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Acronyms and Abbreviations

ACF	Advanced chemical fingerprinting
ASTM	American Society for Testing and Materials
BGS	Below ground surface
BTEX	Benzene, toluene, ethylbenzene, and xylenes
DRO	Diesel range organics
DTW	Depth to water
ESI	Expanded Site Investigation
FOIA	Freedom of Information Act
GC/FID	Gas chromatography/flame ionization detector
GC/MS	Gas chromatography/mass spectrometry
GRO	Gasoline range organics
GWERD	Ground Water and Ecosystem Restoration Division (of USEPA)
HPLC/MS/MS	High-performance liquid chromatography/mass spectrometry/ mass spectrometry
NWIS	National Water Information System
NURE	National Uranium Resource Evaluation
QA/QC	Quality assurance and quality control
QAPP	Quality assurance project plan
RCRA	Resource Conservation and Recovery Act
SOP	Standard operating procedure
SVOC	Semi-volatile organic compound
TBA	*tert*-Butyl alcohol
TCLP	Toxic Characteristic Leaching Procedure
TD	Total depth
TDS	Total dissolved solids
TPH	Total purgeable hydrocarbons
USBOR	U.S. Bureau of Reclamation
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey
VOC	Volatile organic compound
VRP	Voluntary Remediation Program
WDEQ	Wyoming Department of Environmental Quality
WOGCC	Wyoming Oil & Gas Conservation Commission
WSEO	Wyoming State Engineer's Office
WWDC	Wyoming Water Development Commission

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Executive Summary

S.S. Papadopulos & Associates (SSP&A) has reviewed the Draft Report by the U.S. Environmental Protection Agency (EPA) "Investigation of Ground Water Contamination near Pavillion, Wyoming" (Draft Report), which was released on December 8, 2011. SSP&A's review indicates that EPA has not provided sufficient data nor analysis to support most of the report's conclusions. The data in the Draft Report do demonstrate the existence of shallow groundwater contamination associated with surface activities at gas drilling and production locations. This contamination was already known, however, and is being actively investigated by Encana Oil & Gas USA, Inc. under the direction of the Wyoming Oil & Gas Conservation Commission (WOGCC) and the Wyoming Department of Environmental Quality Voluntary Remediation Program (WDEQ VRP). Notably, EPA has not been able to identify the source of taste and odor problems in domestic wells that initiated the study.

The Pavillion area is unusual in that the aquifer and gas-producing formations occur within the same geologic unit. For any study to conclusively address impacts from hydraulic fracturing activities, USEPA must adequately distinguish between potential natural impacts and those from gas drilling activities. Our review of the Draft Report suggests that EPA has not completed the work necessary to distinguish these potential sources. Specific shortcomings include:

- poor study design, lack of appropriate conceptual model, and failure to fully evaluate alternative hypotheses;
- a lack of both baseline and background data for key parameters, including methane, and naturally occurring organic compounds that would be detected and reported as diesel-range organics (DRO) and gasoline-range organics (GRO);
- analytical concerns related to false positives, inappropriate quantification, and lack of appropriate validation of laboratory data and methods;
- problems with construction, development (purging) and sampling of the deep monitoring wells;
- the fact that EPA's conclusions regarding the impact of hydraulic fracturing fluids are based primarily on a total of four samples, two from each of two deep monitoring wells; and
- the fact that EPA never adequately addressed the original project aims of determining the source of taste and odor complaints in residential wells.

EPA's most noteworthy conclusion, that hydraulic fracturing fluids have impacted groundwater, rests primarily on analytical results from deep monitoring wells MW01 and MW02. These wells were only sampled twice, and information provided by EPA show significant concerns with those results. Field notes on well construction indicate that the wells were built, developed and sampled so that the water samples were in contact with cement grout, cuttings and other additives that could have caused elevated levels of potassium (K), pH, and

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organic compounds including glycols observed in the deep monitoring well samples. Calculations of the amount of water contained in borehole storage suggest that the samples from MW01 and MW02 likely contained significant amounts of borehole water and other possible contaminants and thus are not representative of the aquifer formation water. Furthermore, there are indications that these two wells (screened at depths of 765-785 feet bgs and 960 to 980 feet bgs) are open to depths where naturally occurring gas horizons may be present, contributing hydrocarbons and chloride (Cl). Both wells appear to be screened deeper than any nearby domestic wells, based upon data from the Wyoming State Engineer's Office.

Analytical and interpretive issues are present for a number of analytes. These issues would be clarified by a full data validation exercise. For example, while EPA reports widespread detections of diesel-range organics (DRO), chromatograms of these samples rarely match standards for the analytical method, calling into question their quantification. Similarly, the chromatograms for gasoline-range organics (GRO) are generally a poor match to standard, and GRO components (e.g. benzene) were not detected in those samples. EPA has not adequately investigated these DRO and GRO results to understand their physical meaning, nor sufficiently qualified them in the report to indicate that they may represent naturally occurring organic compounds. A number of petroleum-related compounds were detected in blank samples, and the correlative samples were not appropriately qualified in the draft report as non-detect or false positives.

For EPA to adequately test their hypothesis that deep groundwater in the Pavillion area is impacted by hydraulic fracturing activities, additional work, including additional sampling of wells MW01 and MW02 is required. Even if additional samples are collected from these wells, however, they will not address all the shortcomings in EPA's study. An improved study design is required that considers the hydrogeologic conditions near sampling locations, the presence of pre-existing, naturally occurring petroleum compounds, and the actual migration pathways between potential sources and receptors, both in the shallow and deep portions of the aquifer.

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REPORT

Section 1
Introduction

S.S. Papadopulos & Associates (SSP&A) has reviewed the Draft Report by the U.S. Environmental Protection Agency (EPA) "Investigation of Ground Water Contamination near Pavillion, Wyoming" (Draft Report) that was released on December 8, 2011 (U.S. EPA, 2011a). As part our review, SSP&A downloaded all files provided by EPA on its Pavillion website (http://www.epa.gov/region8/superfund/wy/pavillion) and pages linked thereto. Additional files uploaded by EPA on January 31, 2012 were also reviewed.[1] Because EPA's production did not include all files related to field sampling activities, SSP&A submitted a FOIA request to EPA for these files on February 7, 2012 (Appendix A). The FOIA files have not yet been received.

SSP&A also reviewed the Wyoming Oil & Gas Conservation Commission (WOGCC) Pavillion Working Group files available at http://wogcc.state.wy.us . SSP&A reviewed the files that were available through February 27, 2012 (EPA's original date for submission of comments on the Draft Report).

Additional information reviewed by SSP&A staff included files maintained at the Wyoming Department of Environmental Quality (WDEQ) offices in Lander, and articles from the scientific literature.

This report presents SSP&A's observations regarding the report's methods, data and conclusions. We have focused on the degree to which the data support EPA's conclusions regarding the impact of hydraulic fracturing activities on groundwater. Because certain aspects of the investigation (e.g. well construction methods, laboratory methods) impact many of the results and conclusions, this report is organized by those subjects. In addition, the final section of this review addresses each of EPA's conclusions (from Section 4 of the Draft Report) individually. Page numbers cited in this review refer to the Draft Report, unless otherwise noted.

To assist in evaluating laboratory data, SSP&A contracted the assistance of QA/QC Solutions, LLC, an analytical chemistry consulting firm. QA/QC Solution's full report is provided in Appendix B. Many of its conclusions are cited within the following discussions.

In addition, Echelon Applied Geoscience Consulting prepared a focused review that specifically addresses methane detections in groundwater samples. This document is included in Appendix C, and referenced in this report.

The review presented here is necessarily incomplete because some documents have not been made available in a timely manner during the public review period. SSP&A reserves the right to alter and/or update our opinions if new information becomes available.

[1] In uploading new files, EPA removed from public access some files that had previously been available. In addition, the file count after January 31, 2012 was lower than the 622 files indicated on EPA's website. After e-mail correspondence with USEPA staff, additional files were uploaded, but there may be a discrepancy between what EPA intended to make available, and what was actually available to the public.

Section 2
Technical Issues in the EPA Draft Report

This review focuses on technical issues in the EPA Draft Report and highlights those issues that may compromise its stated conclusions. Some of these shortcomings (e.g. too few samples from the deep monitoring wells) can be resolved in a relatively straightforward manner. Other shortcomings (e.g. lack of baseline data) are more difficult to address, and also suggest a study design that is insufficient to support its conclusions. The Pavillion area is unusual in that the aquifer and gas-producing formations occur within the same geologic unit. For any study to conclusively address impacts from human activities, USEPA must adequately distinguish between potential natural impacts and those from gas drilling activities. Our review of the Draft Report suggests that EPA has not completed the work necessary to distinguish these potential sources. In addition, there are important questions about the quality of data collection and analytical methods used, casting doubt on the limited data set used to support EPA's conclusions.

Briefly, the areas of concern fall into the following categories:

- Poor study design, lack of appropriate conceptual model, and failure to fully evaluate alternative hypotheses;
- A lack of both baseline and background data for key parameters, including methane, and naturally occurring organic compounds that would be detected within the diesel-range organics (DRO) and gasoline-range organics (GRO) windows;
- Analytical concerns related to false positives, inappropriate quantitation, and lack of appropriate validation of laboratory data;
- Problems with construction, development (purging) and sampling of the deep monitoring wells. These issues may have compromised the results for Total Dissolved Solids (TDS), chloride (Cl), potassium (K), pH, and organic compound used to support EPA's interpretation of impact on these wells from hydraulic fracturing fluids; and
- EPA's conclusions regarding the impact of hydraulic fracturing fluids are based primarily on two samples each, from the two deep monitoring wells.

2.1 Chemical Compounds in Domestic Wells

EPA's most noteworthy conclusion in the draft report, that hydraulic fracturing fluids have impacted groundwater, rests primarily on analytical results from deep monitoring wells MW01 and MW02 installed and sampled in Phases III and IV (Figure 1). The vast majority of samples, however, were collected from domestic wells ("PGDW" samples in Figure 1) and shallow monitoring wells associated with pits ("PGMW" samples in Figure 1) in Phases I and II.

Notably, EPA did not demonstrate actual impacts of hydraulic fracturing on domestic wells in Phases I and II. Thus the Phase III and IV focus almost entirely on deep monitoring wells is puzzling. As will be discussed later, this reflects the lack of an adequate conceptual model for the site investigation.

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EPA's approach would be understandable if it assumed that methane, gasoline-range organics (GRO) and diesel-range organics (DRO) must be evidence of anthropogenic impact on domestic wells. But EPA did not provide sufficient information on background or baseline concentrations of methane to demonstrate an anthropogenic impact on domestic wells. As will be discussed in greater detail later, the DRO and GRO results from the domestic wells are potentially derived from natural organic compounds unrelated to gas drilling activities, and are generally inconsistent with the standards used to quantify these results.

2.1.1 Methane

During Phases I and II, EPA did demonstrate that methane was present in wells situated over a broad area centered on the Wind River-Fort Union structural high (Mueller, 1989) and the Pavillion gas field (Figure 2). In reality, several hypotheses for the presence of methane in the water supply wells arise from these associations:

- The structural high is an area that has naturally occurring methane in Wind River formation water-bearing sandstone lenses; and/or
- Methane is entrained in fluids leaked historically from pits or other structures at gas drilling and production locations; and/or
- Methane in the Wind River aquifer reflects enhanced migration associated with gas well drilling and construction activities (including hydraulic fracturing).

None of these scenarios is adequately addressed in the Draft Report, however.

The presence of thermogenic methane in shallow or deep wells does not necessarily indicate enhanced migration in these areas due to hydraulic fracturing activities. In fact, the existence of a background methane component in Pavillion groundwater is not surprising given the location of the investigation over a structural high in an area known to have shallow gas deposits. The Draft Report (p. 27) notes evidence for methane based on a review of open-hole geophysical logs. These indicate the presence of gas-filled porosity at three locations at depths of 198, 208, and 252 meters (650, 682, and 827 feet) between the years 1965 and 1973. These results would suggest the presence of natural gas in groundwater at depths used for domestic water supply prior to extensive commercial development. Additionally, a U.S Bureau of Reclamation report documenting work on the Riverton irrigation project (USBOR, 1951; excerpts in Lander DEQ files) describes a water supply well in the Wind River formation 3 miles east northeast of MW01 that required plugging after it reached a depth of 500 feet below ground surface (bgs) due to gas in the water. EPA dismisses shallow gas indications (page 27), but without sufficient documentation and discussion to adequately address the point.

The presence of gas in non-producing areas of other sedimentary basins is well known. For example, in the Piceance Basin in western Colorado, several domestic wells drilled into Tertiary sedimentary rocks similar to the Wind River formation have thermogenic methane concentrations in excess of 1 mg/L (S.S. Papadopulos & Associates, 2008). These wells are located on the apex of the Divide Creek anticline, but are more than one mile south of the actively producing Mamm Creek gas field. Recent studies on the Appalachian basin also indicate that baseline methane detections are common in other petroliferous regions (Baldassare et al., in press; see Appendix C).

