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# DRAFT

Investigation of Ground Water Contamination near Pavillion, Wyoming



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

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### Notice

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### 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.

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### **Extended Abstract**

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

The Agency conducted four sampling events (Phase I - IV) beginning in March 2009 and ending in April, 2011. Ground water samples were collected from domestic wells and two municipal wells in the town of Pavillion in Phase I. Detection of methane and dissolved hydrocarbons in several domestic wells prompted collection of a second round of samples in January, 2010 (Phase II). During this phase, EPA collected additional ground water samples from domestic and stock wells and ground water samples from 3 shallow monitoring wells and soil samples near the perimeter of three known pit locations. Detection of elevated levels of methane and diesel range organics (DRO) in deep domestic wells prompted the Agency to install 2 deep monitoring wells screened at 233 - 239 meters (MW01) and 293 - 299 meters (MW02) below ground surface, respectively, in June 2010 to better evaluate to deeper sources of contamination. The expense of drilling deep wells while utilizing blowout prevention was the primary limiting factor in the number of monitoring wells installed. In September 2010 (Phase III), EPA collected gas samples from well casing from MW01 and MW02. In October 2010, EPA collected ground water samples from MW01 and MW02 in addition to a number of domestic wells. In April 2011 (Phase IV), EPA resampled the 2 deep monitoring wells to compare previous findings and to expand the analyte list to include glycols, alcohols, and low molecular weight acids.

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

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

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 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.

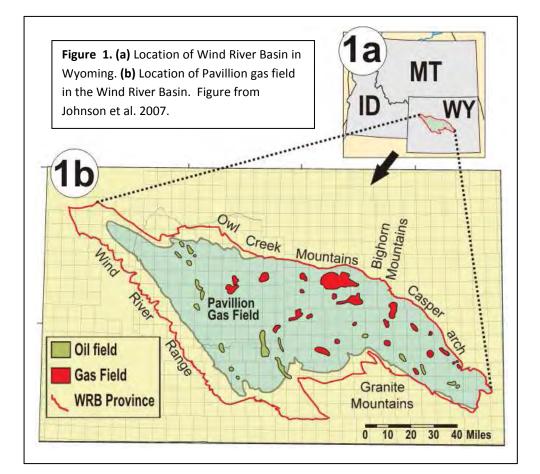
A similar lines of reasoning approach was utilized to evaluate the presence of gas in monitoring and domestic wells. A comparison of gas composition and stable carbon isotope values indicate that gas in production and monitoring wells is of similar thermogenic origin and has undergone little or no degradation. 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.

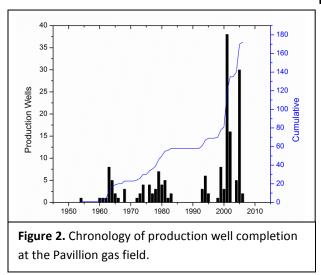
Elevated levels of dissolved methane in domestic wells generally increase in those wells in proximity to gas production wells. Near surface concentrations of methane appear highest in the area encompassing MW01. Ground water is saturated with methane at MW01 which is screened at a depth (239 meters below 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 to domestic wells.

## **1.0** Site Background

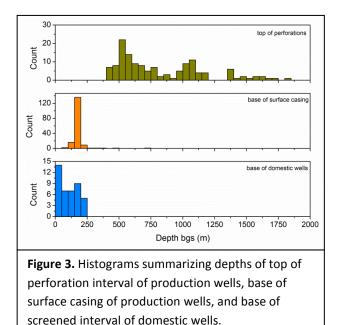
In early 2008, the U.S. Environmental Protection Agency (EPA) received complaints from several domestic well owners near the town of Pavillion, Wyoming regarding sustained objectionable taste and odor problems in well water following hydraulic fracturing at nearby gas production wells. In response to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

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





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**).

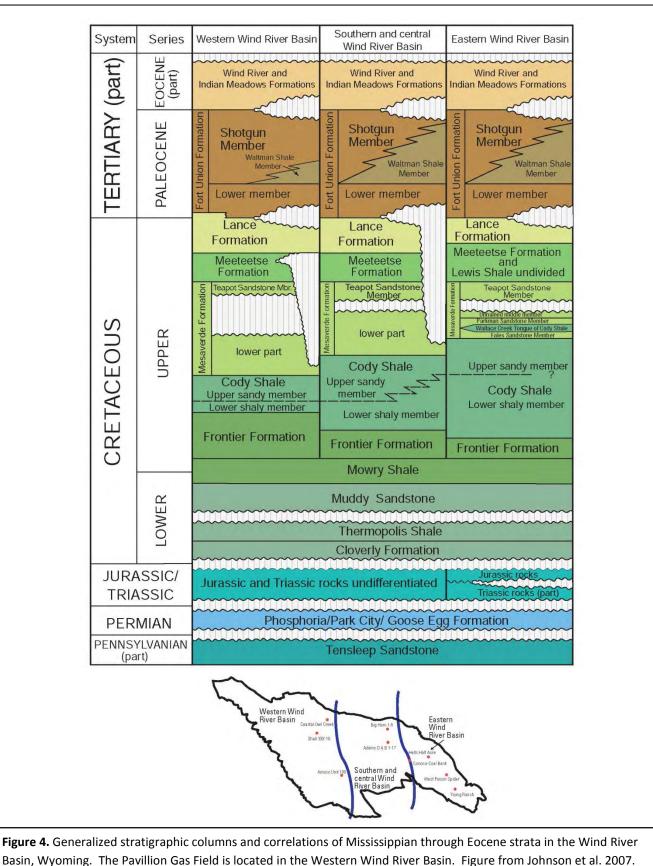


Gas extraction occurs from both the lower Eocene Wind River Formation and underlying Paleocene Fort Union Formation (Figure 4). The Wind River Formation consists of interbedded layers of sandstones and shale with coarse-grained meandering stream channel deposits (Osiensky et al. 1984) and extends from 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

$$\delta^{13}C(\text{\%o}) = \left[\frac{\binom{13}{1^{13}}C^{/12}C}{\binom{13}{1^{12}}C}\frac{1}{1^{13}}C^{-1}\right]x1000$$

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

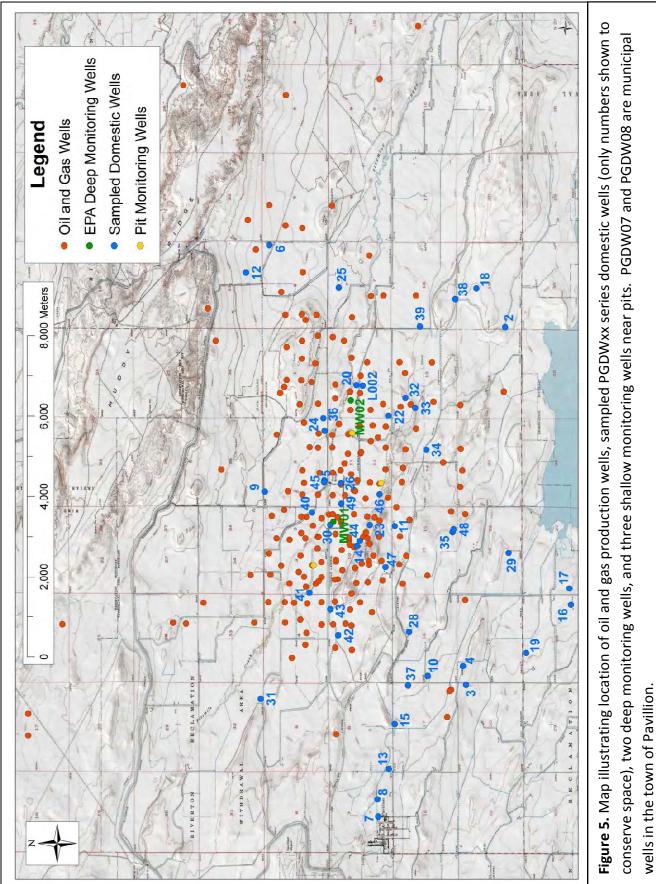
Four sampling events (Phase I - IV) were conducted commencing in March 2009 and ending in April 2011. In March 2009 (Phase I), EPA collected aqueous samples from 35 domestic wells (including two samples from post reverse osmosis systems) in the area of investigation and 2 municipal wells in the town 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



