – Quality Assurance and Quality Control (QA/QC) for Analysis B1

Appendix C – Photographic Log of Deep Monitoring Well Construction C1

Appendix D – Photographic Log of Ground Water Sampling D1

Appendix E – Examples of Cement Bond/Variable Density Log Interpretation E1

EPAPAV0037750

Figures

Figure 1. (a) Location of Wind River Basin in Wyoming. **(b)** Location of Pavillion Gas Field in the Wind River Basin. Figure from Johnson et al. 2007 1

Figure 2. Chronology of production well completion at the Pavillion Gas Field 2

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 2

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 3

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 6

Figure 6a. Schematic illustrating construction of MW01 9

Figure 6b. Schematic illustrating construction of MW02 10

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..... 11

Figure 8. Variation of water level as a function of time in MW01 during Phase 4 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 12

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) 13

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 16

Figure 11. Durov diagram showing ground water chemistry trends obtained in Phase I - IV sampling events and the composition of irrigation water 17

Figure 12. Depth trends of chloride, pH, sulfate, and potassium (filled black squares = domestic wells, filled red circles = monitoring wells) 18

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 19

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) 21

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 22

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) 22

Figure 17. Organic compounds detected in deep monitoring wells MW01 and MW02 during Phase III and IV sampling events 25

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. δD was not determined for PGDW32. Oxidation pathway (enrichment of ^{13}C of remaining CH_4 with biodegradation) is illustrated. **(c)** Methane concentration in domestic and monitoring wells as a function of proximity to production wells and depth. Values of 1.0 were used for non-detection (detection limit 5 μg/L) 28

Figure 19. Map illustrating transect used to develop lithologic cross section and evaluation of CBL/VDLs 30

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 31

Figure C1. Photograph of drilling rig on platform with shakers for mud recirculation at MW02 ..... C2

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

Figure C3. Photograph of blowout preventer for drillstem C2

Figure C4. Photograph of bit and drillstem with bit for mud rotary drilling at MW02 ..... C3

Figure C5. Photograph of water truck used to transport water to mix mud C4

Figure C6. Photograph of Quik-Gel bentonite (Halliburton) used to create mud for drilling C4

Figure C7. Photograph of mud additives EZ Mud Gold (Halliburton) and Dense Soda Ash C4

EPAPAV0037752

Figure C8. Photograph of mud additive Penetrol (Halliburton) C4

Figure C9. Photograph of flow of mud and cuttings from borehole at MW02 ..... C5

Figure C10. Photograph of monitoring of mud and cuttings using a Thermo Scientific TVA-1000B FID/PID at MW02 ..... C5

Figure C11. Photograph of pump used to transport mud and cuttings to shakers at MW02 ..... C6

Figure C12. Photograph of flow of mud and cuttings to shakers at MW02 ..... C6

Figure C13. Photograph of shakers separating mud from cuttings at MW02 ..... C7

Figure C14. Photograph of cuttings transported to disposal bins at MW02 ..... C8

Figure C15. Photograph of pumping of mud back to borehole at MW02 ..... C9

Figure C16. Photograph of injection of mud to borehole at MW02 ..... C10

Figure C17. Photograph of collection of cuttings for lithologic characterization at MW02 ..... C11

Figure C18. Photograph of removal of mud from cuttings at MW02 ..... C11

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 C11

Figure C20. Photograph of setting of stainless-steel pre-packed screen and sand basket into borehole at MW02 ..... C12

Figure C21. Photograph of securing sand basket and casing above screen..... C13

Figure C22. Photograph of placement of sand in sandbasket C13

Figure C23. Photograph of well development at MW02 ..... C14

Figure D1. Photograph of flow from submersible pump through flowmeter at MW02..... D2

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

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

Figure D4. Photograph of water (foaming) flowing into YSI flow cell at MW02 ..... D3

Figure D5. Photograph of sampling at MW02. The sample train was split prior to entry into purge water disposal container D4

Figure D6. Photograph of field filtering samples for metals analysis at MW02 ..... D4

Figure D7. Photograph of sample collection at PGDW14 ..... D5

Figure D8. Photograph of cooler packed with samples for shipment D5

EPAPAV0037753

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 E2

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 E3

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 E4

Figure E3b. Example of "sporadic bonding" Pavillion Fee 11-11B between 2350-3200 feet below ground suface. 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 E5

Figure E4. Example of "Sporadic Bonding" at Tribal Pavillion 24-02. Hydraulic fracturing occurred at 1538 feet bgs. Arrow denotes interval of hydraulic fracturing E6

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. E7

Tables

Table 1. Drilling additives, properties and product use recommendations 7

Table 2. Analytical results of additives (compounds listed are those detected in ground water) 8

Table 3. Geochemical impacts in deep ground water monitoring wells 24

Table 4. Association of inorganic and organic anomalies with compounds used for hydraulic fracturing 26

Table A1. Summary of subsurface sample locations, depth of sample collection, times (phases) of sampling, target analytes, laboratories utilized, and analytical methods A2

Table A2a. Geochemical results for Pavillion ground water A8

Table A2b. Charge balance calculations for deep monitoring wells A9

Table A3a. Summary of aqueous analysis of light hydrocarbons A10

Table A3b. Summary of gas and headspace analysis of light hydrocarbons A12

Table A3c. Summary of isotopic data for dissolved, gas phase, and headspace analysis A14

Table B1. Sample collection containers, preservation, and holding times for ground water samples B2

Table B2. Field QC samples for ground water analysis B3

EPAPAV0037754

Table B3. QA/QC requirements for analysis of metals and major ions B3

Table B4. QA/QC requirements for analysis of dissolved gases, DIC/DOC, VOCs, low molecular weight acids and stable isotopes of water B4

Table B5. QA/QC requirements for analysis of semi-volatiles, GRO, and DRO B5
Table B6. QA/QC requirements for LC/MS/MS analysis of glycols B6

TableB7a. ICP-OES blank results for Phase III and Phase IV sampling B7

Table B7b. ICP-OES blank results for Phase III and Phase IV sampling B7

Table B7c. ICP-MS blank results for Phase III and Phase IV sampling B8

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 B8

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

Table B10. Blank results for Volatile Organic Compounds (µg/L) in Phase IV sampling (ORD laboratory, Ada, OK) B11

Table B11. Blank results for Semi-Volatile Organic Compounds (µg/L) in Phase III and Phase IV sampling (Region 8 laboratory, Golden, CO) B12

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) . B13

Table B13. Duplicate data for selected major ions, DOC, and DIC in ground water samples collected during Phase III and Phase IV sampling activities B14

Table B14. Duplicate data for methane and selected dissolved organic compounds in ground water samples collected during Phase III and Phase IV sampling activities B15

Table B15. QA/QC requirements for analysis of $\delta^{13}C$ of DIC B16

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

Table B17. QA/QC requirements for analysis of fixed gases and light hydrocarbons for aqueous and gas samples B16

Table B18. Summary of quality control samples, purpose, method, and frequency to support gas analysis B17

Table B19. Summary of analytes, instruments, calibration, and check standards for portable gas analyzers B17

Table B20. QA/QC Requirements for portable gas analyzers B17

EPAPAV0037755

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 mulitiple

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

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.

EPAPAV0037758

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).

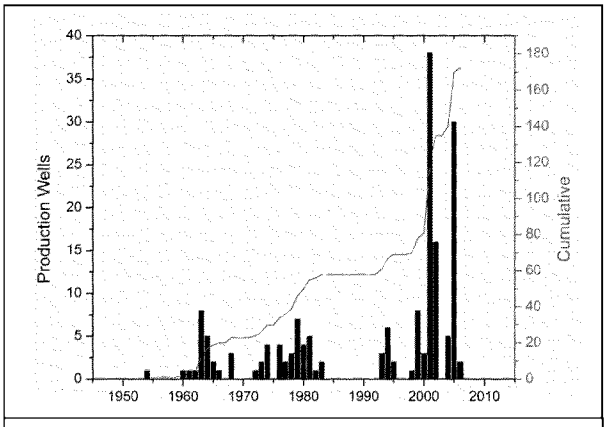

Figure 2. Chronology of production well completion at the Pavillion gas field.

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**).

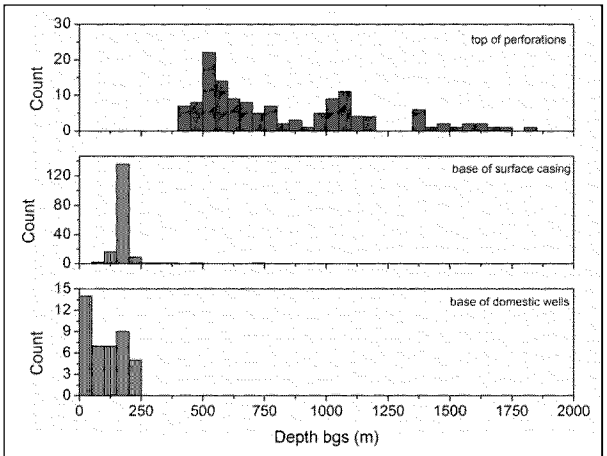

Figure 3. Histograms summarizing depths of top of perforation interval of production wells, base of surface casing of production wells, and base of screened interval of domestic wells.

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 $\delta^{13}C$ 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. $\delta^{13}C$ is defined as

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

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

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

EPAPAV0037764

Table 1. Drilling additives, properties and product use recommendations

Ingredient	Manufacturer	Purpose	Composition from MSDS	Specific gravity	Recommended mixture with water (wt/wt)	pH	Properties
Aqua-Clear PFD	Halliburton	Dispersant/ mud removal	anionic polyacrylamide (30-60%)	1.2-1.4	1:2500	neat 6.5 to 7.5	liquid
Penetrol	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
EZ-Mud Gold	Halliburton	Clay/shale stabilizer	"no hazardous substances"	0.8-1	1:1400 to 1:350	1% solution 7.75	solid
Dense Soda Ash	OCI Chemical Corp	Improve bentonite	Sodium carbonate (100%)	2.5	1:100 to 1:50	5% solution 11.5	solid
Quik-Gel	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
Quik-Trol Gold	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

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

Figure 6b. Schematic illustrating construction of MW02.

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**).

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.

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

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

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.

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 $\delta^{13}C/\delta D$ of methane were not filtered. δD is defined as

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

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), $\delta^{13}C$ of dissolved inorganic carbon, and $\delta^{18}O/\delta D$ of water were filtered onsite using 0.45-micron pore-size, disposable-capsule filters. $\delta^{18}O$ is defined as

$$\delta^{18}O(‰) = \left[\frac{(^{18}O/^{16}O)_{sample}}{(^{18}O/^{16}O)_{standard}} - 1\right] x1000$$

where the standard is the VSMOW.