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2.1.2 Other Organic Compounds

The Pavillion study began in 2008 as an investigation of taste and odor complaints in domestic wells, yet the Draft Report failed to find contamination or source(s) of contamination that caused these complaints. Confirmed detections of significant groundwater contamination at depths shallower than MW01 and MW02 occurred only in the pit monitoring wells, locations where historical surface sources of contamination were known, and are currently undergoing investigation and/or remediation. At this time, no confirmed detections that could conclusively be tied to hydraulic fracturing activities have been shown for any of the domestic wells sampled throughout the four phases of the EPA investigation.

Notably, EPA did not provide a summary of organic compounds detected in domestic and pit monitoring wells. Table 1 is a summary of the potentially anthropogenic compounds reported by EPA as being detected in domestic wells (wells with the prefix "PGDW"). The vast majority of these compounds were detected at sub-ppb or low-ppb concentrations, and a large fraction were only detected in qualified results for which no confirmation was pursued. As can be seen from this table, many of the compounds are unlikely to be associated with hydraulic fracturing (chlorofluorocarbons) or have many potential sources (pentanes, toluene).

In the Draft Report, EPA has identified the adamantanes as potentially indicative of hydraulic fracturing impact. Adamantanes are naturally-occurring compounds found in hydrocarbons and natural gas condensate (Stout and Douglas, 2004). All of the Phase II results for 1,3-dimethyl adamantine were qualified due to holding time issues, and all of the Phase IV detects were also qualified. 1,3-Dimethyl adamantine was also reported as a TIC in a Phase IV blank sample. For adamantane, a single unqualified result was reported in Phase IV (PGDW 32 at 0.12 ! g/l). Although this result might have survived a full laboratory validation, it is insufficient evidence to attribute to the results of natural gas production activities in the Pavillion area.

Clearly, there has been substantial difficulty in quantifying and validating the presence of adamantanes in domestic wells. And since none of the other detections make a clear or strong case for impact of hydraulic fracturing fluids or petroleum products, it is premature for EPA to use these data to establish such impact.

2.1.3 Inorganic Compounds

EPA failed to adequately consider other factors potentially contributing to taste and odor problems in domestic wells and whether or not these have changed over time. Water quality in domestic wells is being impaired, at least in part, by naturally-occurring dissolved inorganic ions and bacteria that affect taste and odor (see Table 11 in URS Phase II Report). As shown in Figures 3 and 4, most shallow groundwater exceeds secondary drinking water quality criteria for total dissolved solids (TDS) and sulfate. These standards (500 mg/L and 250 mg/L, respectively) are non-enforceable guidelines regarding contaminants that may cause aesthetic effects (such as taste, odor, or color). The high concentrations of TDS and sulfate are consistent with other studies in Fremont County that discuss a similar natural quality of groundwater resources (USGS, 1995; USGS, 1996; WWDC, 2011). They are also consistent with specific conductance data from the U.S. Geologic Survey's NWIS and NURE data sets (USGS, 2012a & 2012b).

Based on USGS water quality samples from the Wind River formation (USGS, 2012a), the concentrations of major ions have not changed over time. This is neither consistent with hydraulic fracturing as the source of well-impairing constituents, nor as a significant factor in overall groundwater composition. A comparison between water quality from EPA's Pavillion Area Study and historical data collected by the U.S. Geological Survey (USGS, 2012a) prior to extensive natural gas production activities is also included in Figures 3 and 4. Figure 3 illustrates the similarity between TDS data from the 1940s to the present. As shown in Figure 4, reported sulfate concentrations were generally higher for the period 1948-1960 than the most recent period of time (2000-present; USGS 2012a). Also, a Durov diagram of this same data (Figure 5) illustrates that the overall water chemistry of shallow groundwater has not changed (symbols representing each time period generally overlap one another in the compositional fields shown in the diagram). Therefore, an increase in total ion abundance over time cannot be demonstrated.

Chloride is an important diagnostic compound associated with deep produced water chloride (Benko and Drewes, 2008). It occurs at low concentrations in shallow domestic wells (Figure 6). As shown in Figures 5 and 6, MW02 and produced water are characterized by high levels of chloride that distinguish it from all shallow groundwater. The relatively low chloride concentrations in shallow domestic wells have not changed over time, suggesting no observable influence from deep groundwater that might have been mobilized with hydraulic fracturing fluids.

2.2 Depths and Locations of Wells MW01 and MW02

The EPA's Pavillion investigation was initiated in response to complaints by domestic well owners regarding objectionable taste and odor problems. The Draft Report, however, provides insufficient information on the location or history of these complaints to understand their context within the results presented. In siting monitoring wells MW01 and MW02, EPA seems to have been pursuing a potential source of deep contamination that could be associated with hydraulic fracturing near domestic wells on the Locker and Randall properties (GWERD QAPP, 2011). If so, this should have been justified and clarified through an illustrated conceptual model including maps of these smaller study areas, a full presentation of the domestic well results, and a detailed narrative of their history, including a review of historical water quality.

EPA's failure to present and illustrate a rationale for the placement of the deep monitoring wells results in the failure to address some key issues associated with them. Specifically, while both monitoring wells are located near producing gas wells, they are also located such that impacts from hydrocarbons, whether naturally occurring or due to gas production activities, would be maximized.

- The monitoring wells are situated on the structural apex of the Wind River-Fort Union dome (Mueller, 1989). Migration of methane is enhanced by naturally occurring bedrock fractures, which would be more abundant in an area of tensional stress such as a dome or anticlinal feature. As noted by Johnson et al. (2007), "there is good evidence that mature

gases from deep sources migrated into units as young as the Eocene Wind River Formation where overlying units are fractured...";

- The monitoring wells are located in areas where gas shows shallower than 1,000 feet bgs have previously been interpreted from electric log analyses (Figure 7) (Likwartz, 2007; Schmit, 2010); and
- The monitoring wells are located in areas where gas shows have been observed in well perforations at shallow depths. For example, in Tribal Pavillion 44-3 (API# 49-13-21906, located ¼ mile north of MW01), one perforation at 699-711 feet showed gas during initial flow testing. These perforations were subsequently cemented shut (squeezed) shortly after the flow testing. (WOGCC website sundry notices, file *1321906008/11.pdf*).

MW01 is screened at a depth of 765-785 feet bgs, deeper than the shallowest gas shows in well 44-3. It is also deeper than the shallowest gas shows interpreted from electrical logs for all the gas production wells within ¼ mile of the monitoring well. Similarly, MW02, which is screened from 960-980 feet bgs, is within ½ mile of five gas wells where electric log interpretations suggest the presence of natural gas at depths less than 1000 feet bgs. It is also less than ½ mile from Tribal Pavillion 42X-11 (20442) which produces gas from perforations in the Wind River formation at depths as shallow as 1,263 feet bgs.

Despite EPA's assertion that well "MW01 ... is screened at a depth ... typical of deeper domestic wells in the area" (p. xiii and 29), it is in fact screened deeper than all, or almost all, of the domestic wells in the Pavillion area (Wyoming State Engineer's Office (WSEO), 2012). EPA's reported depth of 800 feet for domestic well PGDW25 could not be independently confirmed from the WSEO database, nor is it consistent with the QAPP (GWERD, 2011), both of which cite a maximum reported depth of 750 feet.

Based on this information, EPA wells MW01 and MW02 were drilled to unusual depths for water supply purposes in the Pavillion area and may be screened within shallow non-economic natural gas-bearing sandstone lenses. EPA may have evaluated some of this information prior to well installation and completion of the Draft Report, however, they provide no substantive evaluation of interplay between regional petroleum geology, local hydrogeology and the monitoring well installation.

2.3 Construction, Development and Sampling of Wells MW01 and MW02

The Draft Report discusses the construction, development, and sampling of MW01 and MW02. EPA also notes precautions taken to protect the wells from shallow contamination and attempts to show that the additives used in the drilling and development process would not cause impacts that could be confused with hydraulic fracturing (pages 5-8). The report, however, does not describe some important complications that occurred in the field with the well construction, development, and sampling process.

Both monitoring wells were constructed in 9 7/8-inch-diameter boreholes using 4-inch-diameter wire-wrapped stainless steel screen and low carbon steel casing. The well screens

included 8 ½-inch-diameter, pre-packed filter sand assemblies with sand baskets welded directly to the top of them.

Based on the information provided by EPA [2], it is clear the samples collected in April 2011 do not unambiguously characterize the water quality for either MW01 or MW02. Complications with well construction, development, and sampling likely had significant consequences on the reported chemistry of the water quality samples from the wells. For an effective case to be made for any hydrogeologic scenario, additional pumping (i.e., development) and sampling of the monitoring wells is first necessary.

2.3.1 Poor Isolation of Cement Grout from the Well Screens

Cement-based grouts are known to have a high pH that may impact water quality in contact with them. Consequently, wells are generally built in such a way that grouts are isolated from the screen interval. Failure to do so could cause a number of sampling issues including high turbidity and high pH in samples.

- MW01 was drilled to a total depth (TD) of 985 feet bgs and then backfilled with cement grout to a depth of 797 feet bgs.[3] The hole was left open for the 12 feet between the top of cement and the bottom of the well screen. Mud and cuttings were circulated out of the hole prior the emplacement of the well screen, leaving the space between the top of cement and bottom of the screen largely devoid of solids (Shaw field notes for August 5, 2010). This construction may have allowed drilling mud and additives and the curing cement beneath the well screen to affect the quality of the water during sampling (especially for the Phase III sampling event).
- In MW01, cement grout was emplaced through a tremie pipe directly onto the sand basket welded to the top of the well screen because the driller indicated it would not be advisable to try to emplace sand prior to grouting the well (Shaw field notes for August 5, 2010). In addition to the cement grout being in direct contact with the water in the screened interval of the well, it is likely that some grout escaped or was washed around the sand basket into the annular space between the well screen and the borehole.
- In MW02, even though Draft Report Figure 6b indicates that the borehole is filled with cuttings that have settled on the bottom of the hole from 997 to 980 feet bgs, when the screen and casing were installed, mud and cuttings were first circulated out of the borehole while the bit was reportedly on the bottom of the hole (Shaw field notes for June 27, 2010). While it is possible that some drill cuttings might have settled in the borehole below the screen, no measurements are reported that confirm the depth to the top of cuttings. It is likely that an unknown quantity of cement grout, drilling mud and other additives are present in the annulus beneath the screen and could potentially impact water quality in the well.
- In MW02, the first attempt to emplace sand on the sand basket welded to the top of the screen was unsuccessful. On June 27, 2010, 15 hours after mobilizing to the site for the

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[2] Primarily from the Shaw Environmental field notes and Boart Longyear driller's notes provided on the EPA Pavillion Draft Report supplemental data webpage.

[3] The backfill depth was not 785 feet bgs as indicated on Figure 6a of the Draft Report.

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day, the driller added 100 lbs. of sand followed by 30 gallons of cement grout to a 2-inch tremie pipe placed directly on the sand basket (Shaw field notes). The drillers spent the following two days trying to unstick the tremie pipe (at 900 feet where it had been left on June 27), repairing broken equipment, and ultimately replacing the clogged tremie pipe (Shaw field notes, June 29, 2010).

On June 30, 2010, in a second attempt to place sand above the sand basket in MW02, the tremie pipe was advanced to 958 feet bgs (2 feet above the sand basket; Shaw field notes). This suggests that a significant quantity of cement from the first attempt to build the well made its way onto and around the sand basket. It is possible that much of this cement settled in the borehole below the well screen, and/or in the annular space between the well screen and the borehole wall. This could have affected both the permeability of the screened interval and the chemistry of the water sampled from the well in both the Phase III and Phase IV sampling.

2.3.2 Grout Invasion and Well Development

Grout invasion into the screen area can substantially alter the ability of a well to collect water from the intended depth interval. During sampling via low-flow pumping (as was used in the Pavillion deep wells), the intent is to collect water that flows from the aquifer, through the screen into the sampling device. If the screen is clogged with grout, water collected during sampling may instead be derived from inside the borehole, resulting in samples that do not meaningfully represent the aquifer.

- According to Shaw field notes, the development of MW02 was initiated on July 14, 2010, with airlifting of drilling mud out of the well. After airlifting, the well was left dry. When 700 gallons of water mixed with Aqua-Clear were pumped into the well the following morning, the well filled entirely, indicating that little water had entered the well overnight. The following morning (July 16) the depth to fluid in the well was measured at 17.6 feet indicating that approximately 11.5 gallons of water/fluid had been lost from the well. Several methods were used to try to develop the well over the next 10 days and in that time the screened interval was opened sufficiently to allow the entry of some high turbidity fluids and some methane gas (Shaw field notes, July 17-26).

  Development activities were suspended on July 27 after almost two weeks of efforts (Shaw field notes). Subsequent measurements from MW02 indicated that the well was making gas, but that groundwater recharge was very slow.