| Table 1. Drilling additives, properties and product use recommendations |                      |                                                 |                                                                                                                                                   |                  |                                              |                                    |            |
|-------------------------------------------------------------------------|----------------------|-------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------|------------------|----------------------------------------------|------------------------------------|------------|
| Ingredient                                                              | Manufacturer         | Purpose                                         | Composition from<br>MSDS                                                                                                                          | Specific gravity | Recommended<br>mixture with<br>water (wt/wt) | рН                                 | Properties |
| Aqua-Clear<br>PFD                                                       | Halliburton          | Dispersant/<br>mud<br>removal                   | anionic<br>polyacrylamide<br>(30-60%)                                                                                                             | 1.2-1.4          | 1:2500                                       | neat<br>6.5 to 7.5                 | liquid     |
| Penetrol                                                                | Halliburton          | Non-ionic<br>wetting<br>agent                   | diethanolamine<br>(1-5%) and coco<br>diethanolamide<br>(10-30%)                                                                                   | 0.98             | 1:400 to 1:100                               | 1%<br>solution<br>9.5              | liquid     |
| EZ-Mud Gold                                                             | Halliburton          | Clay/shale<br>stabilizer                        | "no hazardous<br>substances"                                                                                                                      | 0.8-1            | 1:1400 to 1:350                              | 1%<br>solution<br>7.75             | solid      |
| Dense Soda<br>Ash                                                       | OCI Chemical<br>Corp | Improve<br>bentonite                            | Sodium carbonate<br>(100%)                                                                                                                        | 2.5              | 1:100 to 1:50                                | 5%<br>solution<br>11.5             | solid      |
| Quik-Gel                                                                | Halliburton          | Viscosifier/<br>bentonite                       | bentonite (60%),<br>crystalline silica<br>quartz (1-5%),<br>crystalline silica<br>cristobalite (0-1%),<br>crystalline silica<br>tridymite (0-1%). | 2.6              | 1:60 to 1:30                                 | 3%<br>solution<br>8.9              | solid      |
| Quik-Trol<br>Gold                                                       | Halliburton          | Ease of<br>mixing and<br>improved<br>filtration | cellulose derivative<br>(polysaccharide)<br>(60-100%)                                                                                             | 0.6 - 0.9        | 1:3500 to 1:200                              | 1%<br>solution<br>6 -8<br>(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 & pxylene were detected in one sample at 6.9, 0.63, and 1.0 µg/L, respectively. Cuttings were disposed offsite in a landfill.

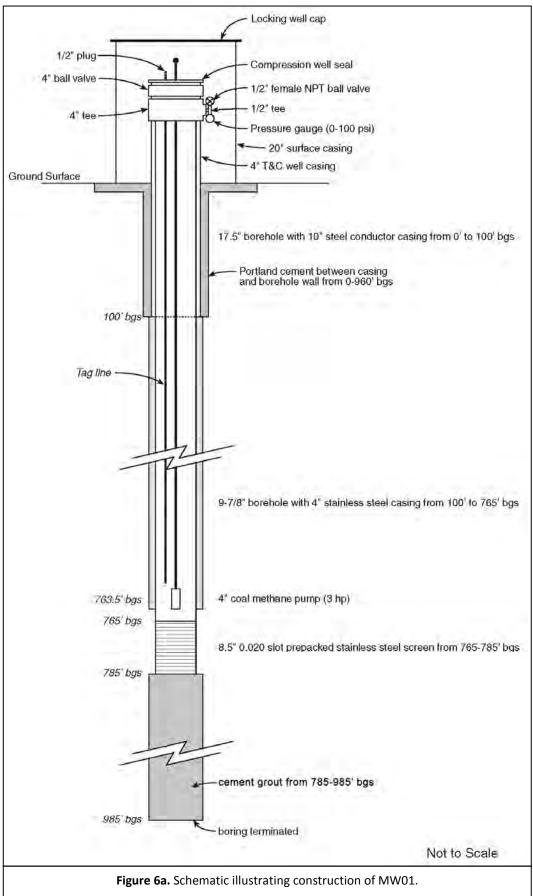
A photographic log of drilling, mud circulation, examination of cuttings, screen placement, and well development is provided in **Appendix C**. Well construction schematics are provided for MW01 and

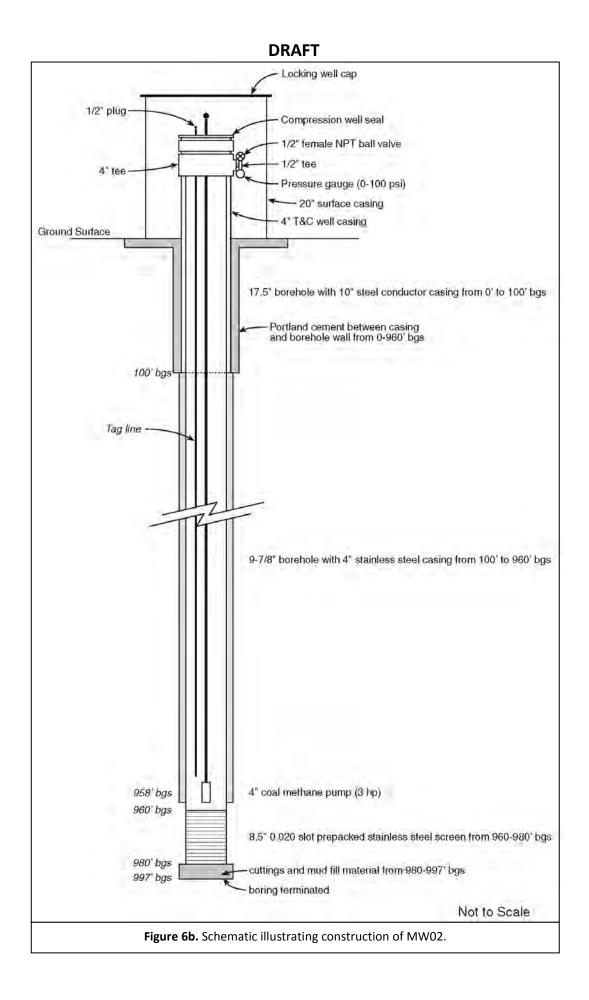
|                                    | Aqua-Clear<br>PFD | Penetrol | EZ-Mud<br>Gold | Dense<br>Soda Ash                     | Quik-Gel | Blank |
|------------------------------------|-------------------|----------|----------------|---------------------------------------|----------|-------|
| Extraction ratio<br>(wt/wt)        | 1:20              | 1:20     | 1:100          | 1:100                                 | 1:100    |       |
| pH measured                        | 7.96              | 8.51     | 6.64           | 11.2                                  | 8.35     |       |
| Specific<br>Conductance<br>(mS/cm) | 13.3              | 0.47     | 0.24           | 15.5                                  | 0.20     |       |
| Dissolved Organic<br>Carbon (ppm)  | 1640 (1650) †     | 1500     | 388            | 0.58                                  | 2.11     | 0.28  |
| Cl (ppm)                           | 214 (230) †       | 85       | 2.22           | 7.03                                  | nd       | nd    |
| SO4 (ppm)                          | 121 (117) †       | 597      | nd             | nd                                    | 3.53     | nd    |
| K (ppm)                            | 0.40 (0.40) †     | 0.63     | 1.16           | 0.12                                  | 0.09     | 0.07* |
| Acetone (µg/L)                     | nd                | nd       | nd             |                                       |          | nd    |
| Tert-butyl alcohol<br>(µg/L)       | nd                | nd       | nd             | ()                                    |          | nd    |
| Isopropanol (µg/L)                 | 85 (87)†*         | 43*      | 27*            | in interaction                        |          | nd    |
| Ethanol (µg/L)                     | 59 (62) **        | 58*      | nd             | sectore 1                             |          | nd    |
| Benzene (µg/L)                     | nd                | nd       | nd             | · · · · · · · · · · · · · · · · · · · |          | nd    |
| Toluene (µg/L)                     | nd                | nd       | nd             | المعيدة 11                            |          | nd    |
| Ethylbenzene<br>(μg/L)             | nd                | nd       | nd             |                                       |          | nd    |
| Xylene<br>(μg/L)                   | nd                | nd       | nd             | 1 (2000)                              | ·        | nd    |
| Trimethylbenzenes<br>(μg/L)        | nd                | nd       | nd             |                                       |          | nd    |
| Naphthalene                        | nd                | 2.00     | nd             | · · · · · · · · · · · · · · · · · · · |          | nd    |
| Ethylene glycol<br>(μg/L)          | nd                | nd       | nd             | ·                                     |          | nd    |
| Diethylene glycol<br>(μg/L)        | nd                | nd       | nd             |                                       |          | nd    |