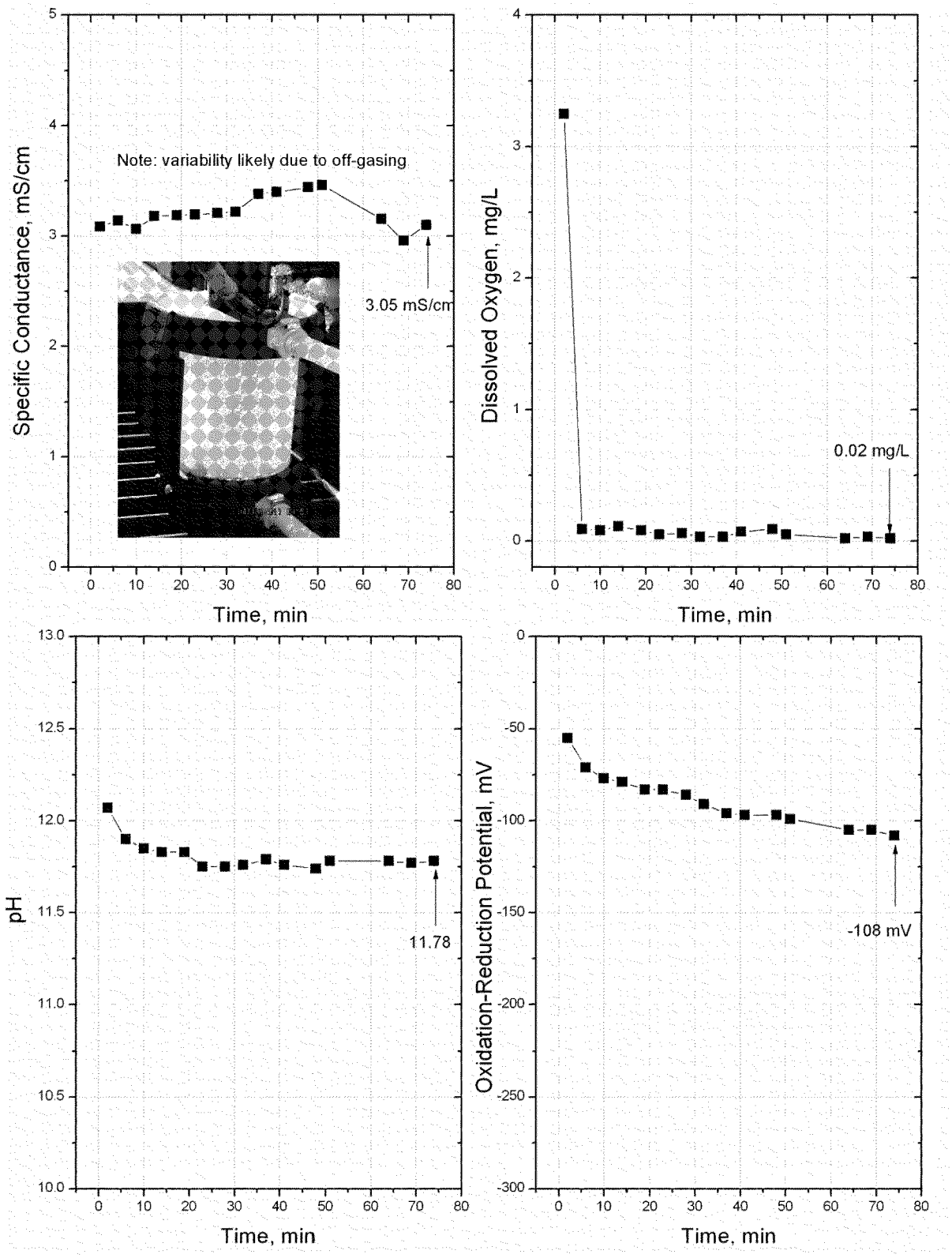

Figure 9. Flow-cell readings as a function of time for specific conductance, dissolved oxygen, pH, and oxidation-reduction potential (well MW02, Phase IV sampling).

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

$$RPD = \left[\frac{x1 - x2}{(x1 + x2)/2} \right] x1000$$

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 detetected 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^+, K^+, Ca^{2+}, Mg^{2+}), anions (Cl^-, SO_4^{2-}, HCO_3^-), 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

the thermodynamic database describing the solubility of KOH (log K= 24.9; $KOH_{(s)} + H^+ = K^+_{(aq)} + H_2O_{(l)}$).

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 till 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 (± 1%) of O_2, CO_2, and 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 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 (Osiensky 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).

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

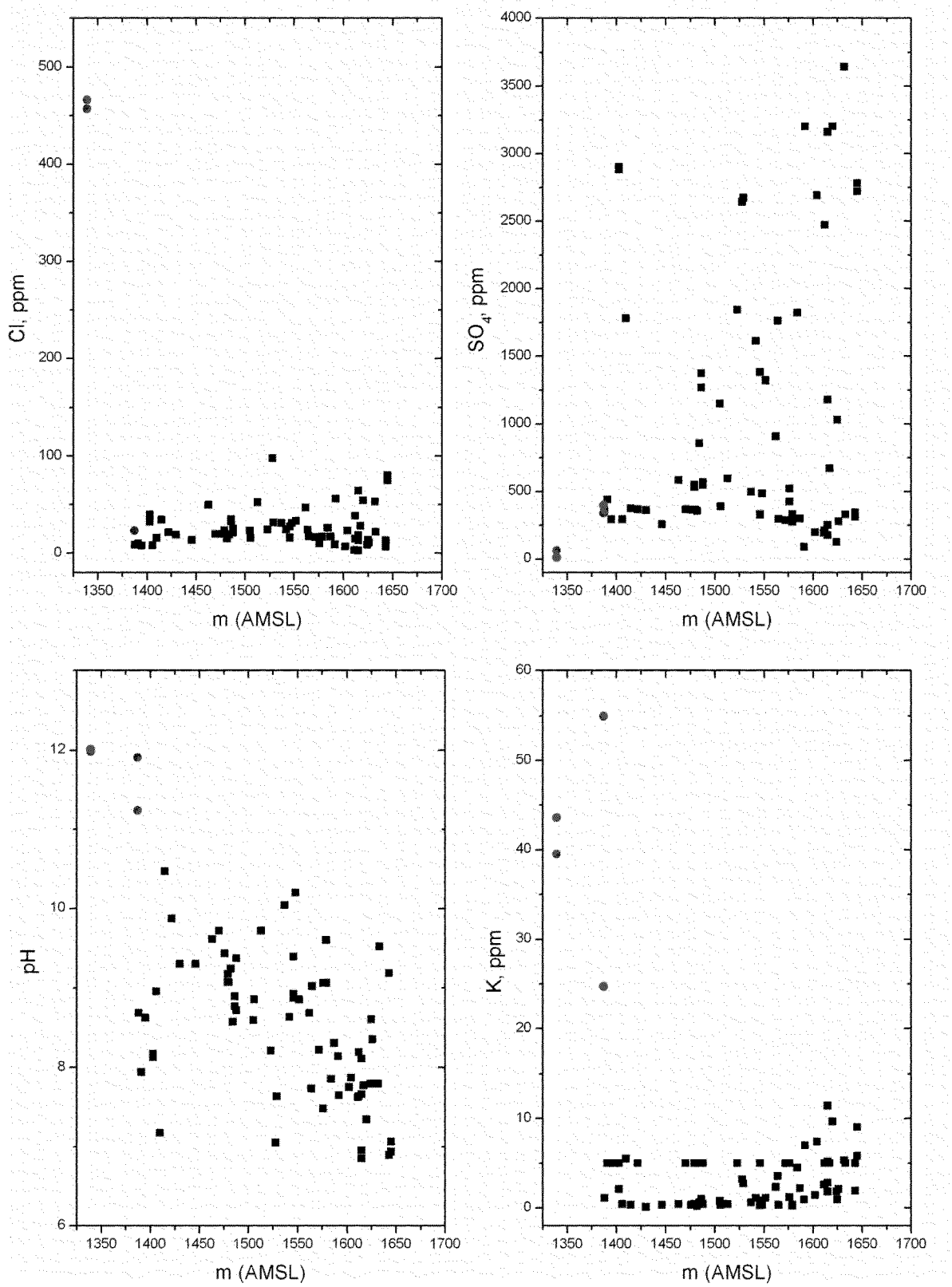

Figure 12. Depth trends of chloride, pH, sulfate, and potassium (filled black squares = domestic wells, filled red circles = monitoring wells).

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 ($CaSO_4 \cdot 2H_2O$) and calcite ($CaCO_3$), 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

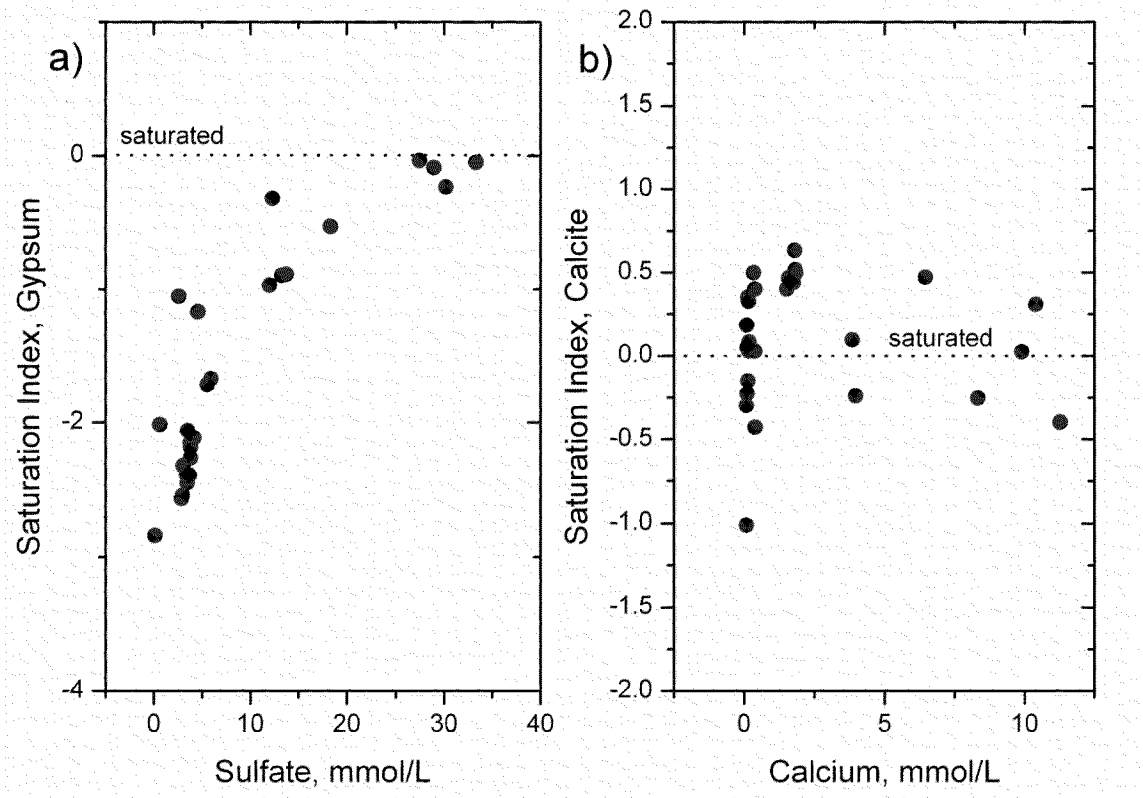

Figure 13. Saturation indices for **(a)** gypsum versus sulfate concentration and **(b)** calcite versus calcium concentration. Saturation Index is equal to the logarithm of the ratio of the ion activity product to the mineral solubility product. A Saturation Index of 0 corresponds to chemical equilibrium;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

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 $\delta^{13}C$ 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_4-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^{2+} and Mg^{2+}, 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_4-type composition) is especially vulnerable to the addition of strong base, with small KOH additions driving significant upward pH changes.