  Final development efforts in MW02 were conducted from September 9 to 11, 2010, by pumping and injecting water and surging the well (Shaw field notes). The last pumping performed during this phase of development was after 200 gallons of water were added to the well after it had been pumped dry. Pumping was terminated when the water level was 944 feet below the top of casing, meaning that 36 feet of imported water remained in the well at the end of development.

- Field notes for July 21, 2010 provide another indication that drilling mud/additives and grout contamination were issues in MW02. At that time, mechanical bailing had been underway for a day, but the well was still capable of producing very little water. Notes for that day indicated "DTW = 927.7 ft. pH still high 11.23." (There are no earlier

references to pH readings in Shaw's field notes.) Two hours later turbidity is reported as "...999 NTU. Brown." The high pH and high turbidity water strongly suggest the influence of cement grout and drilling mud and other additives on the chemistry of the water.

2.3.3 Phase III and Phase IV Deep Monitoring Well Sampling

There are several problematic aspects regarding the sample collection, especially as it bears on the source of the water sampled.[4] Our calculations suggest that a significant part of the water sampled in Phases III and IV was derived not from the aquifer, but from water introduced into the well during development, and is therefore not representative of the formation.

- The GWERD QAPP (p. 13) specifies that low-flow sampling be used to sample the deep monitoring wells, and that water level measurements be collected at minimum of every ten minutes during purging to ensure an appropriate, stabilized drawdown. There is no documentation provided to indicate that these guidelines were followed for the Phase III sampling. During the Phase IV sampling of MW01, drawdown during purging of well MW01 was more than 100 feet, yet the field crew did not respond for thirty minutes, at which point the water level rebounded by approximately 60 feet (pages 11-12).
- For MW02, both the Draft Report and the Technical System Audit Report (Neptune and Company, 2010) indicate that the water levels in MW-02 could not be monitored during sampling, and the available field notes do not indicate pre- and post-sampling water levels. The inability to measure water levels during purging is inconsistent with the QAPP (also see USEPA Region 1 Procedures for Low-Stress Sampling (EPA Region 1, 2010)), and indicates that there is no method by which the success of the low-flow purging could be determined. Failure to properly follow the purge procedures can result in samples that include a significant fraction of casing storage rather than formation water.
- Further, as it relates to low-flow sampling, it is unclear why the intake levels of the pumps used to purge and sample wells MW01 and MW02 were not placed within the screened intervals of the wells, as is specified in low-flow sampling guidance documents (e.g. Puls and Barcelona, 1996; EPA, 1998; ASTM, 2002).
- Calculations of water volumes removed from wells MW01 and MW02 suggest a significant contribution of borehole storage. Based upon the likely static water levels in these wells prior to the start of Phase III sampling, there were approximately 1,390 liters of water in the casing above the screen in MW01 and 1,720 liters above the screen in MW02.[5] Water levels, pump depths, and specific pump rates were not provided for the Phase III sampling. However, given the modest purge volumes relative to casing

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[4] There are limited field notes available for Phase III and Phase IV groundwater sampling and the information provided in the Draft Report is not sufficient to verify reliability of the field procedures. Phase III field purging logs (flow-cell logs) were provided by USEPA on January 31, 2012, but these constitute an incomplete record of field sampling activities. Further, the October 2011 log for Well MW02 indicates that the record is "continued on [the] back" of the page; however, that page was not provided in EPA documents released on January 31, 2012.

[5] Static water levels in MW01 and MW02 in April 2011 prior to the Phase IV purging were 200 and 264 feet below the top of casing, respectively. We have assumed that static levels were similar in October 2010 to their levels prior to the Phase IV Sampling

volumes and the likelihood that pump rates were high enough to draw down the water levels, it is probable that the Phase III samples contain water from casing storage.

- For MW02 this would mean that sampled water was derived from casing storage, and was also, in part, water that had been introduced into the well during the final development on September 11, 2010. The water sampled probably reflects both an imported source and contact with cement grout and drilling mud and other additives introduced into the well during construction and development.
- For MW01, the high pH and elevated potassium concentration in the Phase III samples and the difference from Phase IV sampling, suggest that a similar case may be hypothesized for the first sample from that well.

- The Draft Report indicates that during the Phase IV sampling approximately 1,117 liters of water was purged from well MW01. Since the total borehole volume in that well is greater (~1,390 liters), and because substantial drawdown during purging is documented, there may have been measureable influence by wellbore water that likely had been exposed to curing cement grout and other additives.

- It is also likely that a significant amount of the Phase IV water sampled from MW02 came from casing storage. Because the well exhibits a poor specific capacity, at a flow rate of nearly 19 L/min (Draft Report, p. 12), significant drawdown would have occurred in the well throughout purging. Only 1,287 liters were purged prior to sampling, while the casing held 1,720 liters of water. Consequently, there would still have been considerable water from casing storage in the well when sampling was initiated.

- There was higher than anticipated turbidity identified in water collected from MW02 that has not been adequately explained and that probably affected water quality in that well. As discussed elsewhere, drilling mud/additives and cuttings and cement grout likely are trapped in the well screen and the annulus around the outside of the screen. It is possible that the high turbidity and the detections of certain compounds in this well may be attributed to the presence of these materials in the well. To the extent cuttings may have contributed to the higher turbidity in MW02, the cuttings may also be biasing high the concentrations of organic compounds due to adsorption to particulate matter.

- An additional indicator that the wells may not be providing solely formation water can be observed in the changes in $\delta^{18}O$ and $\delta^{2}H$ of water in both MW01 and MW02. Scrutiny of Draft Report Figure 16 and Table A3c shows that there is an error in the Figure. As shown in Figure 8 (this Report), when the correct Phase III $\delta^{18}O$ and $\delta^{2}H$ results for MW01 and MW02 are plotted, changes in the isotopic composition of the water between sample events for each well are clear. The degree and directionality of the changes suggests that source water in the wells varied between the sampling rounds. Because there are only two samples from each well to date, the continuing effect of this contamination cannot be determined.

2.4 Evaluation of Geochemical Results

2.4.1 Methane and Other Light Hydrocarbons

Methane and C2-C6+alkane hydrocarbons (ethane, propane, butanes, n-pentane, hexane+) were detected in several domestic wells as well as in EPA's deep monitoring wells and EPA's samples from the shallow VRP monitoring wells (Figure 2). For all wells except the deep monitoring wells, the methane concentrations were less than 1 ppm (1,000 ppb) in water. These concentrations are well below both the solubility of methane in water (approximately 28 ppm).

As indicated in the Draft Report's Figure 18, for the samples where sufficient methane was present to measure ^{13}C and D isotopes, the isotopic signatures suggest a thermogenic source for the gas, with it having undergone varying amounts of oxidative degradation, depending on the location of the sample.[6] Gas samples from MW01 and MW02, and the comparison of ^{13}C to C1/(C2+C3) for the two wells indicate the gas is similar to what might be expected from Wind River or Fort Union gas wells in the area. The gases from domestic well PGDW20 show a moderate amount of oxidation, while the gases from PGDW30 and PGDW32 are less depleted in heavier carbon and hydrogen isotopes and more depleted in C2 and C3 hydrocarbons, indicating greater migration/degradation or a different gas source (see Appendix C).

2.4.2 Analysis of DRO and GRO

EPA's reporting of DRO and GRO results is problematic. GRO and DRO are multi-peak response mixtures containing hundreds of compounds, and the data reported do not provide sufficient information to interpret the data. There are a number of distinct issues associated with the DRO and GRO results. At the very least, EPA should perform a complete data validation on these results and provide appropriate data qualifiers to assist in interpretation. The key issues are as follows:

- Chromatograms for DRO and GRO results indicate that few of the samples show a good match with GRO and DRO standards, making the quantification of these results questionable;[7]
- Characteristic water-soluble compounds of gasoline and diesel (BTEX) are generally not present in the samples with GRO and DRO detections;
- BTEX compounds and DRO occur within a number of sample blanks at levels that would cause the results to be flagged as "non-detect" with appropriate data validation; and

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[6] Table 14 of the Phase II report provides several ^{13}C and D isotope results: the results, however, are quite different for the two domestic wells where results overlap and have results from gas wells that are not as depleted in ^{13}C as would be expected. It is assumed that EPA has rejected these results although there is no indication that this is the case.

For comparative purposes it would have been valuable to have isotope data from the shallow monitoring wells. The failure to conduct these analyses is somewhat puzzling given that EPA's investigation in the Pavillion area originally was focused on the possible connection between surface contamination sources and the domestic wells.

[7] EPA has not provided sufficient information to determine how quantification was achieved, and to determine the physical meaning of these results.

- It is not clear if the GRO analyses were completed using acid-preserved or unpreserved samples. Nor is it clear if the samples used for DRO analyses were subjected to silica gel column cleanup to remove potential biogenic interferences that may be present. If this cleanup is not completed, analyses of DRO often exhibit a high bias or are false positives.

EPA does state on page 36 that "detection of gasoline range organics does not infer the use of gasoline for hydraulic fracturing." But, this limited statement misses the greater point that EPA has not identified what the organic chromatogram peaks in the DRO and GRO ranges actually represent. EPA has not eliminated the possibility that these are naturally occurring organic compounds. Consequently, the use of the phrases "diesel-range organics" and "gasoline-range organics" throughout the report is misleading, as it implies the presence of manufactured petroleum hydrocarbons, when that has not been demonstrated. EPA should provide all data required to recalculate the results reported. Advanced chemical fingerprinting (ACF) analytical methods should be considered to verify the absence and/or presence of petroleum hydrocarbon compounds.

2.4.3 Gasoline Range Organics (GRO)

During Phases I and II, GRO was primarily detected in groundwater samples associated with the shallow monitoring wells at pits; concentrations in these wells ranged from hundreds to thousands of ug/L. GRO was detected in only three domestic wells (PGDW05, PGDW30, and PGDW32), at concentrations lower than 50 ug/L.

For all domestic wells, evaluation of chromatograms indicates a poor match to standard, and therefore a potentially erroneous quantification. In addition, GRO constituent compounds that should be detected in the volatile organic compound (VOC) analyses are widely not present in the domestic well samples. If GRO were present, then benzene, toluene, ethylbenzene and xylenes (BTEX) and other related petroleum hydrocarbon VOCs would be reported as detected in VOC analyses completed using gas chromatography/mass spectrometry (GC/MS).[8] Consequently, the physical significance of the GRO results and their quantification are suspect in these domestic well samples.

In Phase III, TPH as gasoline was reported as detected in Sample MW01 at 389 ug/L. If GRO compounds were present, then BTEX and other gasoline-related components should have been detected in the VOC analyses by GC/MS. Only toluene, however, was detected (as a false positive) at a low concentration. Review of the corresponding VOC data shows that toluene was reported as detected in the field-, trip-, and equipment rinsate-blanks associated with this sample. Following data validation protocols, all toluene results at a concentration of ≤2.7 ug/L should be restated as undetected (U). Taking this into account, BTEX and other VOCs cannot be considered as detected in MW01 during Phase III, and the presence of GRO (as gasoline) is unlikely.

In Phase IV, TPH as gasoline was reported as detected in Sample MW01 at 592 ug/L. Review of the corresponding VOC data shows toluene and m, p-xylenes. In the two field blanks, however, m, p-xylene was also detected at 0.690 ug/L and 0.700 ug/L. After taking into account

[8] The relatively low reported concentrations of GRO could complicate such detections in some samples.

contribution of VOC due to blank contamination, only toluene would be considered as present in MW01 during Phase IV and there is no indication that GRO (as gasoline) is present.

The reported detection of TPH as gasoline in MW02 during the Phase III and IV investigations appears to be representative of a gasoline-range hydrocarbon compound and the chromatographic result is supported by the VOC by GC/MS results. A thorough review should be completed for all of the qualitative and quantitative data used by the laboratory for the TPH as gasoline analysis.

2.4.4 Diesel Range Organics (DRO)

As with the GRO, the highest concentrations reported for DRO results were in the shallow pit monitoring wells (up to 62,100 ug/L). Lower concentrations (mostly less than 100 ug/L) were reported for 18 domestic well samples and one municipal well sample.[9] Intermediate concentrations were reported for the deep monitoring wells MW01 and MW02.

The quantification of DRO is suspect in most samples based on review of the sample chromatograms. There is a poor match to the diesel #2 standard used, and early eluting peaks not indicative of a diesel fuel product were primarily used for both qualitative and quantitative purposes.[10] There is also a lack of agreement to other supporting data (e.g., analyses for semivolatile organic compounds (SVOCs) using GC/MS). The results also likely exhibit a high bias due to inclusion of non-petroleum related compounds (such as unidentified chromatographic peaks and plant waxes of likely terrigenous origin. Because of the poor match to standard, and insufficient supporting data to understand how these results were quantified, these DRO results provide only qualitative information. It is likely that many of the low detections of DRO reported for the domestic wells in the Phase II investigation represent false positive values.