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

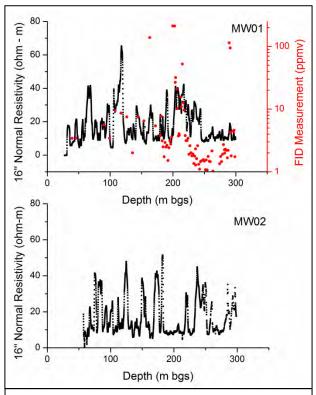
MW02 in **Figures 6a** and **6b**, respectively. During installation of MW02, cuttings were allowed to settle at the cessation of drilling and form a 5 m (17 ft) base for placement of the screen. Cuttings were never added to the borehole. Since a significant vertical distance existed between the depth of drilling and screen placement at MW01, cement grout was utilized to form the base for screen placement. No lubricants were used to attach sections of casing or casing to screens. Well screens, sections of casing and tremie pipe were mounted above ground (never touched soil) and power washed (no detergents used) prior to (deployment. Locations of both MW01 and MW02 were in fields used for alfalfa hay production away from production wells, pads, and pits.

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





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 coarsegrained 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).



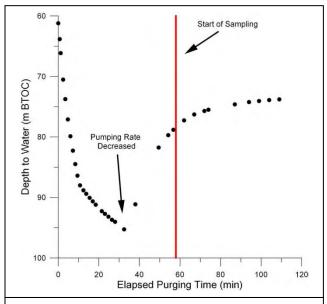
**Figure 7.** Resistivity as a function of depth in MW01 and MW02. MW01 and MW02 were screened at 233 - 239 m and 293 - 299 m bgs, respectively, corresponding to elevated resistivity and presence of coarse-grained sandstone. FID readings in MW01 denote detections of methane during open air logging of 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.



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

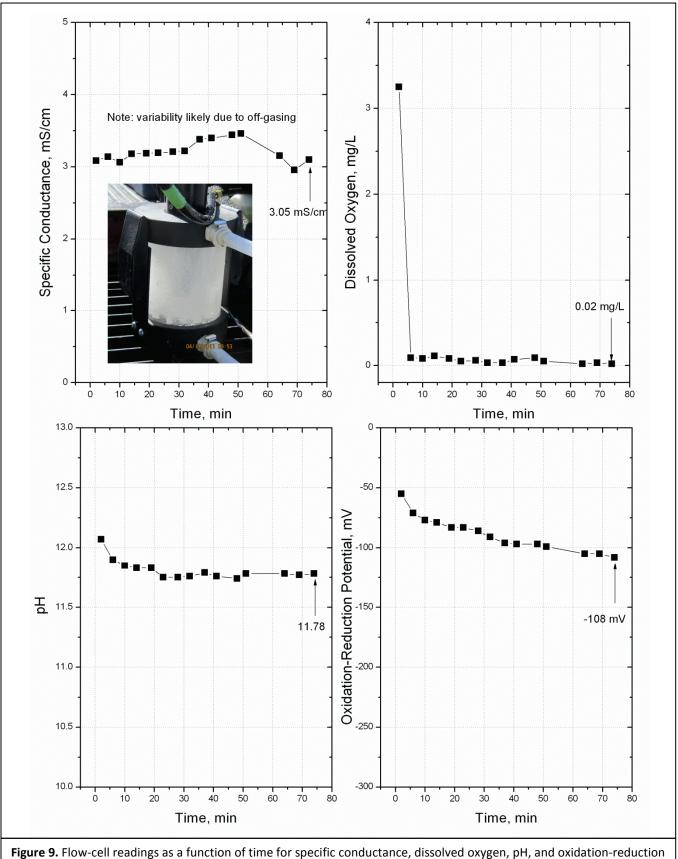
An example of flow-cell readings through the purging of well MW02 is shown in Figure 9. The electrode readings show fairly rapid equilibration of pH and dissolved oxygen. Oxidation-reduction potential steadily decreased with the rate of change falling into the desired range (<2 mV per minute) by the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

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

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

$$\delta^{18}O(\%) = \left[\frac{\binom{18}{18}O^{16}O}{\text{sample}} - 1\right]x1000$$

where the standard is the VSMOW.



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 matrixspike 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  $\mu$ g/L), m,p-xylene (up to 0.7  $\mu$ g/L), toluene (up to 0.5  $\mu$ g/L), benzoic acid (3  $\mu$ g/L), and tetraethylene glycol (3  $\mu$ g/L). Concentrations of these analytes in MW01 and MW02 in Phase III and Phase IV sampling ranged from: 80 to 641 µg/L (acetone), nondetect to 750 µg/L (total xylenes), 0.6 to 617 µg/L (toluene), 209 to 457 µg/L (benzoic acid), and 7 to 27  $\mu$ g/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  $\mu$ g/L). Concentrations of DRO in the deep monitoring wells ranged from 634 to 4050  $\mu$ g/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

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

where x1 = sample and x2 = sample duplicate. RPDs for methane, volatile organic compounds, and semivolatile 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<sub>(s)</sub> + H<sup>+</sup> = K<sup>+</sup><sub>(aq)</sub> + H<sub>2</sub>O<sub>(l)</sub>).

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<sup>™</sup> and a Leur-taper Quick-Mate<sup>™</sup> 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<sub>2</sub>, CO<sub>2</sub>, and CH<sub>4</sub> readings on a GEM-2000 Plus CES-LANDTEC portable gas analyzer.