Paired values of $\delta^{18}O$ and $\delta^{2}H$ in ground water samples plot below the Global Meteoric Water Line (**Figure 16**; -16.6 to -12.4‰ $\delta^{18}O$ and -129.2 to -97.4‰ $\delta^{2}H$). Shallow ground water samples generally tend to be depleted in ^{18}O and ^{2}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 $\delta^{18}O$ versus $\delta^{2}H$ trajectory established by the domestic well data, suggesting similar recharge and evolutional paths (e.g., Bartos et al. 2008).

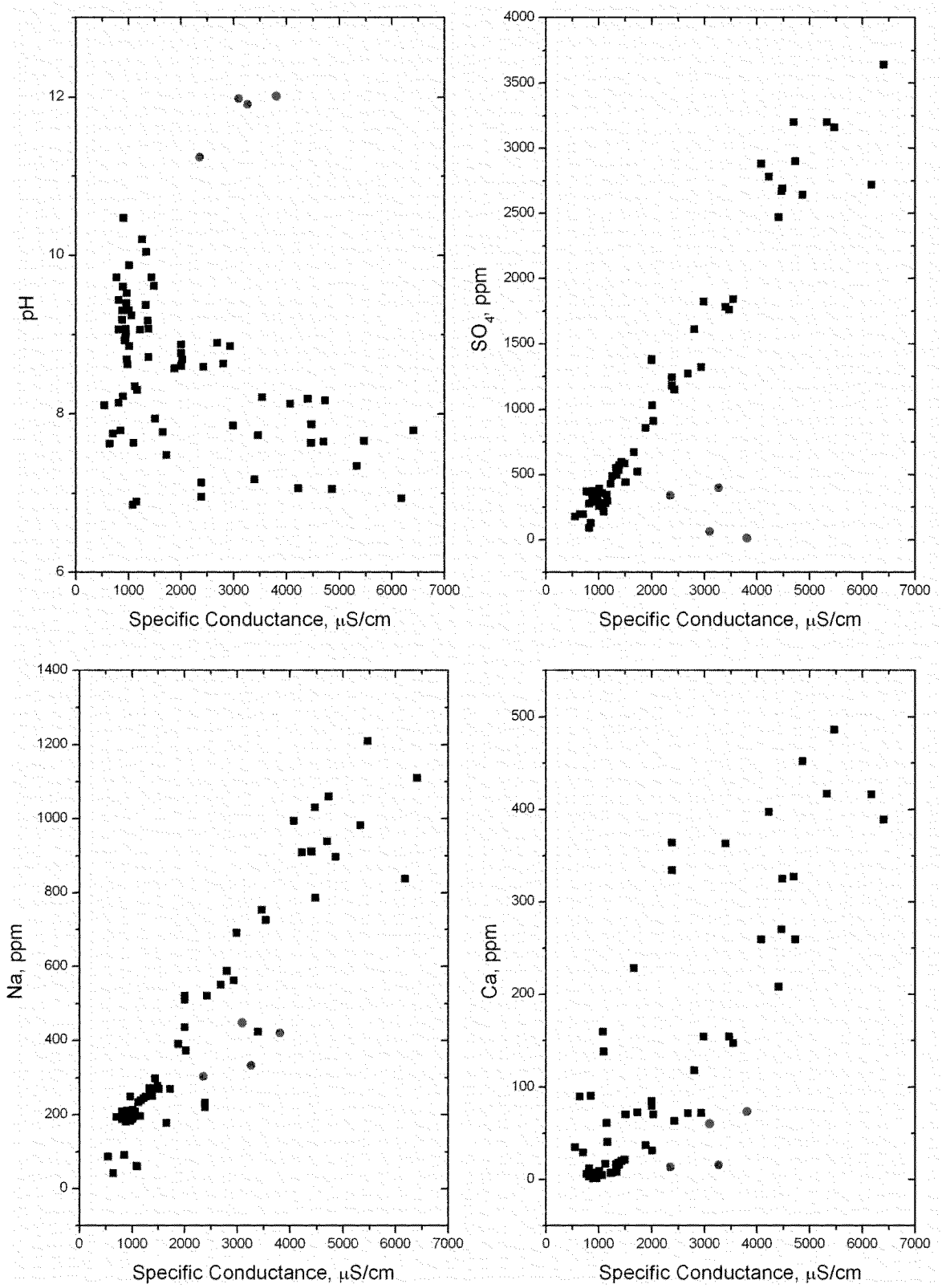

Figure 14. Concentration trends versus specific conductivity. Note the monitoring wells show high pH and low sulfate, calcium, and sodium relative to the general trend observed in the domestic wells (filled black squares = domestic wells, filled red circles = monitoring wells).

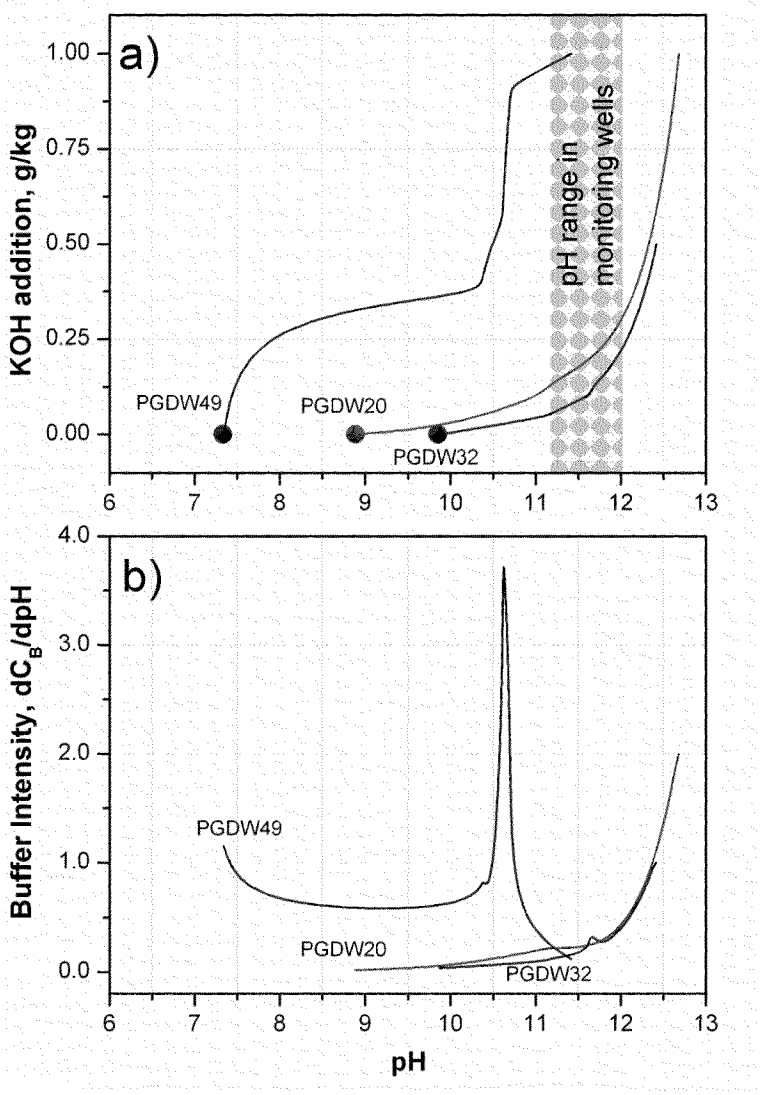

Figure 15. (a) Results of KOH titration models plotted as pH versus grams of KOH added per kilogram of solution. Initial water compositions are from PGDW49, PGDW20, and PGDW32. Model accounts for reactions taking place in solution as KOH is added and equilibrated. pH range in deep monitoring wells shown 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.

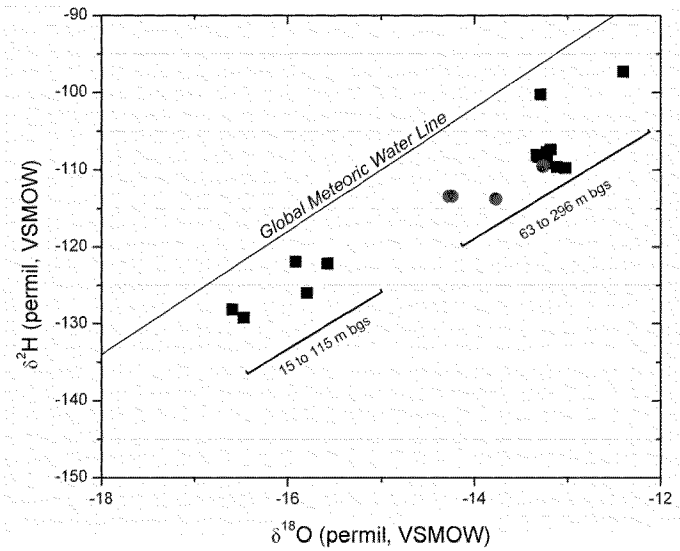

Figure 16. Hydrogen and oxygen isotope values (permil, Vienna Standard Mean Ocean Water, VSMOW) for ground water samples (black squares=domestic wells; red circles=deep monitoring wells) relative to the Global Meteoric Water Line from Craig (1961).

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 µg/L to 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 µg/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 µg/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.

Table 3. Geochemical impacts in deep ground-water monitoring wells

Compound	MW01 Phase 3 10/6/2010	MW02 Phase 3 10/6/2010	MW01 Phase 4 4/20/2011	MW02 Phase 4 4/19/2011
pH	11.9	12.0	11.2	11.8
K, mg/L	54.9	39.5	24.7	43.6
Cl, mg/L	23.3	466	23.1	457
CH_4, mg/L	16.0	19.0	17.9	18.8
Benzene †	nd	246	nd	139
Toluene	0.75 [d]	617	0.56	336
Ethylbenzene	nd	67	nd	21.5
Xylenes (total)	nd	750	0.89 [d]	362
1,2,4 Trimethylbenzene	nd	69.2	nd	18.5
1,3,5 Trimethylbenzene	nd	35.5	nd	nd
Diesel Range Organics	634	1440	924	4050
Gasoline Range Organics	389	3710	592	2800
Phenol [a]	11.1	56.1	20.9	64.9
Naphthalene [b]	nd	6.06	nd	6.10
Isopropanol	-----	-----	212	581
Tert-Butyl Alcohol	-----	-----	nd	4470
2-Butanone	-----	-----	nd	120
Diethylene Glycol	-----	-----	226	1570
Triethylene Glycol	-----	-----	46	310
Tetraethylene Glycol	-----	-----	7.3 [c, d]	27.2
2-Butoxyethanol *	-----	-----	nd	nd
2-Butoxyethanol **	nd	nd	12.7	nd
Acetone	-----	-----	79.5	641
Benzoic Acid	212	244	457	209
Acetate	-----	-----	8050	4310
Formate	-----	-----	112	558
Lactate	-----	-----	69	213
Propionate	-----	-----	309	803

† All values in µg/L unless otherwise noted.
----- not analyzed.
nd - not detected.
[a] Includes phenol, 2,4-dimethylphenol, 2-methylphenol, 3&4 methylphenol.
[b] Includes naphthalene, 1-methylnaphthalene, and 2-methylnaphthalene.
[c] Value below quantitation limit of 10 µg/L.
[d] Chemical detected in a blank sample at a similar level
* 2-Butoxyethanol determined by HPLC-MS-MS.
** 2-Butoxyethanol determined by GC-MS.