While a fuel product may be present in the Phase II samples, DRO was also reported as detected in the associated field blank at 26.5 ug/L. Therefore if these data were validated following guidance specified USEPA functional guidelines (U.S. EPA 2008), the results reported for PGMW01, PGMW02, and PGMW03 would be restated as undetected (U) because the concentrations prior to adjustment of the dilution factors were ≤5 times the concentration found in the field blank.

DRO was reported as detected in MW01 at 634 ug/L during the Phase III investigation and at 924 ug/L during the Phase IV investigation. For MW02 in the Phase III investigation, DRO was reported as detected at 1,440 ug/L and in the Phase IV investigation at 4,050 ug/L (and 4,200 ug/L in the duplicate sample). The DRO (as a petroleum product) detections are suspect in these samples because there is a poor match with the diesel #2 standard and there were many early eluting peaks that are not indicative of a diesel-range fuel product that were used for both

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[9] Reported DRO results exceeded 100 ug/l for four of the domestic well samples. In all of these wells, DRO concentrations were, however, substantially lower in other samples. For example, concentrations dropped by more than 50% from Phase II to Phase IV for PGDW41 (479 to 132 ug/L) and for PGDW49 (130 to 59.1 ug/L). The reported concentration in PGDW22 varied from 27.1 ug/L in Phase I to 154 ug/L in Phase II.

[10] The chromatogram for Sample PGDW30, however, may be representative of mineral spirits, stoddard solvent, or other similar type petroleum hydrocarbon; the laboratory annotated this chromatogram with the phrase "early diesel?". Residual range oil product eluting after the DRO range may possibly be present in some samples (e.g., PGDW05). The chromatograms of other samples (e.g., the trap sample) are indicative of alkanes representative of plant waxes of likely terrigenous origin.

qualitative and quantitative purposes. There were a few chromatographic peaks within the applicable carbon range, but the fingerprint did not appear to be that of an unweathered or weathered diesel fuel product.

2.4.5 Analysis of Glycol

EPA's reporting of glycol detections in domestic wells is misleading. On page 27 of the Draft Report, EPA states that the detection of glycols in several samples analyzed using a GC/FID technique (e.g. SW-846 Method) were likely reported as false positives. The Agency further states the glycol detections could not be confirmed using a liquid chromatography with tandem mass spectroscopy analysis.[11] It is well established that analysis by MS/MS is a significantly more accurate analytical technique and subject to fewer interferences than a GC/FID analytical method. As such, the confirmatory non-detected results should be used for interpretative purposes and not the GC/FID results for the domestic wells.

In contrast, the glycol analyses for the deep monitoring wells conducted during Phase IV (by HPLC/MS/MS) appear to be acceptable and these data are of generally good quality. These data tentatively indicate that glycol target compounds are present in MW01 and MW02. These analyses were, however, completed using a non-peer reviewed method on samples that may have been compromised by contact with cement during purging/sampling (see Section 2.3).

It is important to note that glycols (including diethylene glycol) are components of widely used cement grinding aids that contribute to the fluidity of crushed cement powder (Ervanne and Hakanen, 2007; Grace Construction Products, pers. comm., 2012; Maslow, 1974; Strohman, 2002).[12] Experiments on glycol-containing admixtures suggest that such compounds are mobile in aqueous solutions in contact with cement (Herterich et al., 2003). Consequently, the presence of glycols in the deep aquifer, rather than as an artifact of poor well construction, should be confirmed through additional sampling and analysis.

2.4.6 Other Qualified Data

EPA consistently uses qualified data in its interpretations, without addressing the significance of this qualification. This includes the use of sample results that should have been reported as non-detect due to blank contamination. Ultimately, this is a failure to use appropriate data validation. For example, there were detections of several target compounds (2-butanone, acetone, toluene) in blank water samples (method blanks, trip blanks, field blanks, and equipment rinsate banks), and if the data were subjected to an appropriate degree of data validation, many results reported as detected would be restated as undetected (U) because the concentrations found in the samples were ≤5 times or ≤10 times the concentrations found in the associated blanks. (In laboratory data validation, a ratio of ≤5 is typically applied to uncommon contaminants, whereas a ratio of ≤10 is used for common contaminants such as acetone for VOC analyses and phthalate compounds for SVOC analyses.) The affected results would then either

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[11] Referenced as GC/MS/MS in the report text.

[12] Glycols are also used in cement admixtures such as superplasticizers. The source of cement used to build wells MW01 and MW02 is not specified in EPA's field notes.

be restated as undetected (U) at the concentration found in the associated blank or at the concentration reported in the samples. Specific examples are provided in Appendix B.

EPA also acknowledges that several of the analytical method standard operating procedures (SOPs) that were used to complete chemical analyses were not official EPA methods, nor were they subject to required peer review (U.S. EPA, 2000a, 2002a). While the applicable methods may be capable of generating acceptable data, the use of non-EPA approved methods, coupled with the lack of appropriate (and required) peer review, may possibly bias or invalidate the affected data until they are subjected to a thorough review and are used by outside analytical laboratories. If a laboratory uses a nonstandard or unapproved method, EPA requires the data user to "provide method validation data to confirm that it will be adequate for the intended use of the data" (U.S. EPA, 2002b). Information that should be reported with the data would include "determination of detection limits, quantitation limits, typical recoveries, and analytical precision and bias" (U.S. EPA, 2002b). The evaluation of such data will "indicate the laboratory's ability to demonstrate control of the method and document the quality of the data obtained" (U.S. EPA, 2002b).

EPA also conducted an incomplete and undocumented analysis of monitoring well drilling fluid additives, and then used the results to contend that the additives were not impacting water quality in MW01 and MW02. For example, there are two unknown samples (i.e., PAV1, and PAV2) from the drilling additives study conducted after well completion (July 2011; see *SampleResults_8OA778SF_SS6163_23993_07-21-11_Headspace.pdf*). These samples are not described in the report, but have high concentrations of some organic compounds (TBA, alcohols, benzene, toluene) that EPA attributes to hydraulic fracturing fluids. In addition, EPA only conducted selected analyses on additive samples (Draft Report, Table 2). Chemical characterization of the dense soda ash, Quik Gel, and Quik-Trol Gold were not completed because "dissolved organic concentrations were low..." Nonetheless, analyses of the dense soda ash, Quik Gel, and Quik-Trol Gold should have been completed for all target organic compounds and all additives should have been analyzed for SVOCs, GRO, and DRO.

2.5 EPA's Interpretation of MW01 and MW02 Analytical Data

While it is unlikely that the analytical results from either MW01 or MW02 provide representative results of the formation water for the screened intervals of the wells, EPA's conclusions in the Draft Report require that they be addressed directly. This section addresses a number of issues with EPA's laboratory data and interpretation thereof, and provides additional detail related to the sample results for MW01 and MW02. Each of these conclusions is also summarized in the final sections of this report. Table 2 presents a general summary (based upon Table 3 in the Draft Report) of the analytical results and their occurrence.

2.5.1 Alkaline pH Values

EPA wrongly discounted the effect of well construction materials on alkaline pH in MW01 and MW02. Furthermore, its argument that measured pH greater than 11 is attributable to potassium hydroxide (KOH) potentially used in hydraulic fracturing fluids is unconvincing.

First, drilling mud, additives and cement grout likely present in MW01 and MW02 below the top of the well screens contain materials with pH values greater than 11. This includes soda ash (with a reported pH of 11.5) and cement (with a pH greater than 12). As discussed above, it

is likely that these materials were present within and adjacent to the filter pack and suspended during sampling, and thus contributed to the high turbidity of groundwater collected from these wells (particularly MW02). The known connection between drilling and grouting materials and alkaline groundwater pH is discussed in EPA's own cited reference (Gibb et al., 1987). A more recent case study illustrating the impact of cement-grout on well water pH (to values > 12) can be found in Mercer et al. (2007).

Despite the known presence of alkaline materials from well construction, EPA discounts the possibility that cement and/or other drilling and well completion additives are the cause of the high pH values observed in MW01 and MW02. For example, they reference a qualified statement in Gibb et al. (1987) that elevated pH caused by cement is on the order of 10-11. In fact, the author of that article correctly states that pH ultimately depends on the grout used and residue present after development and purging. EPA also wrongly concludes that because groundwater is undersaturated with Portlandite cement, that cement cannot be the cause of the high pH in MW01 and MW02. In reality, pH values in the presence of cement-type phases can range from approximately 9.0 to 12.8, depending on the amount of dissolution that occurs (Berner, 1992). Undersaturation caused by incomplete dissolution and/or dilution, will produce pH values below 12.8, within the range of MW01 and MW02.

Additional evidence that alkaline pH may not be caused by hydraulic fracturing fluids includes the following:

- a pH of 11.23 in MW01 was recorded in field logs during well development during a time when drilling mud was being recovered by the bailer (Shaw field notes, July 21, 2010);
- the pH in produced water from the formation where hydraulic fracturing fluids were actually injected is relatively low (pH = 5.90 to 8.9) (WOGCC website produced water sample results obtained at shttp://wogcc.state.wy.us/warchoiceMenu.cfmee); and
- there is a lack of evidence that KOH was actually used in hydraulic fracturing fluids in the Pavillion Area; and the stated use of KOH is to buffer pH to maintain the effectiveness of crosslinkers. It is not used as a strong base to generate hyperalkaline groundwater pH.

2.5.2 Potassium and Chloride Concentrations

EPA did not adequately address alternative explanations for elevated potassium and chloride concentrations in deep monitoring wells (particularly in MW02). These include dissolution of cement grout and/or the presence of deeper groundwater with ionic compositions that differ from shallow groundwater found in the Wind River aquifer.

Potassium (like hydroxide alkalinity) is likely related to the dissolution of cement-type phases. As discussed in Berner (1992) and Steefel and Lichtner (1994), cement dissolves incongruently, with KOH components dissolving first. Evidence for cement impacting groundwater quality is the high turbidity and pH of groundwater from MW01 and MW02 (as discussed above). Incomplete purging prior to sampling, as likely happened in the deep monitoring wells, can also impact water quality (Gibb et al., 1987).

A plausible explanation for the observed chloride is that MW02 is screened in or close to the natural gas producing units where chloride is naturally elevated. As shown in Figure 6, chloride concentrations in MW02 are more similar to produced water in the Pavillion Area than the shallow groundwater. This result is consistent with chloride generally being the dominant anion in natural gas formations (Benko and Drewes, 2008) and with Wind River formation produced water samples obtained on the WOGCC website (http://wogcc.state.wy.us).

Although EPA cites the reported uses of KOH, potassium chloride, and potassium metaborate as evidence of impacts of hydraulic fracturing fluids, they do not provide documentation that these constituents were specifically used at Pavillion, or adequately explain how they would be present at the levels observed in the deep monitoring wells. For example, Figure 9 shows that there is no significant difference in boron concentrations between MW01, MW02, and groundwater sampled in the Pavillion Area prior to hydraulic fracturing. This result is inconsistent with potassium concentrations being influenced by the potential use of potassium metaborate. Similarly, were KCl (also used in gas well development) the primary source of K and Cl seen in MW01 and MW02, the ratios of these compounds would be different than actually observed.

2.5.3 Petroleum Hydrocarbon Concentrations

The Draft Report concludes that constituents associated with hydraulic fracturing have been released into the Wind River drinking water aquifer at depths above the current production zone based on the presence of petroleum hydrocarbons in MW01 and MW02. EPA specifically contends that the following reported compounds are evidence of hydraulic fracturing fluids (pg. 35-36):

- Gasoline-range organics in MW01 and MW02 at 592 and 3,710 ug/L, respectively;
- Diesel-range organics in MW01 and MW02 at 924 and 4,050 ug/L respectively;
- Benzene, toluene, ethylbenzene, and xylenes (BTEX) in MW02 at concentrations of 246, 617, 67, and 750 ug/L, respectively;
- Trimethylbenzenes in MW02 at 105 ug/L; and
- Naphthalene in MW02 at 6 ug/L.

These conclusions are based on analytical data of questionable quality due to deep monitoring well drilling and construction complications, field/laboratory contamination, and misinterpreted chromatograms (see above). The deeper of the two wells (MW02) additionally exhibits characteristics of produced water from petroleum reservoirs in the Wind River basin. Although petroleum hydrocarbons occur in produced water, EPA did not consider how these natural occurrences may have affected the reported water composition. Tables 9 and 10 in the Phase II data report show the presence of all these compounds in Pavillion gas field produced waters.

2.5.4 Field/Laboratory Contamination

There was higher than anticipated turbidity identified in water collected from MW02 that is not adequately explained in the Draft Report. This elevated turbidity may be one reason for the

detection of higher concentrations of selected organic constituents than were found in other wells. These higher detected concentrations may be representative of constituents not in an aqueous phase, but partitioned to a solid phase (e.g., particulate matter). Evidence for the influence of particulate matter on petroleum hydrocarbon compounds is the detection of toluene and xylenes during Toxic Characteristic Leaching Procedure (TCLP) tests conducted on drilling mud and cuttings from the monitoring well.