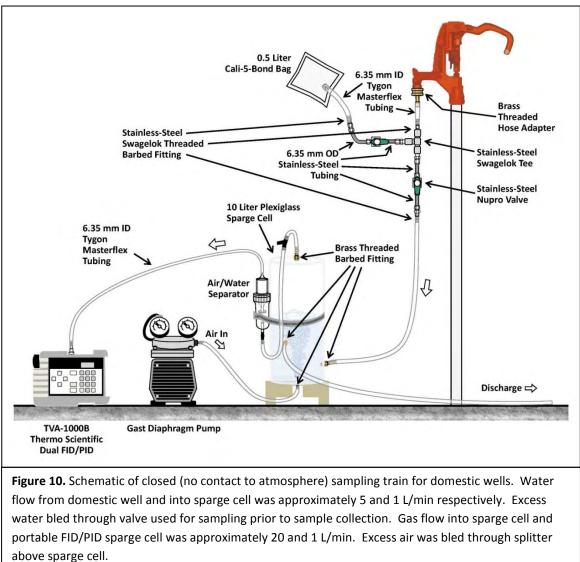
### Domestic Well Sampling for Methane Using a Closed System in Phase IV

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<sub>2</sub> 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

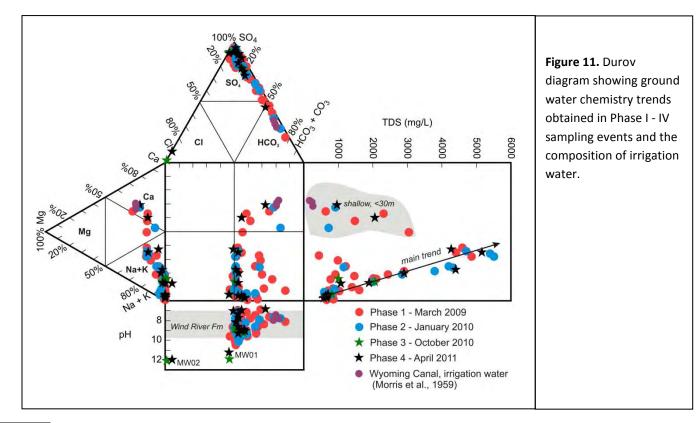
### Ground Water and Soil Sample Results Near Three Pits

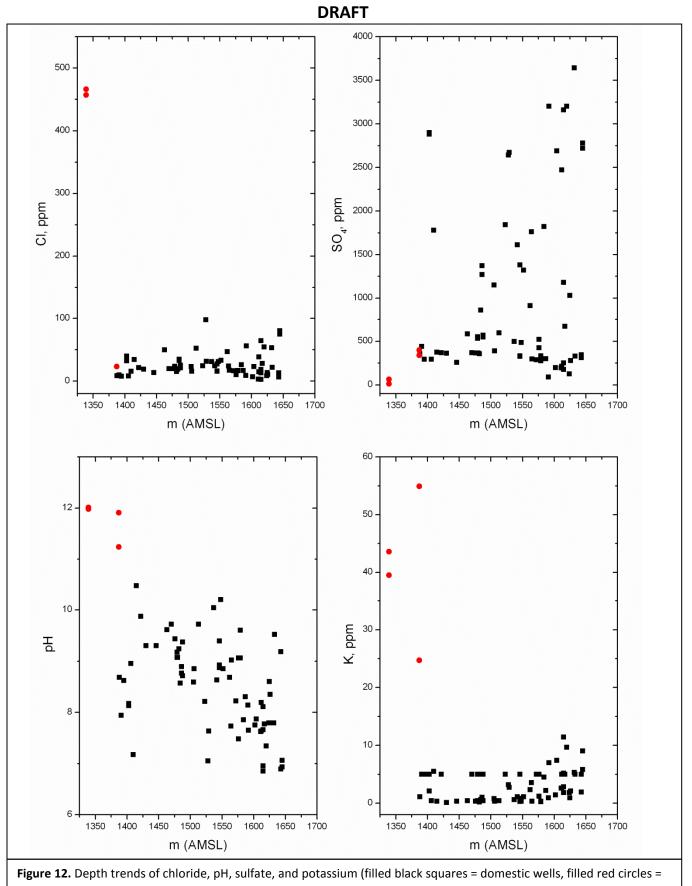
There are at least 33 pits previously used for storage/disposal of drilling wastes, produced water, and flowback fluids in the area of investigation. Discussions are ongoing with stakeholders to determine the location, delineate the boundaries, and extent (areal and vertical) of contamination associated 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, pxylene were detected at concentrations up to 390 and 150  $\mu$ g/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  $\mu$ g/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  $\pm$  0.4, n = 19) (**Figure 12**) and display calciumbicarbonate composition. With increasing depth, ground water becomes moderately alkaline (pH 9.0  $\pm$  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





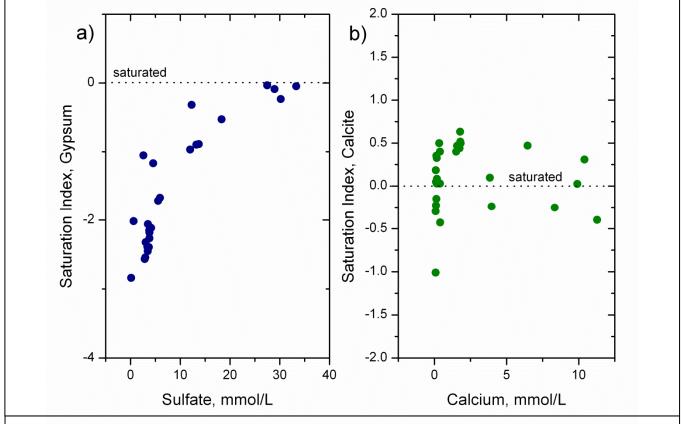
monitoring wells).

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<sub>4</sub>·2H<sub>2</sub>O) and calcite (CaCO<sub>3</sub>), 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



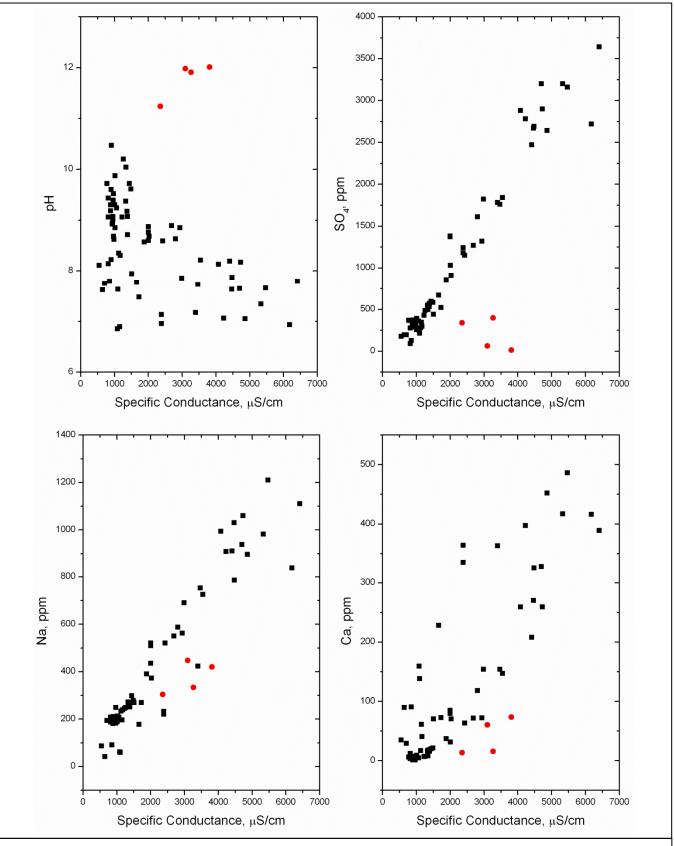
**Figure 13.** Saturation indices for **(a)** gypsum versus sulfate concentration and **(b)** calcite versus calcium concentration. Saturation Index is equal to the logarithm of the ratio of the ion activity product to the mineral solubility product. A Saturation Index of 0 corresponds to chemical equilibrium; 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**).