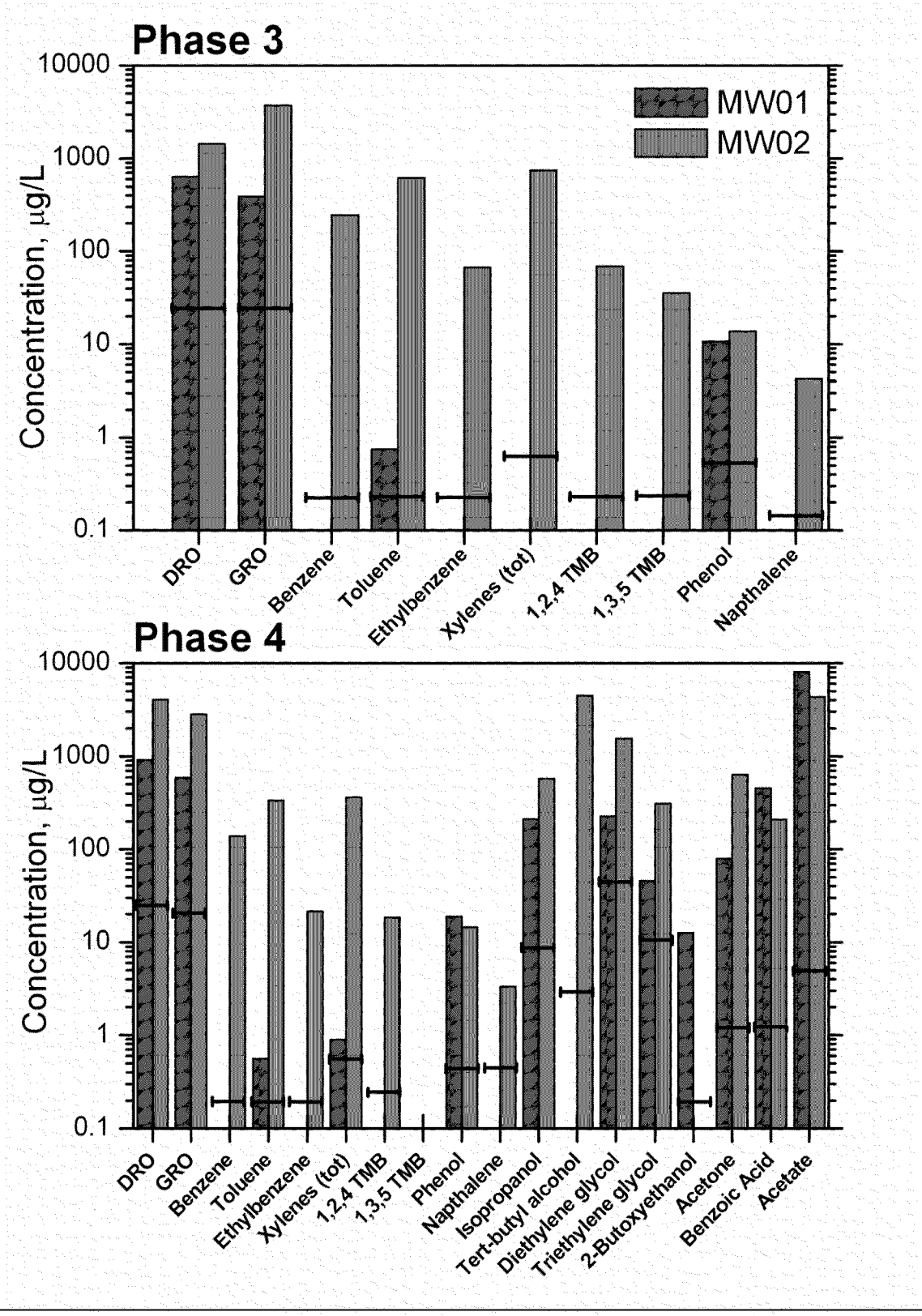

Figure 17. Organic compounds detected in deep monitoring wells MW01 and MW02 during Phase III and IV sampling events. Horizontal bars show method reporting limits for the individual analytes.

Table 4. Association of inorganic and organic anomalies with compounds used for hydraulic fracturing

Compound/ Compound Class	Information from MSDSs and Well Completion Reports
pH	KOH was used in a crosslinker (<5%) and in a solvent (85-100%).
K, Cl	The formulation of fracture fluid provided for foam jobs typically consisted of CO_2, 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%).
Cl	Ammonium chloride was used in crosslinker (1-27%).
BTEX	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 naptha (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).
Trimethylbenzenes	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 naptha (mixture of paraffinic, cycloparaffinic and aromatic hydrocarbons) was used in surfactants (5-10%, 10-30%, 30-60%) and in a solvent (10-50%).
DRO and GRO	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 naptha (mixture of paraffinic, cycloparaffinic and aromatic hydrocarbons) was used in surfactants (5-10%, 10-30%, 30-60%) and in a solvent (10-50%).
Naphthalene	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%).
Isopropanol	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%).
Tert-Butyl Alcohol	No MSDS listing. Breakdown product of methyl *tert*-butyl ether and *tert*-butyl hydroperoxide - found in gel breakers. See discussion.
Glycols	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%).
2-Butoxyethanol	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%).
Acetone	Breakdown product of *tert*-butyl hydroperoxide - found in gel breakers. See discussion.
Benzoic Acid, Acetate, Formate, Lactate, Propionate, 2-Butanone, Phenols	Natural breakdown products of organic contaminants (e.g., BTEX, glycols, etc.).

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

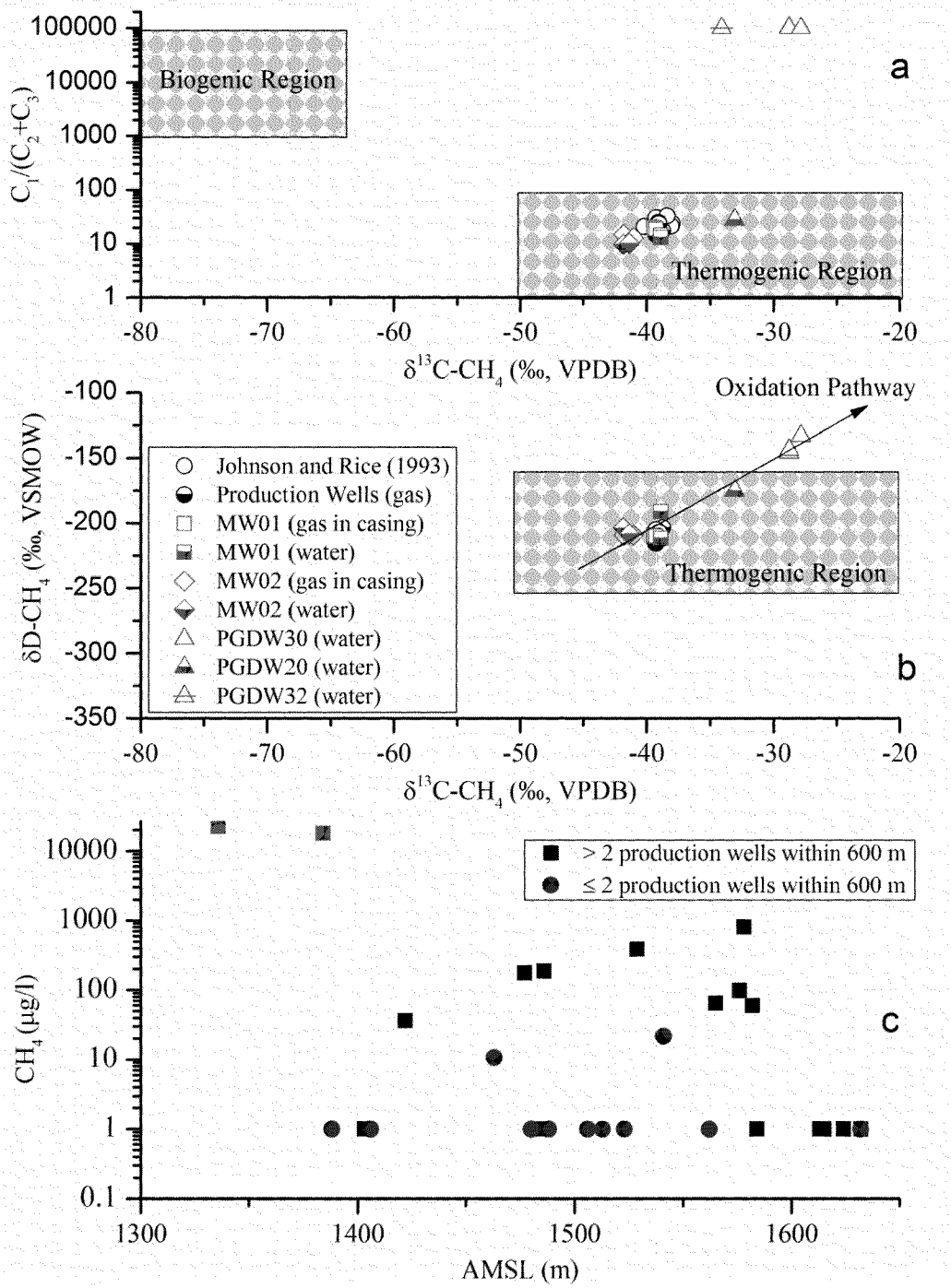

Figure 18. (a) Stable isotope ratios of carbon of methane versus ratio of methane (C_1) to ethane (C_2) and propane (C_3) in gas from production wells, monitoring wells, and domestic wells. Values of 100,000 are used to denote non detection of ethane and propane in samples. **(b)** Stable isotope ratios of carbon versus hydrogen of methane in gas from production wells (both literature and measured values), monitoring wells, and domestic wells. δD 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 µg/L).

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 $\delta^{13}C$ values for methane, ethane, propane, isobutane, and butane between gas production and monitoring wells and plots of $\delta^{13}C$-CH_4 versus δD -CH_4 (**Figure 18b**) and $\delta^{13}C$-CH_4 versus $C_1/(C_2 + C_3)$ (**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 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 ($\delta^{13}C$-CH_4 from to -40.24 to -38.04‰) and as previously stated, dry (Johnson and Rice 1993, Johnson and Keighin 1998). Values of $\delta^{13}C$-CH_4 and δD -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 $\delta^{13}C$-CH_4 and δD-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 $\delta^{13}C$ and δD. This observation is consistent with a pattern of dispersion and degradation with upward migration observed for organic compounds. Values of $\delta^{13}C$-CH_4 more positive than -64‰ and $C_1/(C_2+C_3)$ 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

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.

EPAPAV0037789

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. <u>High pH values</u>

   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

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

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

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

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

between gas production and monitoring wells and plots of $\delta^{13}C$-CH_4 versus δD -CH_4 and $\delta^{13}C$-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 $\delta^{13}C$-CH_4 and δD-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 µg/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 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.

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

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.

5.0 References

American Public Health Association; American Water Works Association; Water Environment Federation (1998a). Method 3500-Fe B. Phenanthroline Method. In: Standard Methods for the Examination of Water and Waste Water, 20th Edition. Editors Clesceri, L.S., Greenberg, A.E., and Eaton, A.D. Washington D.C.