As discussed above, there were also detections of several target compounds in many of the associated blank water samples (e.g., method blanks, trip blanks, field blanks, and equipment rinsate banks), and if the data were subjected to an appropriate degree of data validation, many results reported as detected would be restated as undetected (U).

2.5.5 Baseline Conditions

The presence of gasoline range hydrocarbons in MW01 and MW02 is not sufficient evidence to indicate the impact of hydraulic fracturing fluids. EPA rightly concludes that "detection of gasoline range organics does not infer the use of gasoline for hydraulic fracturing." Gasoline range hydrocarbons are expected to be naturally present in groundwater in the Pavillion Area, particularly at depths associated with oil and gas deposits. For example, BTEX compounds are ubiquitous in produced water, as evidenced by a review of produced water data that included the Wind River Basin (Benko and Drewes, 2008). Additionally, C3-C10 range hydrocarbon fingerprint analyses conducted for the Phase II investigation (URS, 2010, Table 17) indicated the presence of BTEX compounds (but not naphthalene, a common component of hydraulic fracturing fluids) in petroleum liquids from three gas wells in the vicinity of the deep monitoring wells. Two of those samples, PGPP05 and PGPP06, were collected from wells where the most recent completion/recompletion activity is reported to have been prior to the year 2000 (Sundry Notices, WOGCC website). Finally, BTEX, naphthalene compounds, and other hydrocarbons are also present in groundwater adjacent to pits (KC Harvey, 2010a, 2010b, and 2010c; URS, 2010).

In order to make a determination as to what petroleum hydrocarbon concentrations might indicate impacts from hydraulic fracturing fluids, it would first be necessary to evaluate background. As per EPA guidelines (EPA, 1992a), Expanded Site Investigation (ESI) data collection for a ground water plume with no identifiable source must include background sampling. To date, background data have not been presented or analyzed for the Wind River formation horizons being monitored by MW01 and MW02.

2.5.6 Synthetic Organic Compounds

EPA concludes that several synthetic organic compounds are evidence of impacts of hydraulic fracturing fluids in deep monitoring wells; however, this conclusion is based on data of questionable quality for the reasons outlined above. As such, the conclusion is premature until it is shown that valid formation water samples have been collected from the wells, and until thorough data verification and validation review is completed.

There are also several issues related to the purported identification of isopropanol, tert-butyl alcohol, and other alcohol compounds in MW01 and MW02. These include the following:

- EPA acknowledges that several analytical method standard operating procedures (SOPs) that were used to complete some chemical analyses were not official EPA methods nor were they subject to required peer review (U.S. EPA,2000a, 2002a);
- Alcohol compounds were detected in drilling fluids in MW01 and MW02. Although EPA states that these concentrations are below those found in the monitoring wells, they also report high concentrations of alcohols from samples PAV1 and PAV2 in the drilling additive study (from July 2011). It is unclear what these samples represent, and therefore, not possible to fully evaluate EPA's conclusions regarding these organic compounds in MW01 and MW02; and
- Several organic compounds (acetone, toluene, and m & p xylene) were also reported from TCLP analysis of monitoring well cuttings (Draft Report, p. 7). To the extent cuttings are contributing to the observed turbidity in MW01 and MW02, they may also be biasing high the concentrations of organic compounds adsorbed to them.
- The confirmation of glycol detections in MW01 and MW02 requires further purging and sampling of these wells to conclusively determine that they were not impacted by cement additives or other extraneous sources.

2.5.7 Purported Breakdown Products of Organic Compounds

There are several issues related to EPA's conclusion that breakdown products of organic compounds are evidence of hydraulic fracturing fluids. EPA is factually correct that "natural breakdown products of organic contaminants like BTEX and glycols include acetate and benzoic acid." (p. 23). The cited compounds (benzoic acid, acetate, formate, lactate, and propionate), however, are naturally-occurring substances related to the breakdown of both petroleum hydrocarbons and natural organic matter (Cozzarelli et al., 1994; Jakobsen and Cold, 2007). As such, they may be ubiquitous in groundwater from gas-charged sandstones in the Wind River formation. EPA does not adequately address this natural source. [13]

EPA also states that the breakdown products of BTEX and glycols (acetate and benzoic acid) are "more enriched" in the shallower of the two the monitoring wells, suggesting and upward/lateral migration with natural degradation and accumulation of daughter products" (p. 23). There are several fundamental problems with this claim. Whereas it is again factually correct that under specific circumstances, the presence of acetate and benzoic may be due to the breakdown of BTEX and glycols, there is no evidence presented substantiating this breakdown pathway. Considering the need for confirmation of the glycol analytical methods, the inference that these results are breakdown products of glycols must be considered speculative at this point. Finally, EPA's provides no justification for asserting that concentration gradients can be discerned from wells MW01 and MW02, which are located nearly 7,400 feet apart.

[13] Formiate and acetate have also been cited as mobile components of cement additives in contact with aqueous solutions (Herterich et cl., 2003).

2.6 Number of Samples from Deep Wells

The collection of monitoring well samples and one field duplicate from two monitoring wells (i.e., MW01 and MW02) during only two sampling events is not sufficient to support EPA's conclusions. The lack of background or baseline data to compare to the current data sets also prevents meaningful conclusions from being drawn.

EPA's sampling is also inconsistent with its own guidance on sample number and representativeness. For example, according to EPA (2000b), the data quality objectives that should be considered in ESI studies include obtaining statistical significance of measured concentrations. If the stated goal is detection monitoring (e.g. EPA's RCRA Guidance, 2009), EPA notes that statisticians generally consider sample sizes of n <= 4 to be insufficient for good statistical analysis. EPA's reliance on two samples each from two sampling events is therefore insufficient. Also, according to EPA (1992a and 1992b), ESI data collection for a ground water plume with no identifiable source must include background sampling (with background being defined as water collected from the same aquifer and depth, where interconnected aquifers are not considered one aquifer). The analyses used by EPA in the Draft Report compare the deep monitoring wells with data from shallower domestic wells, rather than data from gas-producing horizons. It is not clear if this is the appropriate comparison for background purposes.

We note that in a similar, recent study, EPA apparently adopted more rigorous standards for its Hydraulic Fracturing Case Study in Bradford-Susquehanna Counties, Pennsylvania (U.S. EPA, 2011b).

2.7 Cement Bond Log Interpretations

In the Draft Report, EPA discusses the potential effects of uncemented wellbore intervals below surface casing and poor cement bonding as conduits for the migration of natural gas or hydraulic fracturing fluids. Pathways below approximately 400 to 600 feet may exist that allow enhanced hydraulic connections in the Wind River formation. This could include vertical migration along wellbores or horizontal migration within fractured sandstone intervals between gas wells (Cramer, 2011). There is good evidence for limitations in these sandstone pathways. The geology of the Wind River formation is characterized by isolated sand lenses (McGreevy, et al., 1969). In addition, WOGCC's 40-and 20- acre spacing orders for the Pavillion field (WOGCC Cause No. 1 Order No 1, Dockets 454-2000, October 11, 2000, and 276-2002, August 13, 2002) testify to the limited extent and interconnection of these lenses.

Anecdotal reports do exist, however, to suggest that such migration is possible. For example, there are reports that in December 2005 during the development of a water supply well located ½ mile east of MW01, a blowout occurred at a depth of 540 feet causing a reduction in gas production of an adjacent gas well (Lustgarden, 2011; GWERD QAPP, 2011). EPA has not, however, documented evidence to support impacts due to local connections between oil and gas activity and the Wind River Formation. EPA's discussion in the Draft Report (pages 27-30) is insufficient to demonstrate enhanced migration of natural gas and hydraulic fracturing fluids into the Wind River Formation aquifer. Additional testing, such as Bradenhead pressure tests, would be appropriate steps to assist in evaluating this potential migration pathway.

2.8 EPA's Conceptual Model for Contaminant Transport

EPA's Pavillion investigation and Draft Report have both been hampered by lack of a coherent model for contaminant fate and transport. The study area for this project encompasses nearly 40 square miles and includes both shallow and deep potential sources. The migration pathways for these contaminants are not identical, nor necessarily consistent across the entire study area. Yet, EPA has attempted to interpret the data with little specific reference to hydrogeology, locations of specific vertical migration pathways, or attempts to pair sources and receptors. A conceptual model (focused primarily on soil gas) is cited in GWERD QAPP (2011) but it is not carried over to the Draft Report. This QAPP (Revision 5) was apparently assembled in stages, with some parts (e.g. well construction diagrams) inserted into the document after a particular activity had already been completed. Revision 5 of the QAPP is dated June 2011, after completion of Phases III and IV. Earlier versions are not available for public review.

Also problematic is EPA's repeated assertion that meaningful concentration gradients can be discerned from concentrations in wells MW01 and MW02. These wells are located nearly 7,400 feet apart. The screened intervals of these two wells are approximately 200 feet apart. Consequently, the wells are 37 times further apart horizontally than they are vertically. There are several gas wells located between MW01 and MW02, and at least 4 domestic wells. Pits sampled in this study are located upgradient to sidegradient of both MW01 and MW02. Considering all these complexities, the large study area, the questionable wisdom of deriving trends from two data points, and the likely non-representativeness of the deep monitoring well samples, it is unwarranted to assume that concentration difference between these two wells can be attributed merely to differences in depth.

EPA states that "hydraulic gradients are currently undefined in the area of investigation." This is not strictly correct. Historic potentiometric maps do exist (e.g. Whitcomb and Lowry, 1968), and static water level data provided in USGS reports, the NWIS database, and the WSEO online database of permit information, can be used to constrain regional hydrogeology. Furthermore, site investigation reports for the VRP sites used by EPA in their study provide local depictions of groundwater gradients. If EPA believed these sources were inadequate, this should have been discussed and/or rectified with appropriate field measurements. Instead, the issue was not addressed.

Finally, EPA states in the Draft Report that "there are flowing conditions in a number of deep stock wells suggesting that upward gradients exist in the area of investigation." This may be true locally, but a review of the data sources cited above indicates that historic static water levels decreased with well depth, indicative of downward gradients. It seems appropriate than an investigation purporting to document migration of contaminants, EPA should have first evaluated whether downward or upward gradient existed in the immediate vicinity of the monitoring wells.

Section 3
Review of EPA's Conclusions in the Draft Report

EPA's conclusions are presented in Section 4.0 of the Draft Report. There are essentially three conclusions, with the final two requiring "multiple lines of reasoning approach common to complex scientific investigations" (page 33). Our review indicates that the last two conclusions cannot be supported by the data provided. The technical details associated with each "line of reasoning" are presented above, but we reiterate them here to illustrate issues with EPA's conclusions.

3.1 Conclusion 1: "...pits are a source of shallow groundwater contamination in the area of investigation ..." (p. 33)

The data provided by EPA, WOGCC, and WDEQ support this conclusion, and the need for further investigation. These investigations are continuing, under the oversight of the WDEQ VRP.

Nonetheless, it is important to note that none of the domestic wells tested in EPA's investigation show a clear impact from the pits. In fact, after completing the Phase I and II sampling of domestic wells, EPA was still unable to identify whether taste and odor problems in certain domestic wells were tied to any specific contaminants traceable to hydraulic fracturing or other hydrocarbon drilling- and production-related activities.

We do not disagree with this conclusion, but SSP&A believes that a more coherent study would have focused on (and clearly identified) a narrower study area where domestic well impacts were documented, and in which specific potential sources were identified and eliminated or confirmed in a systematic manner. Were such a study undertaken, EPA might not have failed to meet its original objectives.

3.2 Conclusion 2: "...constituents associated with hydraulic fracturing have been released into the Wind River drinking water aquifer at depths above the current production zone."(p. 33)

EPA provides seven "lines of evidence" to support this conclusion. Each is addressed separately below.

1. High pH Values

EPA concludes that high pH values in wells MW01 and MW02 are evidence of potassium hydroxide use during hydraulic fracturing operations, and dismisses the possibility that such pH values reflect the impact of well construction materials. In fact, mud and grout in MW01 and MW02 contained materials including soda ash (reported pH of 11.5) and cement (pH >12). It is likely that these materials were suspended during sampling, contributed to the high turbidity of groundwater and impacted the pH.

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2. Elevated Potassium and Chloride

EPA cites the elevated levels of chloride and potassium, relative to shallow groundwater as evidence for the impact of hydraulic fracturing fluids. Potassium in wells MW01 and MW02 is likely related to the dissolution of cement-type phases that dissolve incongruently, with KOH components dissolving first.

The elevated chloride in MW02 is most simply explained by the well's position close to the natural gas producing units in which chloride tends to be the dominant anion in natural gas formations.

3. Detection of Synthetic Organic Compounds

EPA cites detections of isopropanol, tert-butyl alcohol, diethylene glycol and triethylene glycol as evidence for potential contamination with surfactants, breakers, foaming agents, and solvents.