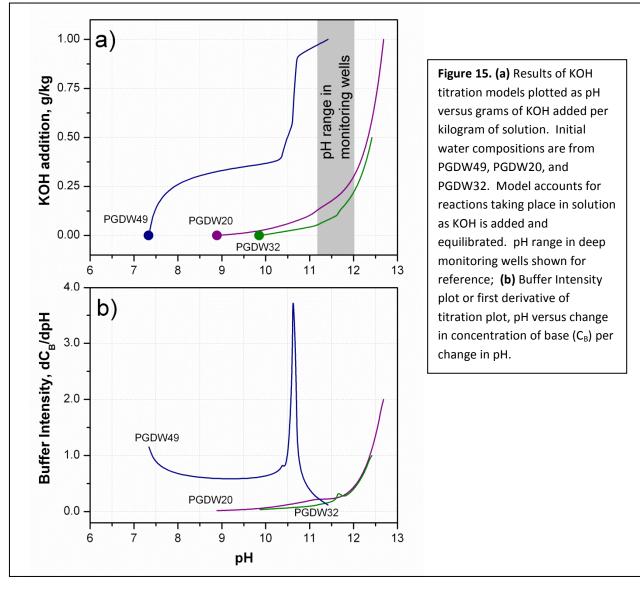
The high pH measured in the deep monitoring wells was unusual and unexpected. Although ground water pH in these wells was >11, total alkalinity was not particularly high (<500 mg/kg), and as already noted up to 94% of the total alkalinity was present as hydroxide (see charge balance calculations, Table 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.

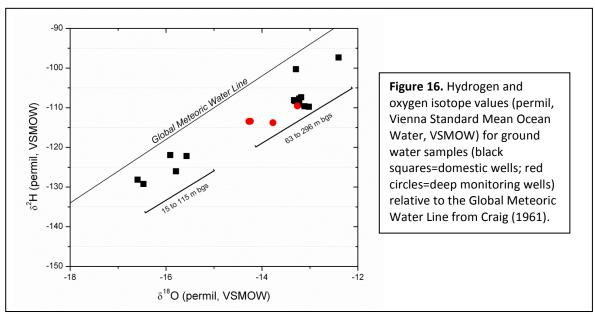
In order to gain additional insight, reaction path modeling was conducted to evaluate pH response to addition of strong base (potassium hydroxide, KOH). Geochemical modeling was carried out by using ground water compositions for PGDW49, PGDW20, and PGDW32 (initial pH 7.3, 8.9, and 9.9, respectively).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

Paired values of  $\delta^{18}$ 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 <sup>18</sup>O and <sup>2</sup>H compared to deeper ground water samples and may be more reflective of local recharge. Ground water isotope data from the deep monitoring wells (red circles, **Figure 16**) follow along the same  $\delta^{18}$ 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).





### **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, 2butoxyethanol, 2-butanone, diethylene glycol, triethylene glycol, and tetraethylene glycol (Figure 17; Table 3). Concentrations of these chemicals range from  $\mu$ g/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(2chloroethyl) ether, bis(2-ethylhexyl) adipate (MW01, Phase IV), butyl benzyl phthalate, and 4-methyl-2pentanone (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, CI, and OH in deep monitoring wells.

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

TBA was detected in MW02 during Phase 4 sampling at a concentration of 4470  $\mu$ g/L. Two possible formation pathways for TBA are: 1) biodegradation of methyl tert-butyl ether (MTBE, synthetic chemical used as a fuel additive) under methanogenic conditions (e.g., Mormile et al. 1994, Bradley et al. 2001); and 2) breakdown of *tert*-butyl hydroperoxide (a gel breaker used in hydraulic fracturing; e.g., Hiatt et al. 1964). TBA biodegradation is generally slow compared to the degradation of MTBE; this suggests that TBA could be present and persist even after complete MTBE removal from ground water impacted by fuel releases (Wilson et al. 2005). MTBE was not detected in either of the deep monitoring wells. A second pathway of TBA production is from the decomposition of the gel breaker tert-butyl hydroperoxide. Hiatt et al. (1964) found that decomposition of tert-butyl hydroperoxide yielded a 10-fold molar quantity of TBA, oxygen, di-tert-butyl peroxide, and acetone. Acetone was detected in MW02 during Phase 4 sampling at a concentration of 641  $\mu$ g/L. This breaker is used in hydraulic fracturing formulations; however, the MSDSs made available to EPA do not indicate whether tert-butyl hydroperoxide was used in the Pavillion gas field for well stimulation. Elevated concentrations of TBA are not expected in unimpacted aguifers 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    | l-water monitor | ing wells                |           |
|------------------------------|-------------------|-----------------|--------------------------|-----------|
| Compound                     | MW01              | MW02            | MW01                     | MW02      |
|                              | Phase 3           | Phase 3         | Phase 4                  | Phase 4   |
|                              | 10/6/2010         | 10/6/2010       | 4/20/2011                | 4/19/2011 |
| рН                           | 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 <sub>4</sub> , mg/L       | 16.0              | 19.0            | 17.9                     | 18.8      |
| Benzene †                    | nd                | 246             | nd                       | 139       |
| Toluene                      | 0.75 <sup>d</sup> | 617             | 0.56                     | 336       |
| Ethylbenzene                 | nd                | 67              | nd                       | 21.5      |
| Xylenes (total)              | nd                | 750             | <b>0.89</b> <sup>d</sup> | 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 <sup>a</sup>          | 11.1              | 56.1            | 20.9                     | 64.9      |
| Naphthalene <sup>b</sup>     | 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 <sup>c, d</sup>      | 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.

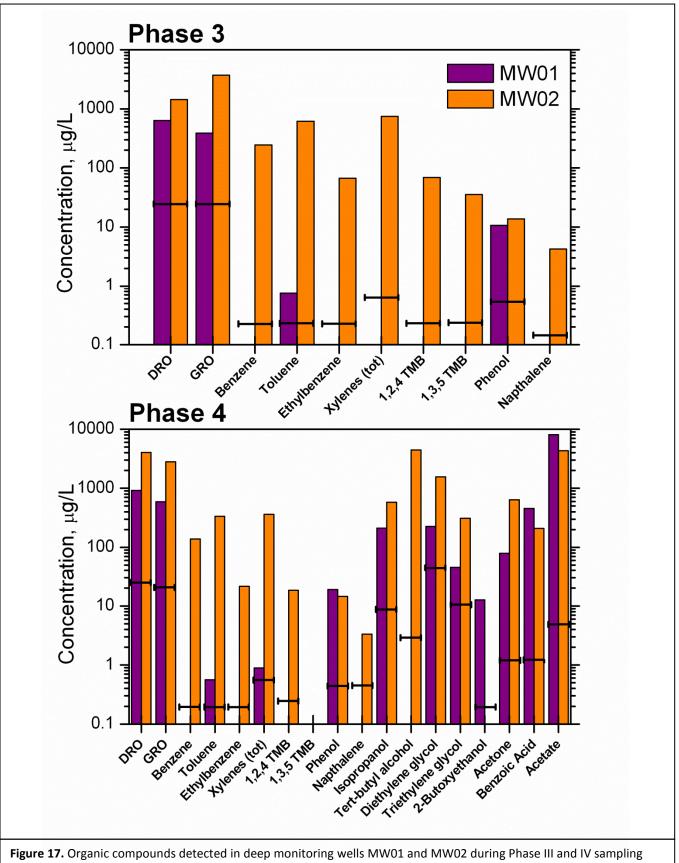
----- not analyzed.

nd - not detected.

nd - not detected.
<sup>a</sup> Includes phenol, 2,4-dimethylphenol, 2-methylphenol, 3&4 methylphenol.
<sup>b</sup> Includes naphthalene, 1-methylnaphthalene, and 2-methylnaphthalene.
<sup>c</sup> Value below quantitation limit of 10 µg/L.
<sup>d</sup> Chemical detected in a blank sample at a similar level
<sup>a</sup> Detected in a blank sample at a similar level

\* 2-Butoxyethanol determined by HPLC-MS-MS.