American Public Health Association; American Water Works Association; Water Environment Federation (1998b). Method 4500-S2- D. Methylene Blue Method. In: Standard Methods for the Examination of Water and Waste Water, 20th Edition. Editors Clesceri, L.S., Greenberg, A.E., and Eaton, A.D. Washington D.C.

Bair, S.E., Freeman, D.C., and Senko, J.M. (2010). Expert Panel Technical Report Subsurface Gas Invasion Bainbridge Township, Geauga County, Ohio, submitted to Ohio Department of Natural Resources Division of Mineral Resources Management, June 2010.

Bartos, T.T., Quinn, T.L., Hallberg, L.L., and Eddy-Miller, C.A. (2008). Quality of shallow ground water in three areas of unsewered low-density development in Wyoming and Montana, 2001. U. S. Geological Survey Scientific Investigations Report 2008-5012, 118 p.

Bethke, C. M. (1996). Geochemical Reaction Modeling. Oxford University Press, New York.

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

Bradley, P.M., Chapelle, F.H., and Landmeyer, J.E. (2001). Effect of redox conditions on MTBE biodegradation in surface water sediments. *Environmental Science and Technology*, v. 35, p. 4643-4647.

Bybee, K. (2007). Cement-bond-log interpretation reliability. *Journal of Petroleum Technology*, Feb. 2007, p. 64-66.

Caldwell, M.E. and Suflita, J.M. (2000). Detection of phenol and benzoate as intermediates of anaerobic benzene biodegradation under different terminal electron-accepting conditions. *Environmental Science and Technology*, v. 34, p. 1216-1220.

Corseuil, H.X., Monier, A.L., Fernandes, M., Schneider, M.R., Nunes, C.C. Rosario, M., and Alvarez, P.J.J. (2011). BTEX plume dynamics following an ethanol blend release: Geochemical footprint and thermodynamic constraints on natural attenuation. *Environmental Science and Technology*, v. 45, p. 3422-3429.

Craig, H. (1961). Isotopic variations in meteoric waters. *Science*, v. 133, p. 1702-1703.

Daddow, R.L. (1996). Water resources of the Wind River Indian Reservation, Wyoming. U.S. Geological Survey Water-Resources Investigation Report 95-4223, 121 p.

Dahm, K.G., Guerra, K.L., Xu, P., and Drewes, J.E. (2011). Composite geochemical database for coalbed methane produces water quality in the Rocky Mountain Region. *Environmental Science and Technology*, v. 45, p. 7655-7663.

Delany J.M. and Lundeen S.R. (1990). The LLNL thermochemical database. Lawrence Livermore National Laboratory Report, UCRL-21658. Lawrence Livermore National Laboratory.

Dwyer, D.F. and Tiedje, J.M. (1983). Degradation of ethylene glycol and polyethylene glycols by methanogenic consortia. *Applied and Environmental Microbiology*, v. 46, p. 185-190.

Flores, R.M. and Keighin, C.W. (1993). Reservoir anisotropy and facies stratigraphic framework in the Paleocene Front Union Formation, western Wind River Basin, Wyoming, *in* W.R. Keefer, W.J. Metzger and L.H. Godwin, eds., Oil and Gas and Other Resources of the Wind River Basin, Wyoming: Wyoming Geological Association Special Symposium, 1993, p. 121–141.

EPAPAV0037798

Gibb, J.P. and Jennings, K.V.B. (1987). Forum: How drilling fluids and grouting materials affect the integrity of ground water samples from monitoring wells. *Ground Water Monitoring and Remediation*, v. 7, p. 33-42.

Harrison, S.S. (1983). Evaluating system for ground water contamination hazards due to gas-well drilling on the glaciated Appalachian Plateau. *Ground Water,* v. 21, 689-700.

Harrison, S.S. (1985). Contamination of aquifers by overpressuring the annulus of oil and gas wells. *Ground Water,* v. 23, 317-324.

Hiatt, R., Clipsham, J., and Visser, T. (1964). The induced decomposition of *tert*-butyl hydroperoxide. *Canadian Journal of Chemistry*, v. 42, p. 2754-2757.

Johnson, R.C. and Rice, D.D. (1993). Variations in composition and origins of gases from coal bed and conventional reservoirs, Wind River Basin, Wyoming, *in* W.R. Keefer, W.J. Metzger and L.H. Godwin, eds., Oil and Gas and Other Resources of the Wind River Basin, Wyoming: Wyoming Geological Association Special Symposium, 1993, p. 319-335.

Johnson, R.C. and Keighin, W.C. (1998). Origins of natural gases from upper Cretaceous reservoirs, Bighorn Basin, Wyoming and Montana, and comparison with gases from the Wind River Basin, Wyoming, In Forty-Ninth Guidebook, Wyoming Geological Association, p. 223- 249.

Keefer, W.R. and Johnson R.C. (1993). Stratigraphy and oil and gas resources in uppermost Cretaceous and Paleocene rocks, Wind River Reservation, Wyoming, *in* W.R. Keefer, W.J. Metzger and L.H. Godwin, eds., Oil and Gas and Other Resources of the Wind River Basin, Wyoming: Wyoming Geological Association Special Symposium, 1993, p. 71-86.

Johnson, R.C., Finn, T.M., Kirschbaum, M.A., Roberts, S.B., Roberts, L.N.R., Cook, T., and Taylor, D.J. (2007). The Cretaceous-Lower Tertiary Composite Total Petroleum System, Wind River Basin, Wyoming, Chapter 4 of Petroleum Systems and Geologic Assessment of Oil and Gas in the Wind River Basin Province, Wyoming. U.S. Geological Survey Digital Data Series DDS–69–J.

Kinnaman, F.S., Valentine, D.L., and Tyler, S.C. (2007). Carbon and hydrogen isotope fractionation associated with the aerobic microbial oxidation of methane, ethane, propane and butane. *Geochimica et Cosmochimica Acta*, v. 71, p. 271-283.

Mormille, M.R., Liu, S., and Suflita, J.M. (1994). Anaerobic biodegradation of gasoline oxygenates: Extrapolation of information to multiple sites and redox conditions. *Environmental Science and Technology*, v. 28, p. 1727-1732.

Morris, D.A., Hackett, O.M., Vanlier, K.E., Moulder, E.A., and Durum, W.H. (1959). Ground water resources of Riverton irrigation project area, Wyoming, Geological Survey Water-Supply Paper 1375, 205 p.

Mueller, C. (1989). Pavillion; Wyoming Geological Association, Wyoming Oil and Gas Fields Symposium, Bighorn and Wind River Basins, p. 356-358.

Nordbotten, J.M., Celia, M.A., and Bachu, S. (2004). Analytical solutions for leakage rates through abandoned wells. *Water Resources Research*, v. 40, W04204.

Nordbotten, J.M., Celia, M.A. and Bachu, S. (2005a). Injection and storage of CO_2 in deep saline aquifers: Analytical solution for CO_2 plume evolution during injection. *Transport Porous Media*, v. 58, p. 339-360.

Nordbotten, J.M., Celia, M.A., Bachu, S., and Dahle, H.K. (2005b). Semianalytical solution for CO_2 leakage through an abandoned well. *Environmental Science and Technology*, v. 39, p. 602-611.

Ohio Department of Natural Resources, Division of Mineral Resources Management, Report on the Investigation of the Natural Gas Invasion of Aquifers in Bainbridge Township of Geauga County, Ohio September 1, (2008).

Osborn S.G., Vengosh, A., Warner, N.R., and Jackson, R.B. (2011). Methane contamination of drinking water accompanying gas-well drilling and hydraulic fracturing. *Proceedings of the National Academy of Sciences*, v. 108, p. 8172-8176.

Osiensky, J.L., Winter, G.V., and Williams, R.E. (1984). Monitoring and mathematical modeling of contaminated ground water plumes in fluvial environments. *Ground Water*, v. 22, p. 298-306.

Pennsylvania Department of Environmental Protection (PADEP) Consent Order and Agreement Cabot Oil and Gas Corporation Dimock and Springville Townships Susquehanna County (2009).

Pennsylvania Department of Environmental Protection (PADEP) Modification to Consent Order and Agreement dated November 4, 2009 - April 15, 2010.

Pennsylvania Department of Environmental Protection (PADEP) Modification to Consent Order and Agreement dated November 4, 2009 - April 15, 2010.

Plafcan, M., Eddy-Miller, C.A., Ritz, G.F., and Holland, J.P.R. (1995). Water resources of Fremont County, Wyoming. U.S. Geological Survey, Water-Resources Investigations Report 95-4095, 133 p.

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

U.S. Department of Energy. Secretary of Energy Advisory Board. Shale Gas Production Subcommittee. Ninety-Day Report – August 11, 2011.

U.S. Department of Energy. Secretary of Energy Advisory Board. Shale Gas Production Subcommittee. Second Ninety-Day Report – November 18, 2011.

Single, E.L. (1969). *in* Wyoming Geological Association 21st Field Conference Guidebook, p. 101-103.

Taylor, S.W., Sherwood Lollar, B., and Wassenaar, L.I. (2000). Bacteriogenic ethane in near-surface aquifers: Implications for leaking hydrocarbon well bores. *Environmental Science and Technology,* v. 34, p. 4727-4732.

U.S. Environmental Protection Agency (1987). Management of Wastes from Exploration, Development, and Production of Crude Oil, Natural Gas, and Geothermal energy, EPA/530-SW-88-003, December, 1987. Available at http://www.epa.gov/osw/nonhaz/industrial/special/oil/rtc1987.pdf

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

U.S. Environmental Protection Agency (2004). Evaluation of Impacts to Underground Sources of Drinking Water by Hydraulic Fracturing of Coalbed Methane Reservoirs, Office of Water Office of Ground Water and Drinking Water (4606M), EPA 816-R-04-003, June 2004.

U.S. Environmental Protection Agency (2009). Site Inspection - Analytical Results Report, Pavillion Area Ground Water Investigation Site, August 8, 2009. available at http://www.epa.gov/region8/superfund/wy/pavillion/

U.S. Environmental Protection Agency (2010). Expanded Site Inspection - Analytical Results Report, Pavillion Area Ground Water Investigation Site, August 30, 2010. available at http://www.epa.gov/region8/superfund/wy/pavillion/

U.S. General Accounting Office (1989). Safeguards are not Preventing Contamination from Injected Oil and Gas Wastes, GAO/RCED-89-97, July 1989.

U.S. Geological Survey Produced Waters Database, Chemistry of Produced Water in the United States, http://energy.cr.usgs.gov/prov/prodwat/tds.htm. Site accessed November, 2011.

Valentine, D.L. et al. (2010). Propane respiration jump-starts microbial response to a deep oil spill. *Science*, v. 330, p. 208-211.

Van Stempvoort, D., Maathuis, H., Jaworski, E., Mayer, B., and Rich, K. (2005). Oxidation of fugitive methane in ground water linked to bacterial sulfate reduction, *Ground Water*, v. 43, p. 187-199.

Whiticar, M.J. (1999). Carbon and hydrogen isotope systematic of bacterial formation and oxidation of methane. *Chemical Geology,* v. 161, p. 291–314.

Whiticar, M.J. and Faber, E. (1986). Methane oxidation in sediment and water column environments-isotopic evidence. *Organic Geochemistry*, v. 10, p. 759-768.