Detection of glycols in domestic well samples analyzed using a gas chromatography/flame ionization (GC/FID) technique, could not be confirmed with more accurate techniques, and therefore, should have been reported as non-detect for interpretive purposes. Detection of glycols in deep monitoring wells appears reliable, but requires additional confirmation due to the untested nature of the analytical methods and the potential impact of contact with cement phases (including glycol-bearing additives).

For the purported identification of isopropanol, tert-butyl alcohol, and other alcohol compounds, EPA failed to identify the nature/source of samples from the drilling additive study (July, 2011) in which similar compounds were detected, and which could have contaminated the wells. Finally, several organic compounds were reported in TCLP analysis of monitoring well cuttings which may have contributed to the concentrations of organic compounds reported.

4. Detection of Petroleum Hydrocarbons

EPA reports detections of BTEX, trimethylbenzenes, GRO and DRO as evidence for the impact of hydraulic fracturing fluids, yet also dismisses the possibility that liquid condensates in the Wind River and Fort Union formations could yield these aromatic and straight-chain hydrocarbons. EPA's own data are inconsistent with this analysis, however. Data in the Phase II data report shows the presence of all these compounds in Pavillion gas field produced waters. Consequently, it is premature to eliminate a natural origin for these compounds on the basis of two samples from each monitoring well.

5. Breakdown Products of Organic Compounds

Purported breakdown products of hydraulic fracturing fluids (benzoic acid, acetate, formate, lactate, and propionate) are also naturally-occurring substances related to the breakdown of both petroleum hydrocarbons and natural organic matter. Their presence does not necessarily indicate that the parent compounds are hydraulic fracturing fluids.

6. Sporadic Bonding outside Production Casing Directly above Intervals of Hydraulic Fracturing

Under certain conditions, the migration of hydraulic fracturing or oil field fluids through uncemented production casing or poorly cemented wellbores is a plausible migration

mechanism. EPA has not provided sufficient evidence to show that this has occurred and resulted in impacts to water supply wells in the Pavillion area, however. Furthermore, to date, there is no reliable evidence that such impacts have occurred to either MW01 or MW02. The bonding log examples provided by EPA in the Draft Report are not sufficient to tie specific sources, migration pathways and receptors into a coherent model of groundwater contamination.

7. Hydraulic Fracturing into Thin Discontinuous Sandstone Units

This "line of reasoning" addresses the lack of a regional geologic barrier to aqueous migration and the possibility of wellbore flow in Pavillion gas wells. EPA's reasoning is difficult to follow, however. For example, if there is "no lithologic barrier...to stop upward vertical migration of aqueous constituents..." [page 37], why must borehole flow be invoked elsewhere in the report as a transport mechanism? In the same paragraph, EPA cites "tortuous paths" within sand lenses as migration pathways. Yet these same tortuous paths would serve not just anthropogenic fluids but also natural liquids and gases including methane. As noted by Johnson and Rice (1993), vertical gas migration is believed to be a natural feature of the Wind River Basin.

3.3 Conclusion 3: "...data suggest that enhanced migration of gas has occurred to ground water at depths used for domestic water supply and to domestic wells." (p. 37)

EPA provides five lines of reasoning to support their conclusion that enhanced migration of gas, presumably due to gas drilling and production activities, has occurred and impacted the domestic water supply wells in the Pavillion area. Unfortunately, EPA has not attempted to define either baseline or background concentrations of methane that pre-dated hydraulic fracturing activities. Thus the notion that EPA can address "enhanced" migration of gas is not supported by any data.

To accept the EPA's conclusion, each of these lines of reasoning has alternate hypotheses that must first be rejected, at least in part. Specifically EPA must evaluate the following alternative hypotheses for which evidence has already been discussed:

- The formations screened in the deep monitoring wells are naturally gas charged;
- The methane detected in the domestic wells in the Pavillion area is naturally occurring due to the location of the wells over the structural apex of a formation that produces natural gas at relatively shallow depths;
- The highest methane concentrations at domestic well depths (e.g. PGDW30) result from localized activities unrelated to hydraulic fracturing. For example, migration of methane along uncemented casings may constitute an anthropogenic enhancement of gas migration, but would not necessarily indicate impacts due to hydraulic fracturing; and
- There are no differences in the water quality in the domestic wells in the Pavillion area that have occurred since the onset of significant natural gas production activities beginning in approximately 2000.

To date, EPA has not demonstrated that any of the above conditions can be rejected. Until a statistically significant number of representative samples have been collected from MW01 and MW02, no conclusions regarding water quality and the nature of the methane in

those wells can be made with any certainty. The inability to evaluate the deep monitoring wells affects the ability to make conclusions about the nature and source of methane in the water supply wells, especially as relates to drawing inferences on the nature and timing of potential methane invasion via wellbores or other pathways.

Correlation is not causation, and EPA has not provided a sufficient argument to show that the dissolved methane in any of the domestic wells is a response to hydraulic fracturing activities. Consistent with this conclusion, EPA's statement that the location of wells on the structural dome "would also facilitate enhanced gas migration" is simply a statement of the geologic conditions at the Pavillion field and cannot be considered proof that the existence of methane is due to hydraulic fracturing.

Finally, elevated concentrations of sulfate and total dissolved solids, which have notable impacts on aesthetic water quality characteristics, are common in many water supply wells in the area. As shown by USGS water sampling efforts conducted prior to 2000, these are not a new phenomenon. (This similarly applies to the presence of iron- or sulfur-reducing bacteria.) EPA's investigation of domestic water wells has not shown that changes were a response to gas production activities.

Section 4
Conclusions

Detailed discussions of many aspects of the Draft Report are provided above. The key conclusions that can be drawn from SSP&A's evaluation of the report are provided below.

- EPA's study design was not sufficient to gather the data, nor draw the conclusions it asserts. The investigation appears to have been completed without an adequate conceptual model of area hydrogeology and contaminant fate and transport. EPA has not provided sufficient data to distinguish between naturally occurring and anthropogenic occurrences of hydrocarbons, nor describe their source(s). Similarly, EPA's inferences regarding depth-related concentration gradients between MW01 and MW02 cannot be supported with the existing data. Overall, the study is not coherent as presented, and is insufficient to support its purported conclusions.
- Deep monitoring wells MW01 and MW02 were beset by well construction, development, and sampling problems that may have impacted or caused the presence of high pH, Cl, K, petroleum hydrocarbons and other organic compounds. Additional development (especially for MW02) and sampling of the wells will be necessary prior to drawing any conclusions regarding potential contamination in these wells. This sampling should encompass a minimum of four rounds for full parameter sets, but only after fully developing each well and ensuring that no interferences from construction or incomplete development are possible. Because the two existing data sets show significant variation, it is recommended that the wells be sampled for a restricted set of parameters until stability of the results—or a definitive trend—can be established during development.
- There are a number of issues with the laboratory methods employed by EPA, and their reporting. The quantification of DRO and GRO results is suspect for nearly all samples, and certain analytical methods remain untested. These should have been recognized and addressed prior to publication of this Draft Report. As it stands, much of the "significant" data is suspect either because of the information provided, and/or because of EPA's failure to provide all necessary backup for a full validation.
- All the "lines of evidence" EPA cites to support their conclusions can be adequately explained with alternative hypotheses addressing either natural background concentrations or sampling/analytical problems. EPA must more fully consider and test these alternate hypotheses before these conclusions will be fully supported.
- If EPA intends to continue with the investigation at Pavillion, a revised QAPP and Field Investigation Work Plan, approved by a qualified peer review committee, are required. A revised report should be prepared only after all the concerns highlighted herein have been addressed.

EPAPAV0050406

Section 5
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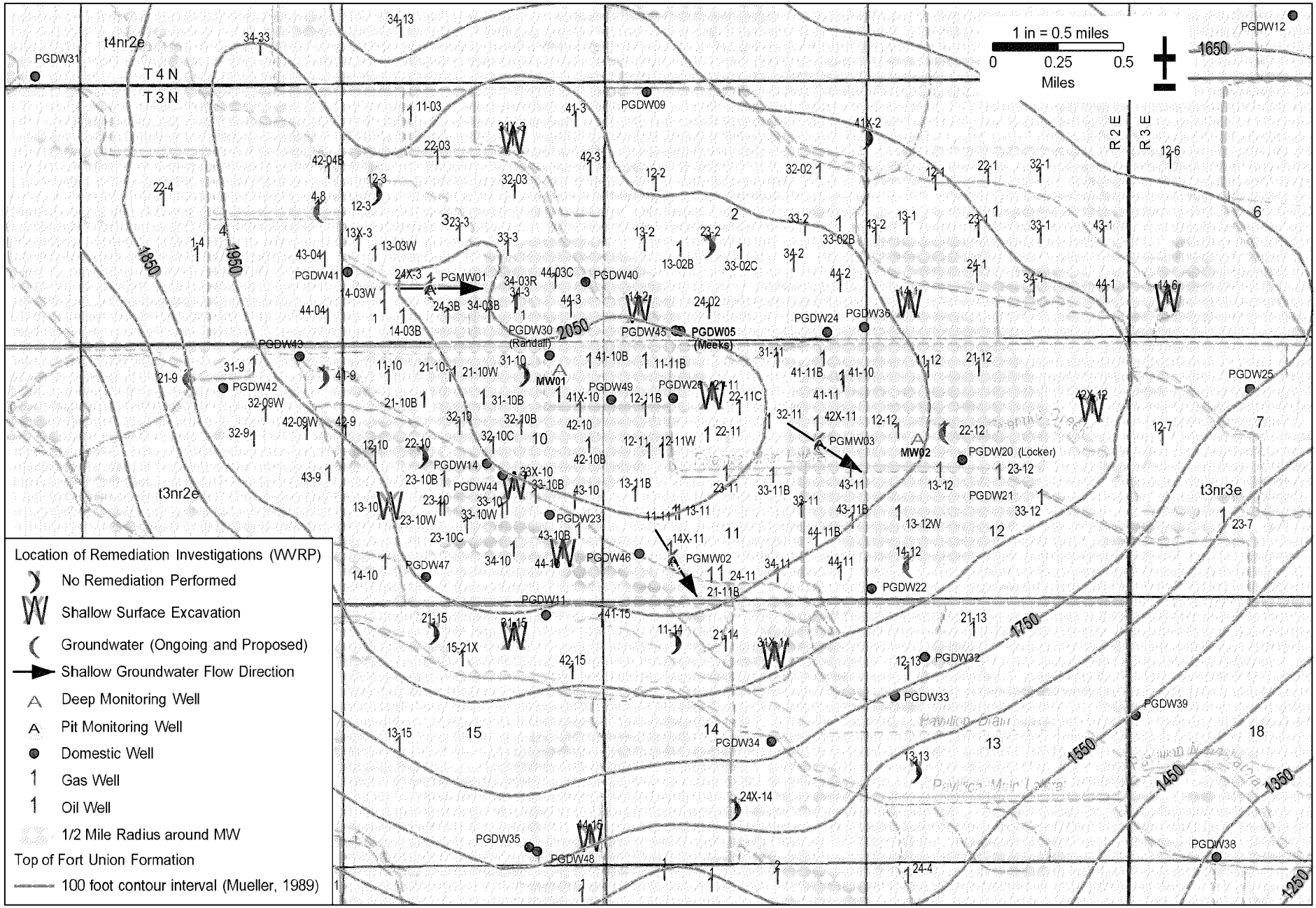