\*\* 2-Butoxyethanol determined by GC-MS.



events. Horizontal bars show method reporting limits for the individual analytes.

| Table 4. Association o                                                            | f inorganic and organic anomalies with compounds used for hydraulic fracturing                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  |
|-----------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Compound/<br>Compound Class                                                       | Information from MSDSs and Well Completion Reports                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              |
| рН                                                                                | 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<br>and aromatic hydrocarbons including naphthalenes and alkylbenzenes) was used in a<br>guar polymer slurry/liquid gel concentrate (30-60%) and in a solvent (60-100%).<br>Petroleum raffinates (mixture of paraffinic, cycloparaffinic, olefinic, and aromatic<br>hydrocarbons) was used in a breaker (<30-60%). Heavy aromatic petroleum naptha<br>(mixture of paraffinic, cycloparaffinic and aromatic hydrocarbons) was used in<br>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 <i>tert</i> -butyl ether and <i>tert</i> -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%).<br>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 <i>tert</i> -butyl hydroperoxide - found in gel breakers. See discussion.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  |
| Benzoic Acid,<br>Acetate, Formate,<br>Lactate, Propionate,<br>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  $(C_1/C_1-C_5 = 0.95 - 0.95)$ 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.

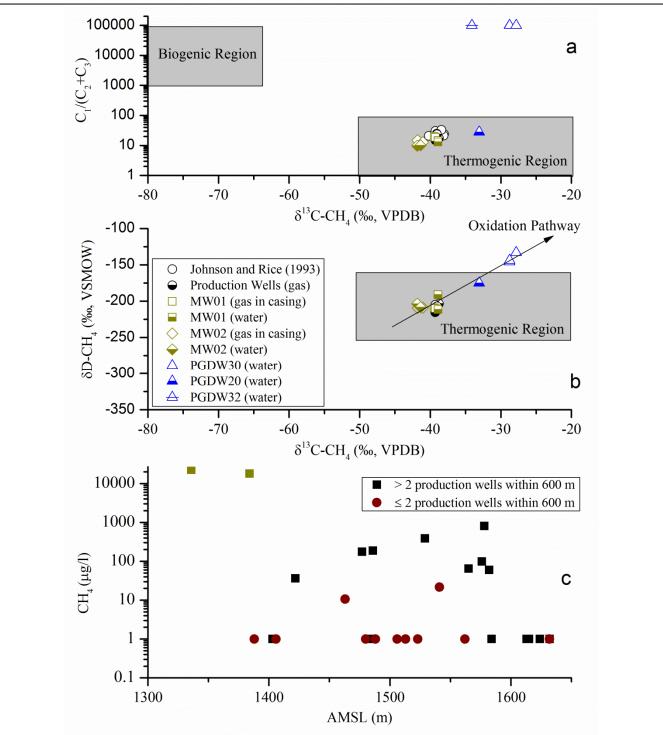
As noted previously, this investigation was prompted by homeowner complaints over perceived changes in water quality. Domestic well results showed: the presence of DRO and GRO (in 23 of 28 samples), and trace levels of exotic organic compounds in some domestic wells including adamantanes, 2butoxyethanol phosphate, phenols, naphthalene, and toluene (EPA 2009, EPA 2010). Methane was detected in 10 of 28 samples at concentration levels below 0.8 mg/L. Foul odors associated with some domestic wells correlate with detections of GRO and DRO. Anomalous trends in inorganic constituents observed in the deep monitoring wells (e.g., K, Cl, pH) were not revealed in domestic well waters. In several instances, glycols were detected in domestic wells using gas chromatography with flame ionization detection (GC-FID; EPA Standard Method 8015). However, glycol analysis using liquid chromatography with tandem mass spectroscopy (GC/MS/MS) failed to replicate these glycol detections, even though the method

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

#### **Natural Gas Migration**

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

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



**Figure 18. (a)** Stable isotope ratios of carbon of methane versus ratio of methane ( $C_1$ ) to ethane ( $C_2$ ) and propane ( $C_3$ ) in gas from production wells, monitoring wells, and domestic wells. Values of 100,000 are used to denote non detection of ethane and propane in samples. (b) Stable isotope ratios of carbon versus hydrogen of methane in gas from production wells (both literature and measured values), monitoring wells, and domestic wells.  $\delta D$  was not determined for PGDW32. Oxidation pathway (enrichment of <sup>13</sup>C of remaining CH<sub>4</sub> 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).

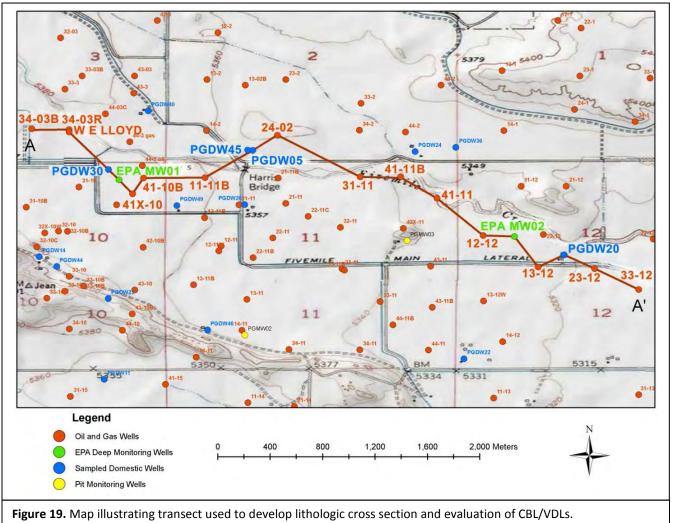
detected at less than 22  $\mu$ g/L, methane was not detected in domestic wells with 2 or less production wells within 600 m (**Figure 18c**). All domestic wells with the exception of PGDW25 with 2 or less production wells within 600 m are located on the periphery of the gas field (**Figure 5**). PGDW25 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  $\mu$ g/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<sub>4</sub> versus  $\delta$ D -CH<sub>4</sub> (**Figure 18b**) and  $\delta^{13}$ C-CH<sub>4</sub> versus C<sub>1</sub>/(C<sub>2</sub> + C<sub>3</sub>) (**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<sub>4</sub> 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  $\delta D$  - $CH_4$  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<sub>4</sub> and  $\delta D$ -CH<sub>4</sub> 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  $\delta D$ . This observation is consistent with a pattern of dispersion and degradation with upward migration observed for organic compounds. Values of  $\delta^{13}$ C-CH<sub>4</sub> 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).