Wilson, J.T., Kaiser, P.M., and Adair, C. (2005). Monitored natural attenuation of MTBE as a risk management option at leaking underground storage tank sites. EPA/600/R-04/1790.

Wyoming State Water Plan, Wyoming Water Development Office, Wind/Bighorn River Basin Plan, Jan. 14, 2003. http://waterplan.state.wy.us/plan/bighorn/techmemos/grnddet.html

EPAPAV0037801

Appendix A
Summary of Analytical Results

EPAPAV0037802

DRAFT

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^1 - Energy Laboratories Inc., Billings, MT. Heterotrophic plate counts, iron reducing bacteria, sulfur reducing bacteria.

E^2 - Energy Laboratories Inc., Billings, MT. GRO, DRO, THE, and TPH.

I^1 - 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. $\delta^{13}C$ and δD for C_1 determined using gas stripping and IRMS in aqueous samples. $\delta^{13}C$ and δD for C_1-C_4 determined using IRMS for gas samples.

I^2 - Isotech Laboratories, Champaign, IL. Fixed gases and light hydrocarbons determined using ASTM D1945-03 in headspace of aqueous samples. $\delta^{13}C$ and δD for C_1 and $\delta^{13}C$ for C_2 and C_3 determined using gas stripping and IRMS in aqueous samples. $\delta^{13}C$ DIC using gas stripping and IRMS.

I^3 - Isotech Laboratories, Champaign, IL. Fixed gases and light hydrocarbons determined using ASTM D1945-03 in headspace of aqueous samples. $\delta^{13}C$ and δD for C_1 , $\delta^{13}C$ for C_2 - C_5, and $\delta^{13}C$ for DIC gas stripping and IRMS in aqueous samples.

I^4 - Isotech Laboratories, Champaign, IL. Fixed gases and light hydrocarbons determined using ASTM D1945-03 in gas samples. $\delta^{13}C$ and δD for C_1 - C_3 using IRMS in gas samples.

I^5 - Isotech Laboratories, Champaign, IL. Fixed gases and light hydrocarbons determined using ASTM D1945-03 in gas samples. $\delta^{13}C$ and δD for C_1 - C_3 using IRMS in gas samples. ^{14}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^1 - EPA, ORD, Ada, OK. SO_4, Cl, F, and Br determined using RSKSOP 276v3 and EPA Method 6500. NO_3 + NO_2 and NH_4 determined using RSKSOP 214v5 and EPA Method 350.1 and 353.2

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

O^3 - EPA, ORD, Ada, OK. 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.

$R8^1$ - 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).

$R8^2$ - U.S. EPA Region 8 Laboratory, Golden, CO. VOCs determined using EPA Method 8260B.

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

$R8^4$ - 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.

$R8^5$ - U.S. EPA Region 8 Laboratory, Golden, CO. Dissolved C_1 in Phase I and dissolved C_1-C_3 in Phase II using EPA Method 524.2.

S^1 - 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^2 - 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^3 - Shaw Inc, Ada, OK . Alcohols, aromatics, and chlorinated hydrocarbons determined using method RSKSOP-259v1.

S^4 - Shaw Inc, Ada, OK. Low molecular weight acids determined using RSKSOP-112v6.

S^5 - Shaw Inc, Ada, OK. Dissolved gases C_1-C_4 determined using RSKSOP 194v4 and 175v5.

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

DRAFT

Abbreviations

I () - Phase I(laboratory/method). Samples collected March, 2009
II() - Phase II(laboratory/method). Samples collected January, 2010
III() - Phase III(laboratory/method). Samples collected September and October 2010
IV() - Phase IV(laboratory/method). Samples collected April 2011.
PG - gas production well
MW - deep monitoring wells
PGM - shallow monitoring wells near pits
PGS - soil samples near pits
DW - domestic wells
PGP - municipal wells in the Town of Pavillion
IRMS - isotope-ratio mass spectrometry
AMS - accelerated mass spectrometry
VOCs - volatile organic compounds
SVOCs - semivolatile organic compounds
PCBs - polychlorinated biphenyls
TICs - tentatively identified compounds
DRO - diesel range organics
GRO - gasoline range organics
TEH - total extractable hydrocarbons
TPH - total purgeable hydrocarbons
DIC - dissolved inorganic carbon
TAL - target analyte list
CLP - U.S. EPA Contract Laboratory Program
C_1 (methane), C_2 (ethane), C_3 (propane), iC_4 (isobutane), nC_4 (normal butane), iC_5 (isopentane), nC_5 (normal pentane), C_6^+ (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.

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.

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_4 (ppm)	F (ppm)	NO_3 (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

Sample ID	T (°C)	pH	SC (µS/cm)	Alkalinity mg/kg	Na (ppm)	K (ppm)	Ca (ppm)	Mg (ppm)	Cl (ppm)	SO_4 (ppm)	F (ppm)	NO_3 (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 $CaCO_3$. 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_4^+ (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_4, meq	CO_3, meq	Cl, meq	F, meq	OH, meq	Σcat, meq	Σan, meq	Balance, %
		cations				*anions*							
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 (%) = $|(\Sigma cat-\Sigma an)/(\Sigma cat+\Sigma an)*100|$. meq OH is calculated as $1000*[a_{OH^-}/\gamma_{OH^-}]$, where $a_{OH^-} = 10^{-(14-pH)}$ and γ_{OH^-} = 0.85 to 0.88. meq CO_3 is estimated from measurements of Dissolved Inorganic Carbon (DIC) as 2*[DIC/12], where DIC is in mg/L.

EPAPAV0037812

Table A3b. Summary of gas and headspace analysis of light hydrocarbons

Sample (matrix)	Phase	Date	C_1 (%)	C_2 (%)	C_2H_4 (%)	C_3 (%)	iC_4 (%)	nC_4 (%)	iC_5 (%)	nC_5 (%)	C_6+ (%)
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

DRAFT

Sample (matrix)	Phase	Date	C_1 (%)	C_2 (%)	C_2H_4 (%)	C_3 (%)	iC_4 (%)	nC_4 (%)	iC_5 (%)	nC_5 (%)	C_6+ (%)
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

DRAFT

DRAFT

Appendix B

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

EPAPAV0037818

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†, pH>10; refrigerate 4°C††	14 days
Metals (filtered)	RSKSOP-213v4 &-257v3 (EPA Methods 200.7 and 6020)	125 mL plastic bottle/1	HNO_3, pH<2; room temperature	6 months (Hg 28 days)
SO_4, Cl, F, Br	RSKSOP-276v3 (EPA Method 6500)	30 mL plastic/1	Refrigerate ≤4°C	28 days
$NO_3 + NO_2$, NH_4	RSKSOP-214v5 (EPA Method 350.1 and 353.2)	30 mL plastic/1	H_2SO_4, 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_3PO_4, 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†, pH>10; refrigerate ≤4°C	14 days
Low Molecular Weight Acids	RSKSOP-112V6 (No EPA Method)	40 mL glass VOA vial/2	TSP†, 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
$\delta^{13}C$ DIC	Isotech: gas stripping and IRMS (No EPA Method)	60 mL plastic bottle/1	Refrigerate ≤4°C	No information
$\delta^{13}C$ 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 ≤4ºC	14 days

† Trisodium phosphate
†† Above freezing point of water
*Spare bottles made available for laboratory QC samples and for replacement of compromised samples (broken bottle, QC failures, etc.).
**EPA Methods 8000C and 8321 were followed for method development and QA/AC limits were applicable.

Table B4. QA/QC requirements for analysis of dissolved gases, DIC/DOC, VOCs, low molecular weight acids and stable isotopes of water

Measurement	Analysis Method	Blanks (Frequency)	Calibration Checks (Frequency)	Second Source (Frequency)	Duplicates (Frequency)	Matrix Spikes (Frequency)
Dissolved gases	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
DIC/DOC	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.
Volatile organic compounds (VOC)**	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)
Low Molecular Weight Acids	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)
O, H stable isotopes of water***	RSKSOP-296v1 (No EPA Method)	NA	Difference of calibrated/true < 1‰ for δ^2H & < 0.2‰ for $\delta^{18}O$ (Beginning, end and every tenth sample)	Working stds calibrated against IAEAstds.† (Beginning, end, and every tenth sample)	Standard deviation ≤ 1‰ for δ^2H and < 0.2‰ for $\delta^{18}O$ (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^2H and ≤ 1‰ for $\delta^{18}O$
†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

Table B5. QA/QC requirements for analysis of semi-volatiles, GRO, and DRO

QC Type	Semivolatiles	DRO	GRO	Frequency
Method Blanks	<RL Preparation or Method Blank, one with each set of extraction groups. Calibration Blanks are also analyzed	<RL Preparation or Method Blank	<RL Preparation or Method Blank and IBL	At least one per sample set
Surrogate Spikes	Limits based upon DoD statistical study (rounded to 0 or 5) for the target compound analyses.	60-140% of expected value	70-130% of expected value	Every field and QC sample
Internal Standards Verification	Every sample, EICP area within -50% to +100% of last ICV or first CCV.	NA	NA	Every field and QC sample
Initial multilevel calibration	ICAL: minimum of 6 levels (0.25 -12.5 ug/L) , one is at the MRL (0.50 ug/L), prior to sample analysis (not daily) RSD≤20%, r^2≥0.990	ICAL: 10-500 ug/L RSD<=20% or r^2>=0.990	ICAL: .25-12.5 ug/L for gasoline (different range for other compounds) RSD<=20% or r2>=0.990	As required (not daily if pass ICV)
Initial and Continuing Calibration Checks	80-120% of expected value	80-120% of expected value	80-120% of expected value	At beginning of sample set, every tenth sample, and end of sample set
Second Source Standards	ICV1 70-130% of expected value	ICV1 80-120% of expected value	ICVs 80-120% of expected value	Each time calibration performed
Laboratory Control Samples (LCS)	Statistical Limits from DoD LCS Study (rounded to 0 or 5) or if SRM is used based on those certified limits	Use an SRM: Values of all analytes in the LCS should be within the 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
Laboratory Control Samples (LCS)	Statistical Limits from DoD LCS Study (rounded to 0 or 5) or if SRM is used based on those certified limits	Use an SRM: Values of all analytes in the LCS should be within the limits determined by the supplier. Otherwise 70-130% of expected value	Use and SRM: Values of all analytes in the LCS should be within the limits determined by the supplier. Otherwise 70-130% of expected value	One per analytical batch or every 20 samples, whichever is greater
Matrix Spikes (MS)	Same as LCS	Same as LCS	70-130% of expected value	One per sample set or every 20 samples, whichever is more frequent
MS/MSD	% Recovery same as MS RPD ≤ 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
Reporting Limits*	0.1 µg/L (generally)[1]for target compounds HF special compounds are higher	20 µg/L[1]	20 µg/L[2]	NA

[1]Based on 1000 mL sample to 1 mL extract
[2]Based on a 5 mL purge

Table B6. QA/QC requirements for LC/MS/MS analysis of glycols

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

RL = Reporting Limit
Corrective Actions: If 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.

DRAFT

EPAPAV0037824

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.