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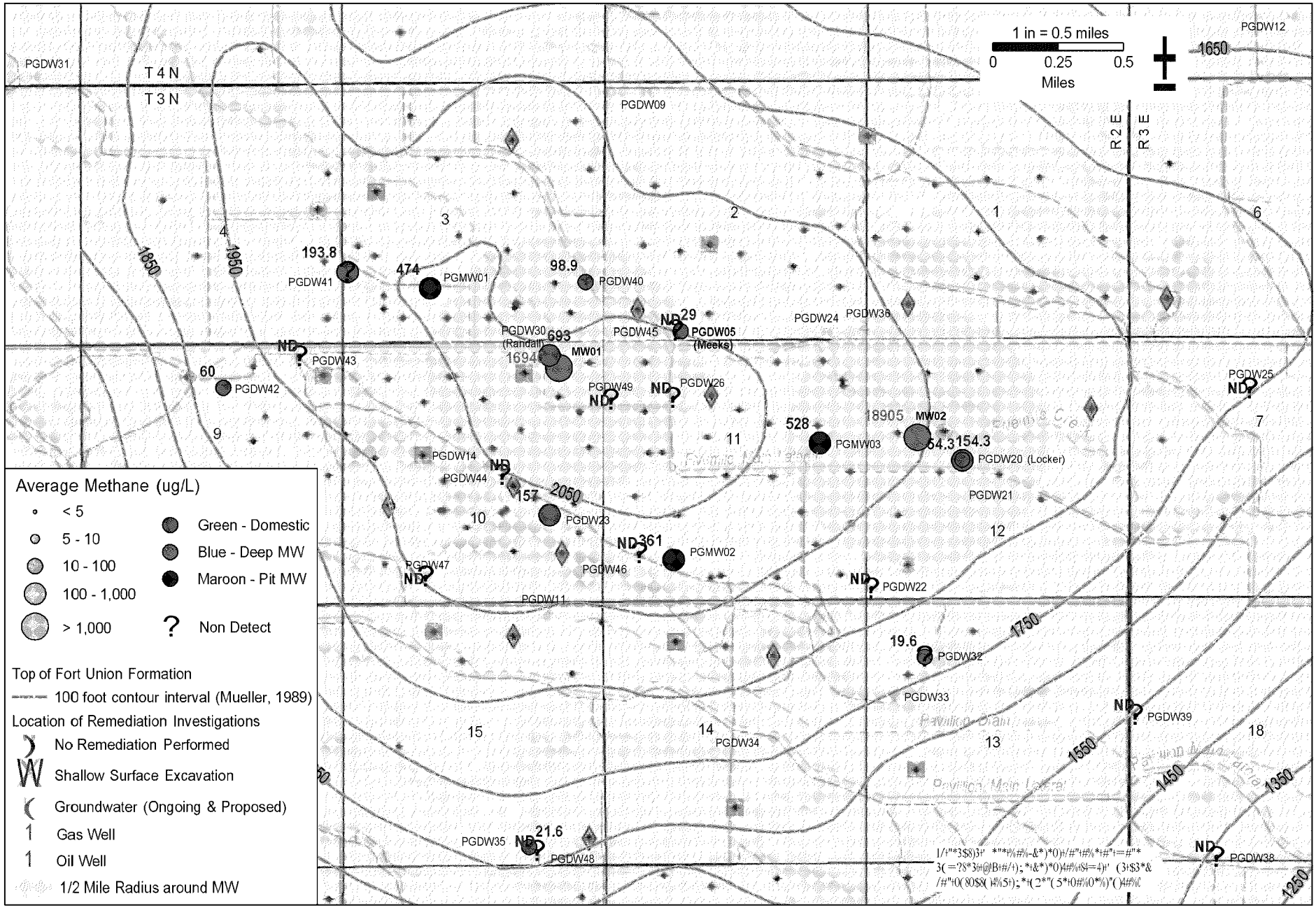

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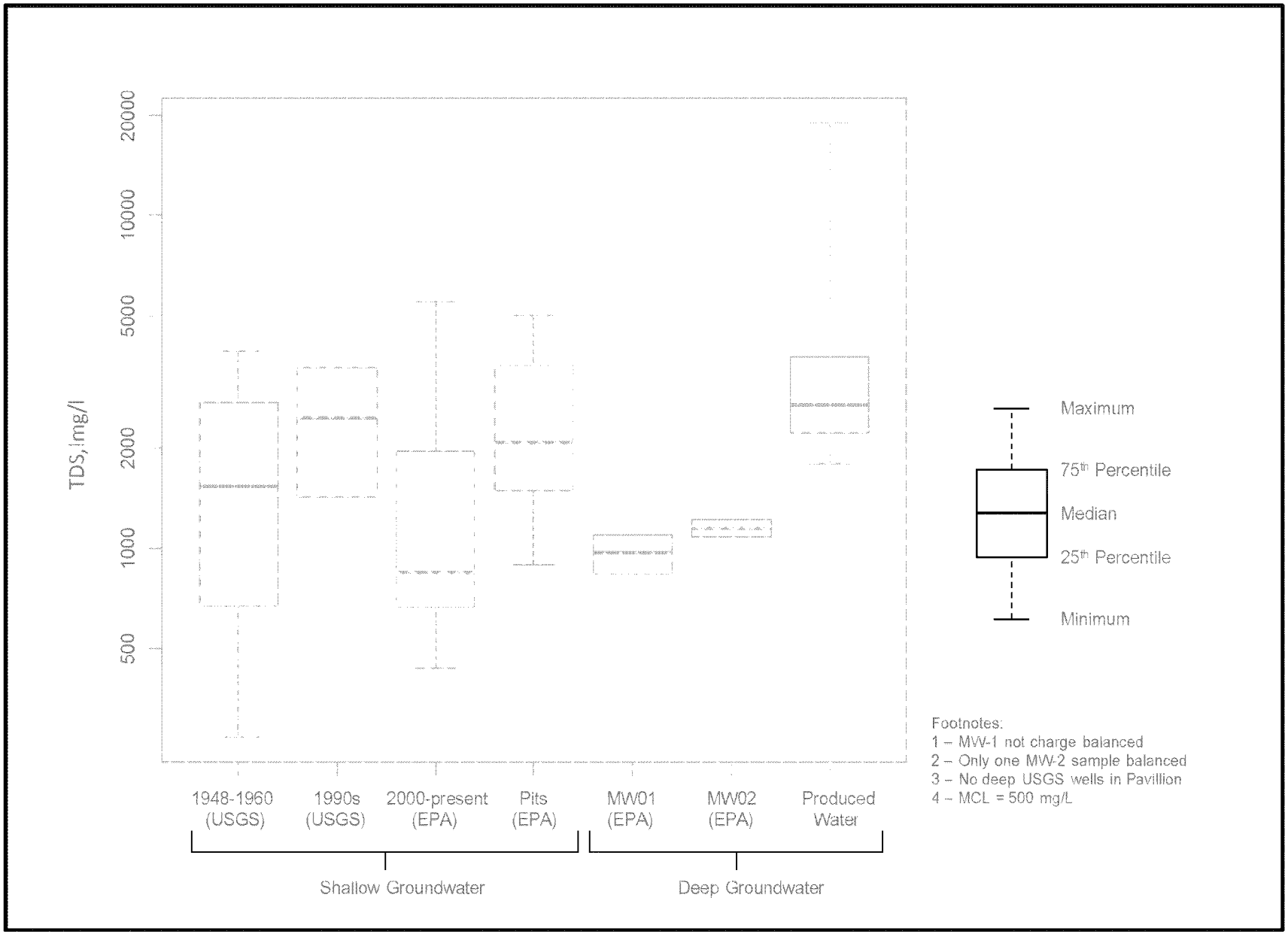

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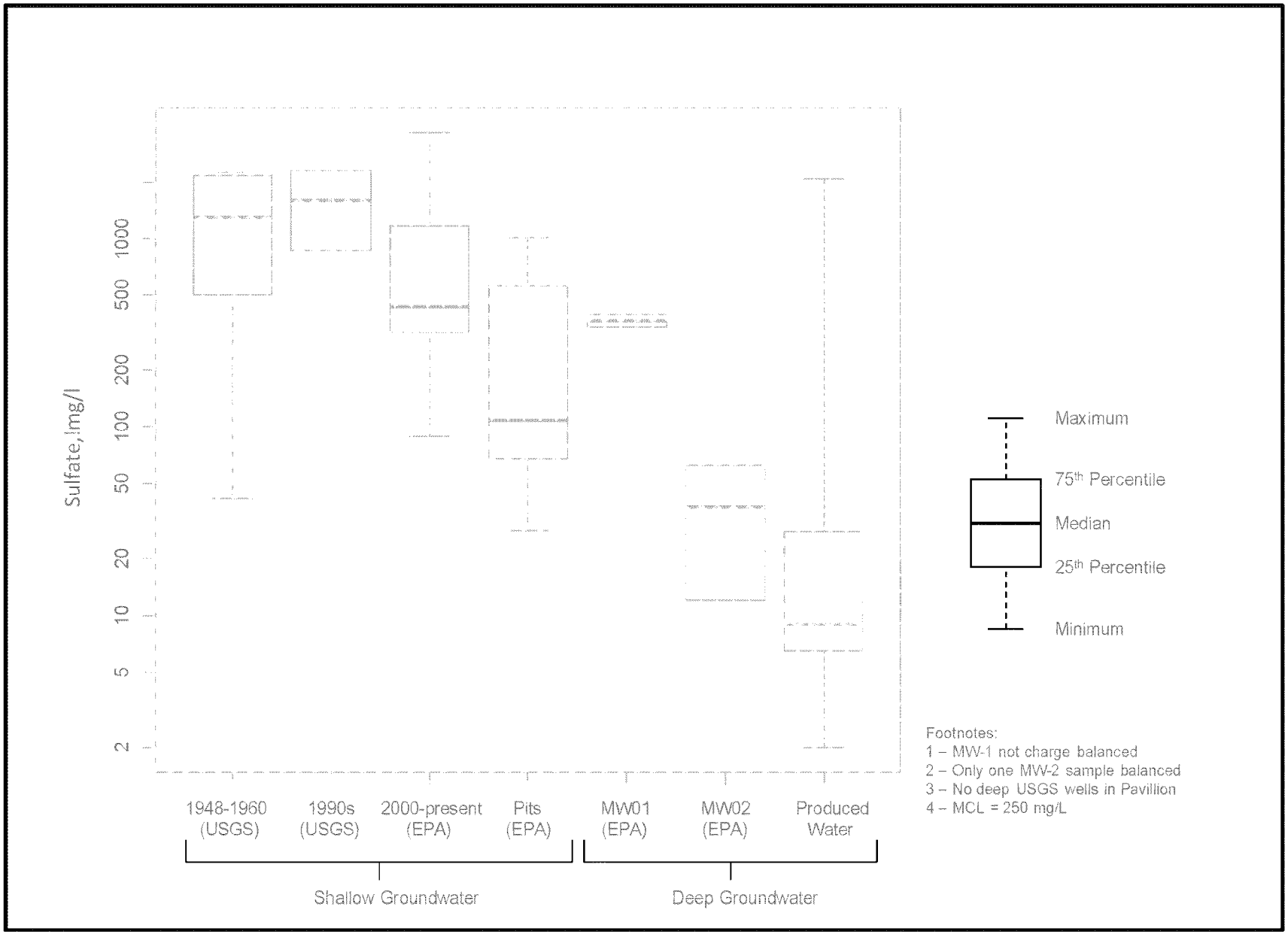

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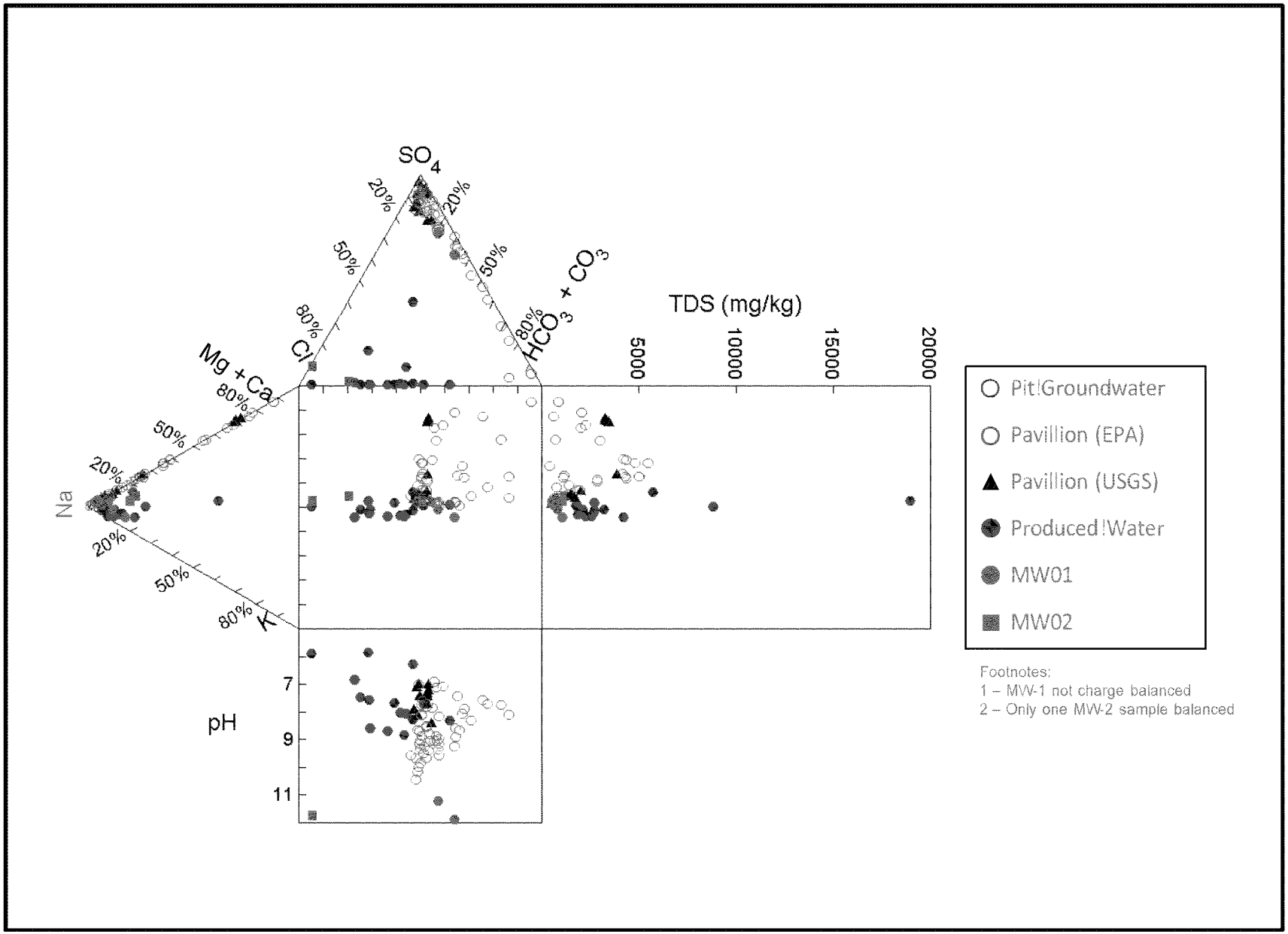