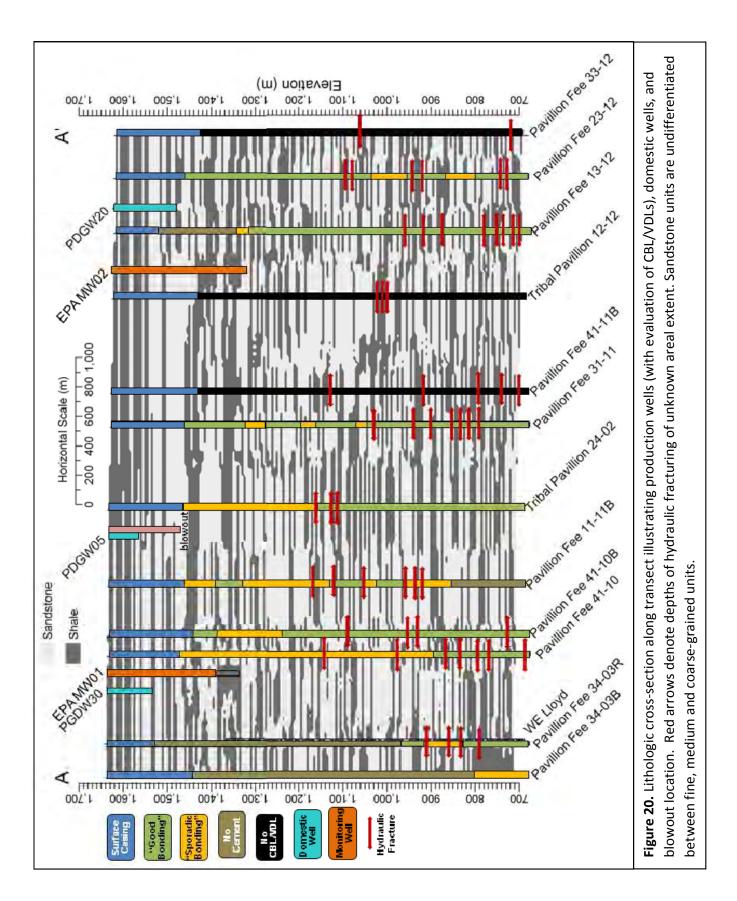
# Evaluation of Cement Bond/Variable Density Logs Along Transect

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.



#### **Potential Migration Pathways**

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

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

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

# **4.0** Conclusions

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

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

Detection of contaminants in ground water from deep sources of contamination (production wells, hydraulic fracturing) was considerably more complex than detection of contaminants from pits necessitating a multiple lines of reasoning approach common to complex scientific investigations. In this approach, individual data sets and observations are integrated to formulate an explanation consistent with each data set and observation. While each individual data set or observation represents an important line of reasoning, taken as a whole, consistent data sets and observations provide compelling evidence to support an explanation of data. Using this approach, the explanation best fitting the data for the deep monitoring wells is that constituents associated with hydraulic fracturing have been released into the Wind River drinking water aquifer at depths above the current production zone.

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

1. High pH values

pH values in MW01 and MW02 are highly alkaline (11.2-12.0), above the pH range observed in domestic wells (6.9-10), and above the pH range previously reported for the Wind River Formation with up to 94% of the total alkalinity contributed by hydroxide. The presence of hydroxide alkalinity suggests addition of base as the causative factor for elevated pH in the deep monitoring wells. Reaction path modeling indicates that sodiumsulfate 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  $\mu$ g/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 tertbutyl 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 noncommercially 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  $\mu$ g/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  $\mu$ g/L respectively. Trimethylbenzenes were detected in MW02 at 105  $\mu$ g/L. Gasoline range organics were detected in MW01 and MW02 at 592 and 3710  $\mu$ g/L, respectively. Diesel range organics were detected in MW01 and MW02 at 924 and 4050  $\mu$ g/L respectively. Naphthalene was detected in MW02 at 6  $\mu$ g/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. <u>Sporadic bonding outside production casing</u> <u>directly above intervals of hydraulic fracturing</u>

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. <u>Hydraulic fracturing into thin discontinuous</u> <u>sandstone units</u>

> 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<sub>4</sub> versus  $\delta$ D -CH<sub>4</sub> 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<sub>4</sub> and  $\delta$ D-CH<sub>4</sub> 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. <u>Elevation of dissolved methane</u> concentrations in proximity to production wells

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

#### 3. Spatial anomaly near PGDW05

Methane concentrations in ground water appear highest in the area encompassing MW01, PGDW30, and PGDW05. Ground water is saturated with methane at MW01 which is screened at a depth (239 m bgs) typical of deeper domestic wells in the area. Methane was detected in PGDW30 at 808  $\mu$ g/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. <u>Shallow surface casing and lack of cement or</u> <u>sporadic bonding outside production casing</u>

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. <u>Citizens' complaints</u>

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

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# **Appendix A** Summary of Analytical Results