EPAPAV0037828

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

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

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

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

Analyte	Instrument (Detector)	Method	Range	Calibration	Check Standard	Accuracy
O_2	GEM-2000 Plus CES-LANDTEC (EC Cell)	RSKSOP-314v1	0 - 21%	4%, 10%, or 20.9%	4% 10%, 20.9%	±1.0% (0-5%) ±1.0% (5-21%)
CH_4	GEM-2000 Plus CES-LANDTEC (IRGA)	RSKSOP-314v1	0 - 100%	2.5% or 50%	2.5%, 50%	±0.3% (0-5%) ±1% (5-15%) ±3% (15-100%)
CO_2	GEM-2000 Plus CES-LANDTEC (IRGA)	RSKSOP-314v1	0 - 100%	5%, 20%, or 35%	5%, 20%, 35%	±0.3% (0-5%) ±1.0% (5-15%) ±3.0% (15-50%)
VOCs	Thermo Scientific TVA-1000B (FID)	RSKSOP-320v1	1.0 – 10,000 ppmv	0.0, 10, 100, 1000, 9000 ppmv CH_4	10, 100, 1000, 9000 ppmv CH_4	±25% or ±2.5 ppmv, whichever is greater, from 1.0 to 10,000 ppmv.
VOCs	Thermo Scientific TVA-1000B (PID)	RSKSOP-320v1	0.5 – 500 ppmv	0.0, 250, 475 ppmv	250, 475 ppmv Isobutylene	±25% or ±2.5 ppmv, whichever is greater, from 0.5 to 500 ppmv.

DRAFT

Appendix C

Photographic Log of Deep Monitoring Well Construction

EPAPAV0037836

EPAPAV0037838

EPAPAV0037848

Appendix D

Photographic Log of Ground Water Sampling

EPAPAV0037854

DRAFT

Appendix E
Examples of Cement Bond/Variable Density Log Interpretation

EPAPAV0037856

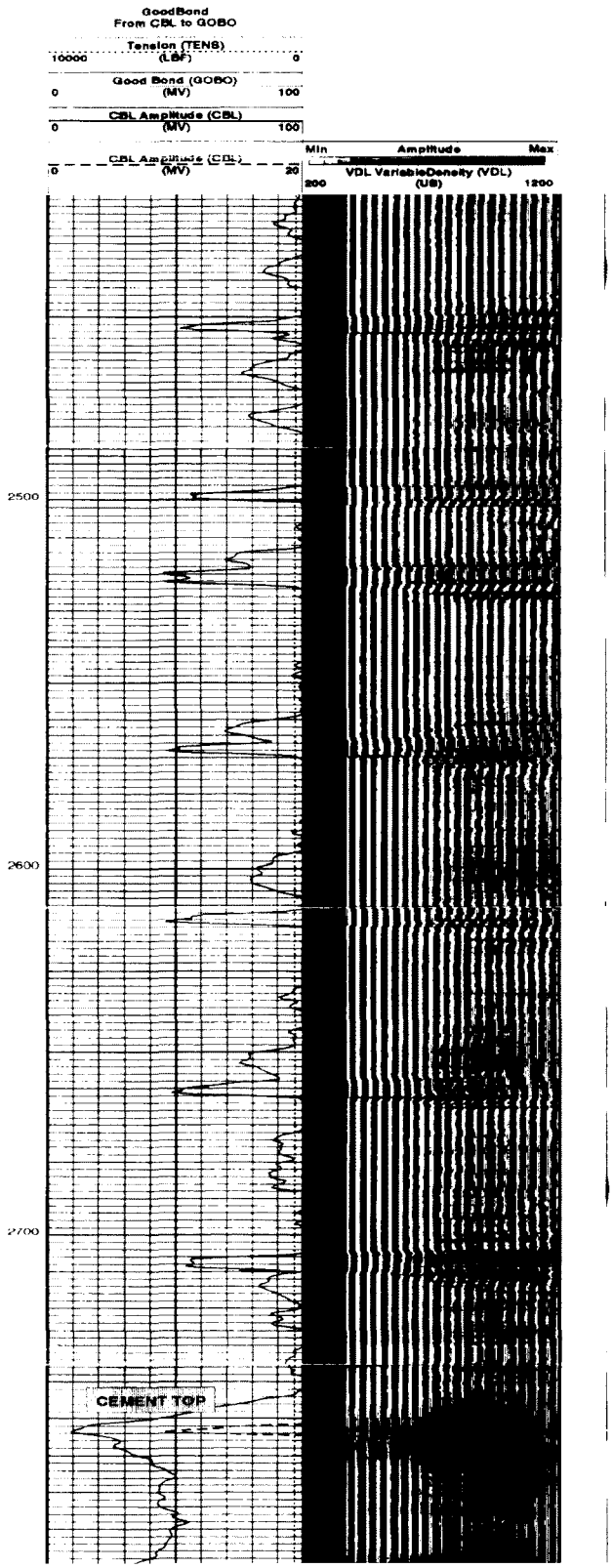

Figure E1. Example of CBL/VDL indicating "no cement" at Pavillion Fee 34-03B. The CBL/VDL indicates no cement 2750 feet below ground surface at the time of logging.

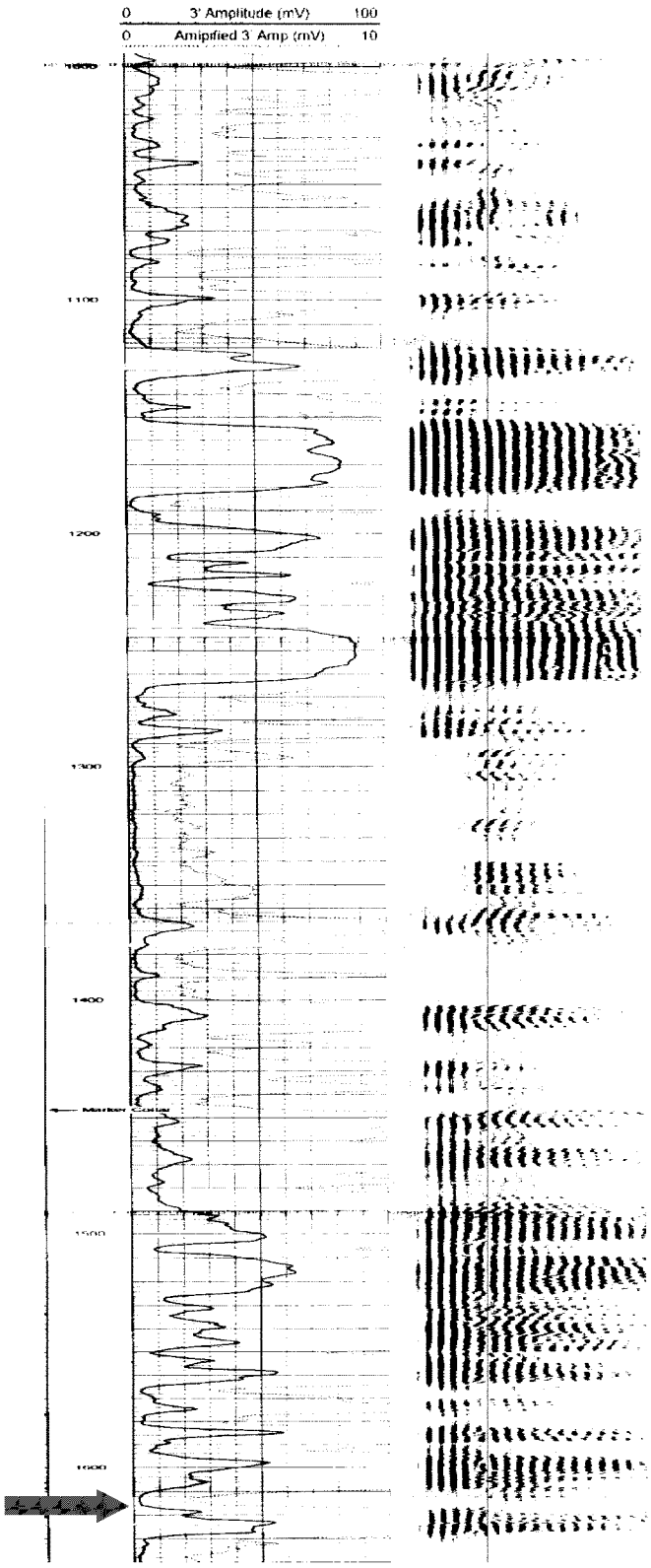

Figure E2. Example of "sporadic bonding" at Pavillion Fee 41-10 from 1000 to 1640 ft bgs. Hydraulic fracturing occurred at 1618 feet below ground surface. Arrow denotes interval of hydraulic fracturing.

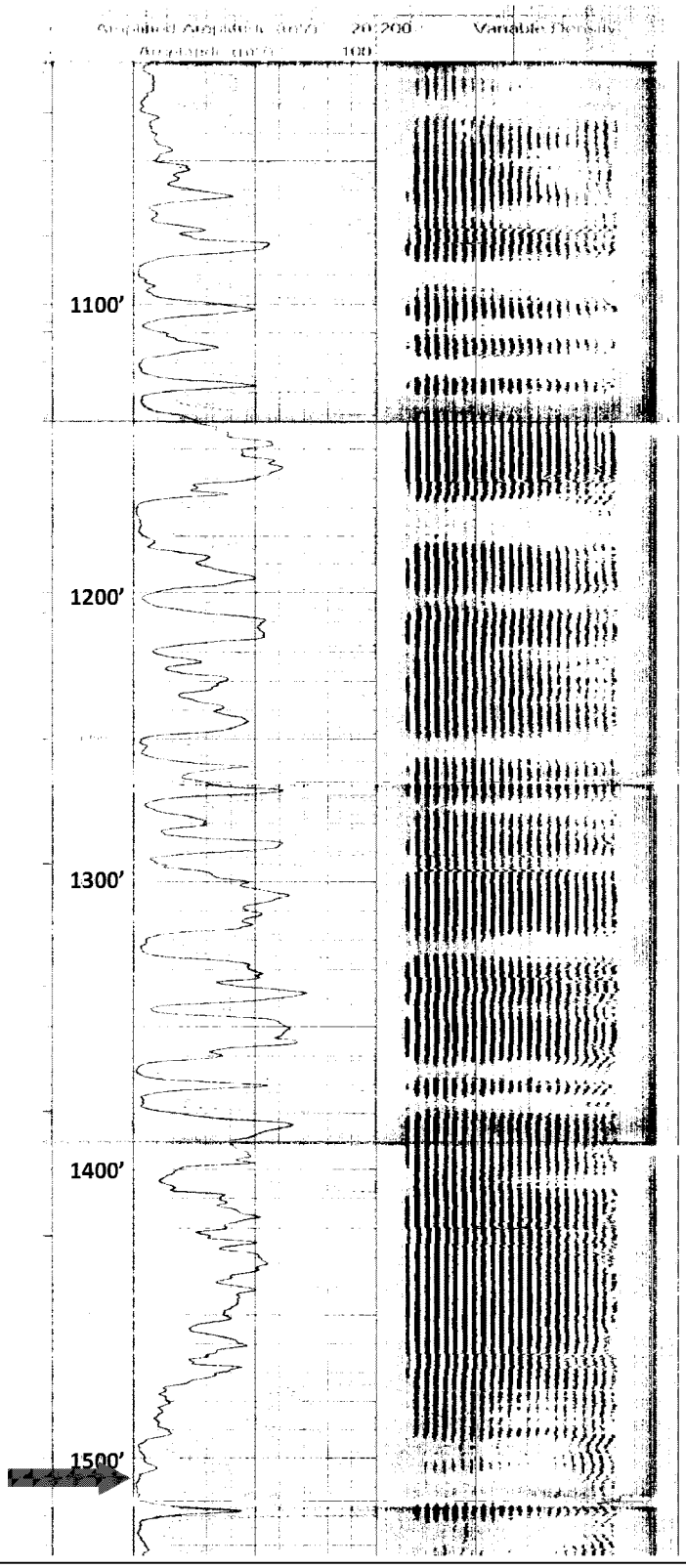

Figure E3a. Example of "sporadic bonding" at Pavillion Fee 11-11B. Hydraulic fracturing occurred at 1516 feet below ground surface. Arrow denotes interval of hydraulic fracturing. Depths on CBL/VDL difficult to read and inserted on left margin.