| Sample                             | Latitude    | Langitude    | Depth<br>(m bgs) | Type | Media         | Major<br>anions and<br>alkalinity<br>phase(lab) | Metals<br>phase(lab)                      | Alcohols<br>and VOCs<br>phase(lab)                                            | Low<br>molecular<br>weight<br>acids, glycols<br>phase(lab) | SVOCs<br>Pesticides<br>PCBs, TICs<br>phase(lab)  | GRO, DRO,<br>THE, TPH<br>phase(lab)                        | Bacteria<br>phase(lab)                 | Fixed gases,<br>C <sub>1</sub> -C <sub>6</sub> +,<br>5 <sup>13</sup> C and 5D C <sub>1</sub> -C <sub>4</sub><br>DOC<br>DIC, 5 <sup>13</sup> C DIC<br>6 <sup>14</sup> C and 6D water<br>ohasellab) |
|------------------------------------|-------------|--------------|------------------|------|---------------|-------------------------------------------------|-------------------------------------------|-------------------------------------------------------------------------------|------------------------------------------------------------|--------------------------------------------------|------------------------------------------------------------|----------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| PGPP01 (Tribal<br>Pavillion 14-10) | 43.24578857 | -108.6356735 |                  | Ъd   | gas/<br>fluid | 1                                               | I                                         | II(R8 <sup>2</sup> )                                                          | Į.                                                         | II(R8 <sup>3</sup> )                             | II(R8 <sup>4</sup> )                                       | 1                                      | ( <sub>t</sub> 1)11                                                                                                                                                                               |
| PGPP02                             | 43.2486496  | -108.6274796 |                  | PG   | gas           | ł                                               | ł                                         | l                                                                             | I                                                          | t                                                | ł                                                          | ŀ                                      | (,)))                                                                                                                                                                                             |
| PGPP04 (Tribal<br>Pavillion 24-02) | 43.25984955 | -108.6116409 |                  | PG   | gas/<br>fluid | 1                                               | 1                                         | II(R8 <sup>2</sup> )                                                          | 1                                                          | li(R8³)                                          | II(R8 <sup>4</sup> )                                       | 1                                      | ( <sub>1</sub> )))                                                                                                                                                                                |
| PGPP05 (Tribal<br>Pavillion 33-10) | 43.2486496  | -108.6274796 | Ľ                | PG   | gas/<br>fluid | Ţ                                               |                                           | II(R8 <sup>2</sup> )                                                          | 1                                                          | II(R8 <sup>3</sup> )                             | II(R8 <sup>4</sup> )                                       | 1                                      | ( <sub>1</sub> )0                                                                                                                                                                                 |
| PGPP06 (Tribal<br>Pavillion 14-2)  | 43.26016998 | -108.6165009 |                  | PG   | gas/<br>fluid | ł                                               | -                                         | II(R8 <sup>2</sup> )                                                          |                                                            | II(R8 <sup>3</sup> )                             | II(R8 <sup>4</sup> )                                       | ł                                      | (L)(I                                                                                                                                                                                             |
| TOWIN                              | 43.25682    | -108.62185   | 233 -<br>239     | MM   | gas/<br>water | (10])<br>(10])                                  | (rs)vi (rs)iii                            | III(R8 <sup>2</sup> ,5 <sup>3</sup> )<br>IV(R8 <sup>2</sup> ,5 <sup>3</sup> ) | IV(S <sup>4</sup> ,R3)                                     | III(R8 <sup>3</sup> )<br>IV(R8 <sup>3</sup> )    | III(R8 <sup>4</sup> )<br>IV(R8 <sup>4</sup> )              | I                                      | III(I <sup>2</sup> ,I <sup>2</sup> ,O <sup>2</sup> ,S <sup>5</sup> ,S <sup>6</sup> )<br>IV(I <sup>3</sup> ,I <sup>4</sup> ,O <sup>2</sup> ,S <sup>5</sup> ,S <sup>6</sup> )                       |
| MW02                               | 43,25293    | -108,59468   | 293 -<br>299     | MM   | gas/<br>water | 111(0 <sup>1</sup> )<br>117(0 <sup>1</sup> )    | III(S <sup>1</sup> ), IV(S <sup>1</sup> ) | III(R8 <sup>2</sup> ,S <sup>3</sup> )<br>IV(R8 <sup>2</sup> ,S <sup>3</sup> ) | IV(S <sup>4</sup> ,R3)                                     | III(R8 <sup>3</sup> )<br>IV(R8 <sup>3</sup> )    | III(R8 <sup>4</sup> ),<br>IV(R8 <sup>4</sup> )             | I                                      | 111(1 <sup>2</sup> ,1 <sup>5</sup> ,0 <sup>2</sup> , S <sup>5</sup> ,S <sup>5</sup> )<br>1V(1 <sup>3</sup> ,1 <sup>4</sup> ,0 <sup>2</sup> , S <sup>5</sup> ,S <sup>5</sup> )                     |
| PGMW01<br>(Pit 24-3#1)             | 43.26122665 | -108.6316147 | 4.6              | PGM  | water         | II(R8 <sup>1</sup> )                            | II(A4)                                    | II(A,R8 <sup>2</sup> )                                                        | 1                                                          | II(A,R8 <sup>3</sup> )                           | II(E <sup>2</sup> ,R8 <sup>4</sup> )                       | II(E <sup>1</sup> )                    | II(R8 <sup>5</sup> )                                                                                                                                                                              |
| PGMW02<br>(Pit 14X-11#6)           | 43.24616241 | -108,613205  | 4.6              | PGM  | water         | II(R8 <sup>1</sup> )                            | II(A4)                                    | JI(A,R8 <sup>2</sup> )                                                        | 1                                                          | II(A,R8³)                                        | II(E <sup>2</sup> ,R8 <sup>4</sup> )                       | II(E <sup>1</sup> )                    | II(R8 <sup>3</sup> )                                                                                                                                                                              |
| PGMW03<br>(Pit 42X-11#4)           | 43.25263977 | -108.6020584 | 4.6              | PGM  | water         | II(R8 <sup>1</sup> )                            | II(A4)                                    | )I(A,R8 <sup>2</sup> )                                                        | 1                                                          | II(A,R8 <sup>3</sup> )                           | II(E <sup>2</sup> ,R8 <sup>4</sup> )                       | 11(E <sup>1</sup> )                    | II(R8 <sup>5</sup> )                                                                                                                                                                              |
| PGSO01<br>(Pit 24-3)               | 43.26117325 | -108.6316071 | < 5<br>5         | PGS  | soil          | 1                                               | J                                         | 1                                                                             | 1                                                          | ll(R8 <sup>3</sup> )                             | II(E <sup>2</sup> ,R8 <sup>4</sup> )                       | 1                                      | I                                                                                                                                                                                                 |
| PGSO02<br>(Pit 14X-11)             | 43.24636841 | -108.6135254 | <5<br><          | PGS  | soil          | ļ                                               | Ą                                         | ĺ                                                                             | I                                                          | II(R8³)                                          | II(E <sup>2</sup> ,R8 <sup>4</sup> )                       | l                                      | I                                                                                                                                                                                                 |
| PGSO03<br>(Pit 42X-11)             | 43.2527504  | -108.6022339 | < 5              | PGS  | soil          | ł                                               |                                           | ļ                                                                             | -                                                          | II(R8³)                                          | II(E <sup>2</sup> ,R8 <sup>4</sup> )                       | ł                                      | 1                                                                                                                                                                                                 |
| PGDW01                             | unknown     | unknown      | ĺ.               | DW   | water         | 1(R8 <sup>1</sup> )                             | I(K)                                      | (1)                                                                           | 1                                                          | I(L,R8 <sup>3</sup> )                            | 1                                                          | 1                                      | 1                                                                                                                                                                                                 |
| PGDW02                             | 43.21848912 | -108.5783117 | 15.2             | MQ   | water         | I(R8 <sup>1</sup> )                             | (K)                                       | I(T)                                                                          | - Sec.                                                     | I(L,R8 <sup>3</sup> )                            | inter a                                                    | ) and                                  |                                                                                                                                                                                                   |
| PGDW03                             | 43.22721318 | -108.6584107 | 152.4            | MQ   | water         | I(R8 <sup>1</sup> )                             | i(K), II(A4)                              | i(L) II(A,R8 <sup>2</sup> )                                                   | 1                                                          | I(L,R8 <sup>3</sup> )<br>II(A,R8 <sup>3</sup> )  | II(E <sup>2</sup> ,R8 <sup>4</sup> )                       | 11(E <sup>1</sup> )                    | ( <sup>1</sup> ,R8 <sup>2</sup> )                                                                                                                                                                 |
| PGDW04                             | 43.22790981 | -108.6542063 | 152.4            | Md   | water         | I(R8 <sup>1</sup> )<br>II(R8 <sup>1</sup> )     | I(K), II(A4)                              | I(L) II(A,R8 <sup>2</sup> )                                                   | ł                                                          | I(L,R8 <sup>3</sup> ),<br>II(A,R8 <sup>3</sup> ) | 1(E <sup>2</sup> )<br>11(E <sup>2</sup> ,R8 <sup>4</sup> ) | I(E <sup>1</sup> ) II(E <sup>1</sup> ) | I(R8°)<br>II(I,R8°)                                                                                                                                                                               |
| PGDW05                             | 43.25884666 | -108.6126481 | 64.0             | MQ   | water         | I(R8), II(R8)<br>IV(0 <sup>1</sup> )            | I(K) II(A4)<br>N/IS <sup>1</sup> 1        | 1(L) 11(A,R8 <sup>2</sup> )<br>11/188 <sup>2</sup> 5 <sup>3</sup> )           | IV(S <sup>*</sup> ,R3)                                     | I(L,R8 <sup>3</sup> )<br>II(A,R8 <sup>3</sup> )  | 1(E <sup>2</sup> )<br>11(F <sup>2</sup> R8 <sup>4</sup> )  | I(E <sup>1</sup> ) II(E <sup>1</sup> ) | II(R8 <sup>5</sup> )<br>II(R8 <sup>5</sup> )                                                                                                                                                      |