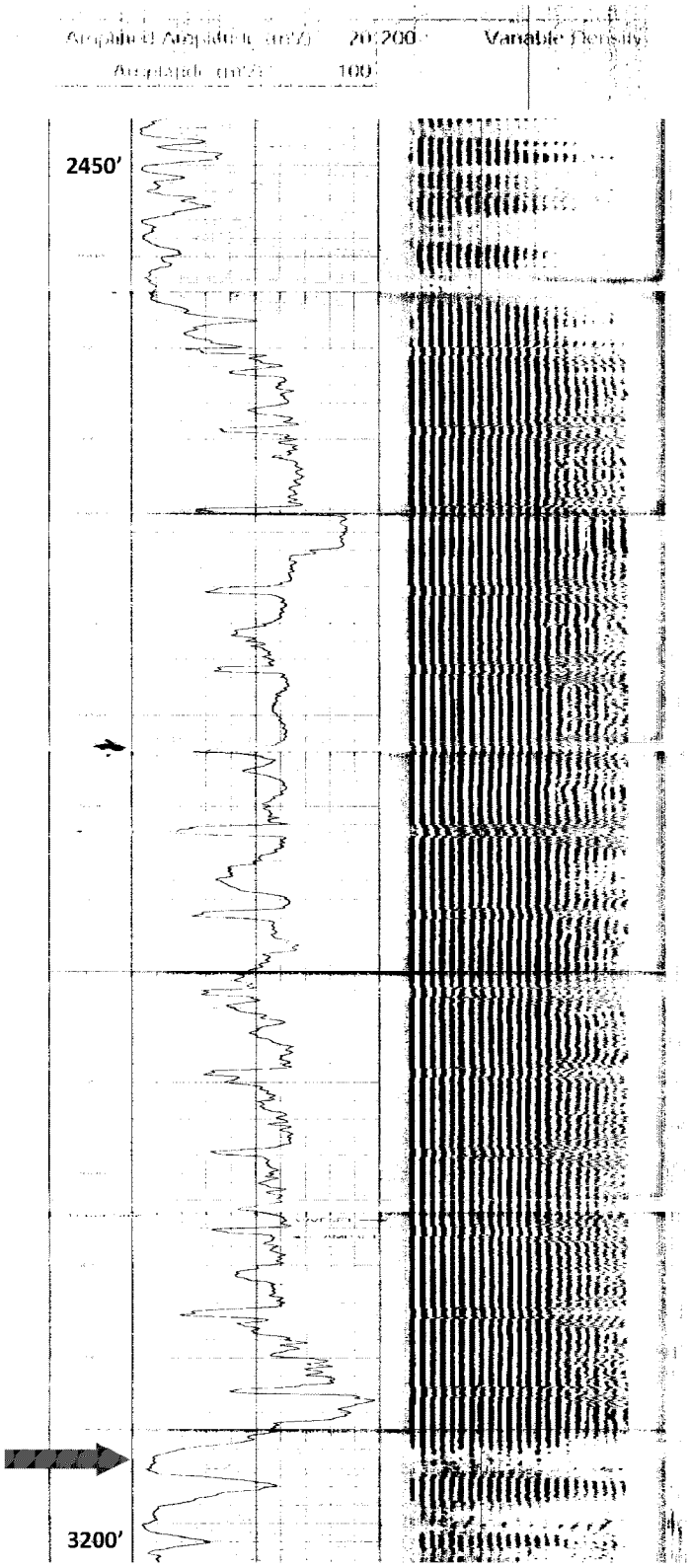

Figure E3b. Example of "sporadic bonding" Pavillion Fee 11-11B between 2350-3200 feet below ground suface. Hydraulic fracturing occurred at 3165 feet below ground surface. Arrow denotes interval of hydraulic fracturing. Depths on CBL/VDL difficult to read and inserted on left margin.

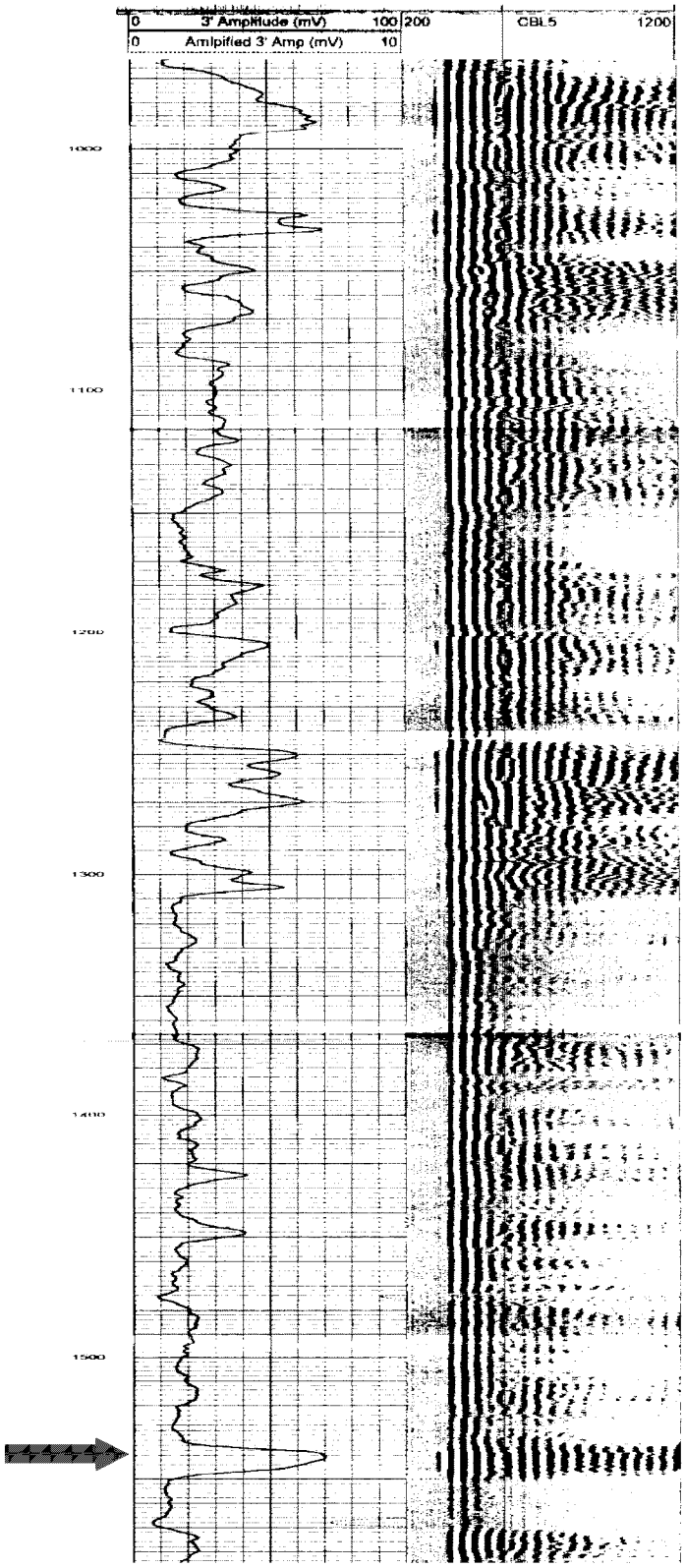

Figure E4. Example of "Sporadic Bonding" at Tribal Pavillion 24-02. Hydraulic fracturing occurred at 1538 feet bgs. Arrow denotes interval of hydraulic fracturing.

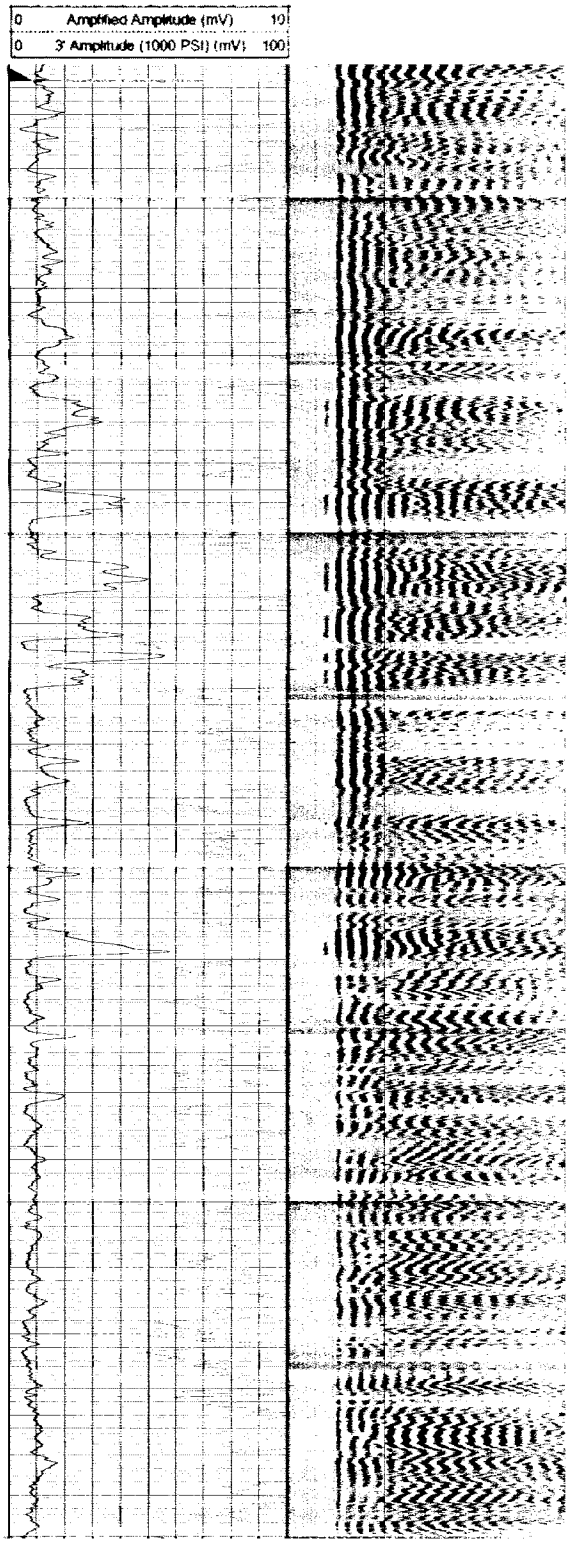

Figure E5. Example of "Good Bonding" (from surface casing at 645 ft bgs to 820 ft bgs) followed by "Sporadic Bonding" (from 820 ft bgs 1310 ft bgs) to "Good Bonding" at 1310 to target depth at Pavillion Fee 41-10B.

DRAFT

DRAFT