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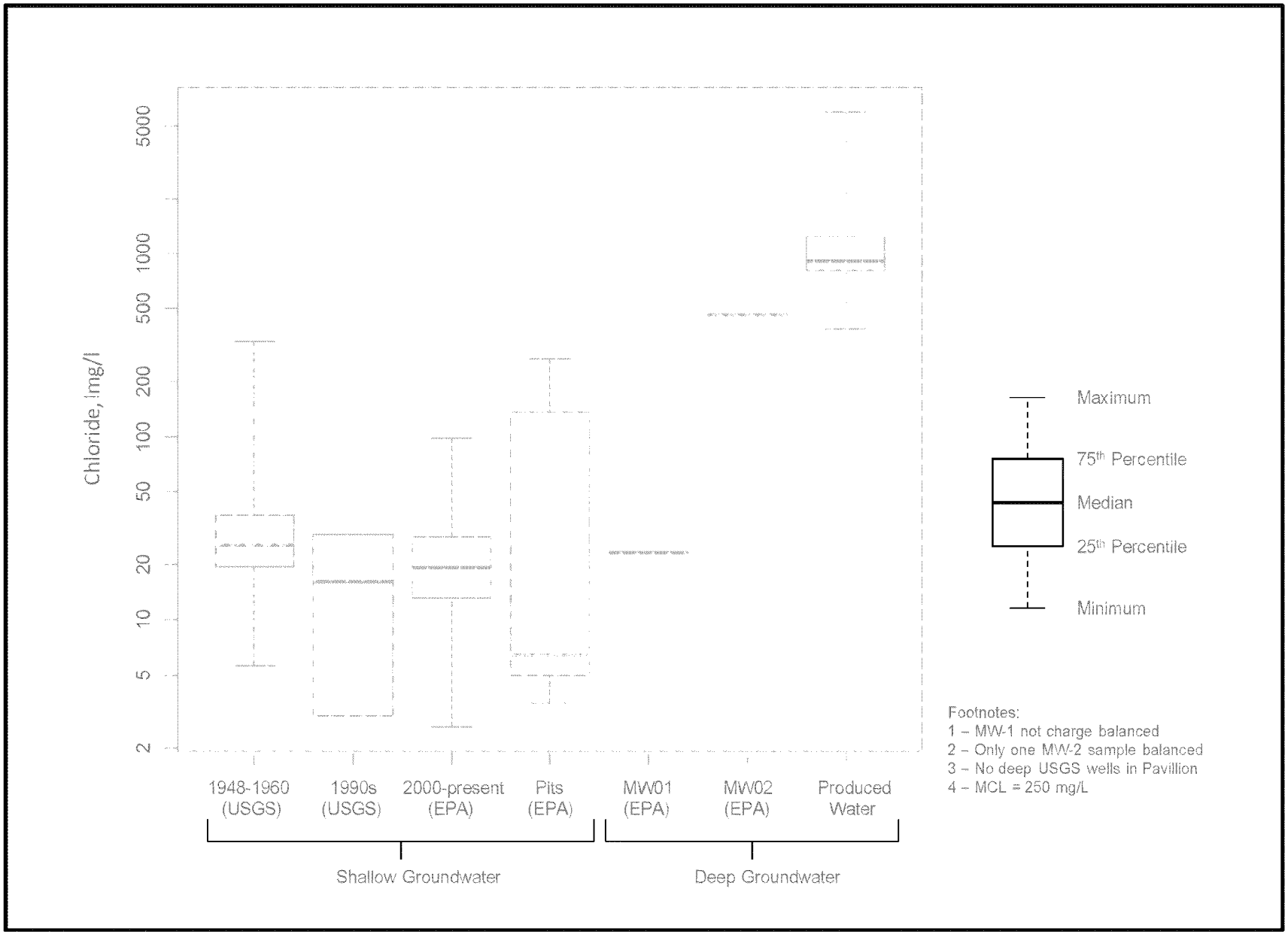

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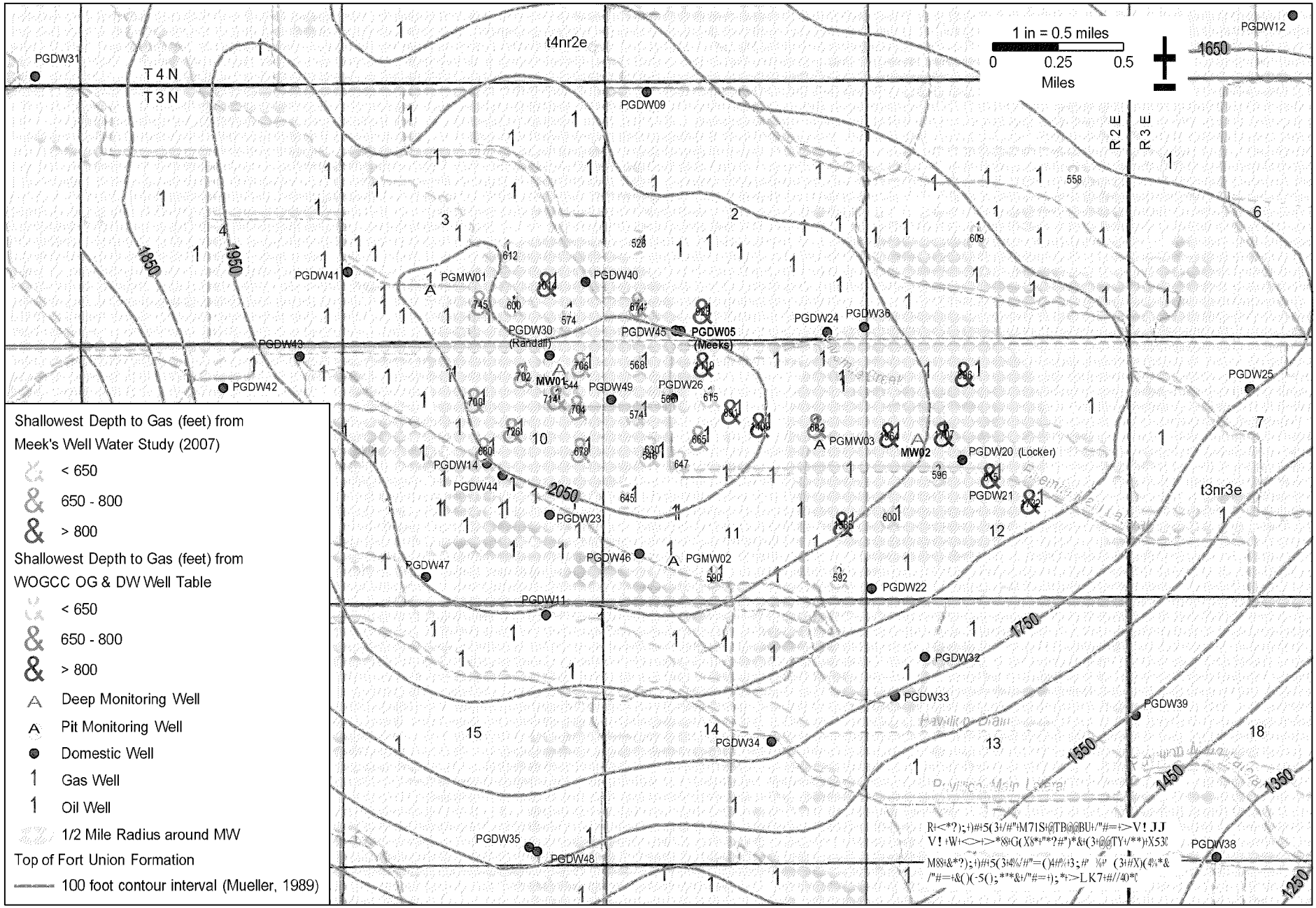

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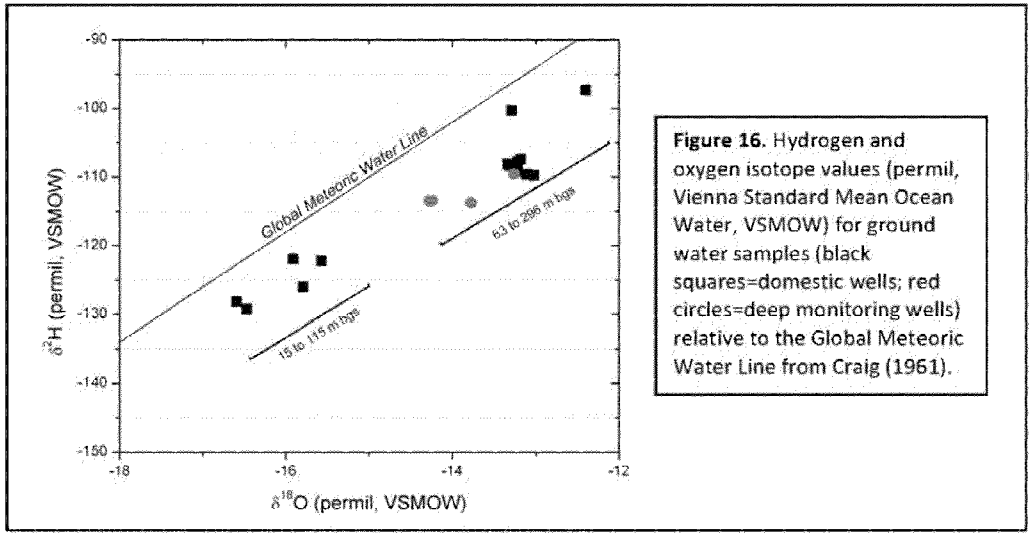

Figure 16. Hydrogen and oxygen isotope values (permil, Vienna Standard Mean Ocean Water, VSMOW) for ground water samples (black squares=domestic wells; red circles=deep monitoring wells) relative to the Global Meteoric Water Line from Craig (1961).

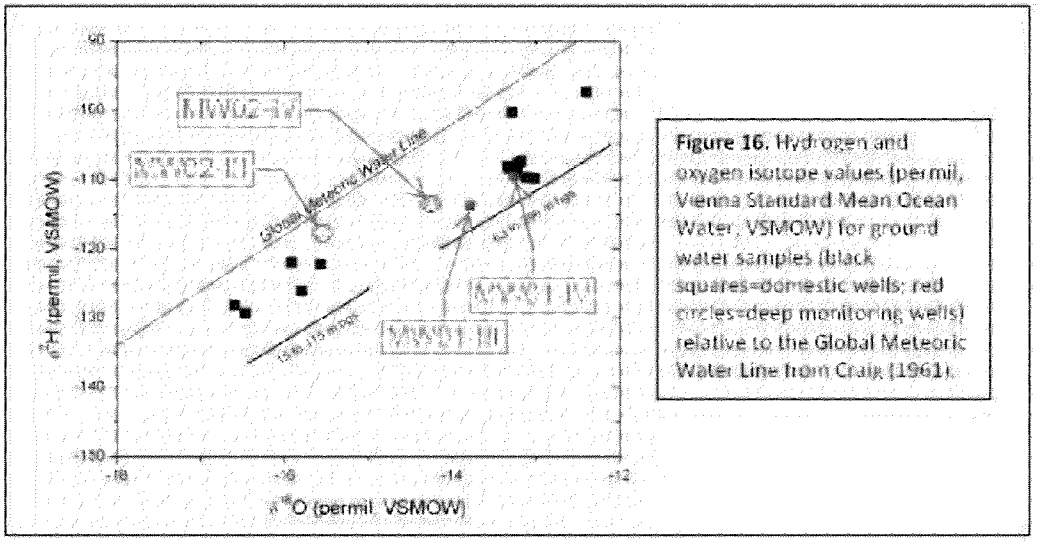

Figure 16. Hydrogen and oxygen isotope values (permil, Vienna Standard Mean Ocean Water, VSMOW) for ground water samples (black squares=domestic wells; red circles=deep monitoring wells) relative to the Global Meteoric Water Line from Craig (1961).

Figure 8 V"454%(8+(%&+J#""*0)*&+L*"34#%+#/-NZ&"#5*%-(%&+VEZ5 *%-13#)#?*+<+(5"(==+H945$"*+@[I+/"#==+-<"(/+K*?#")

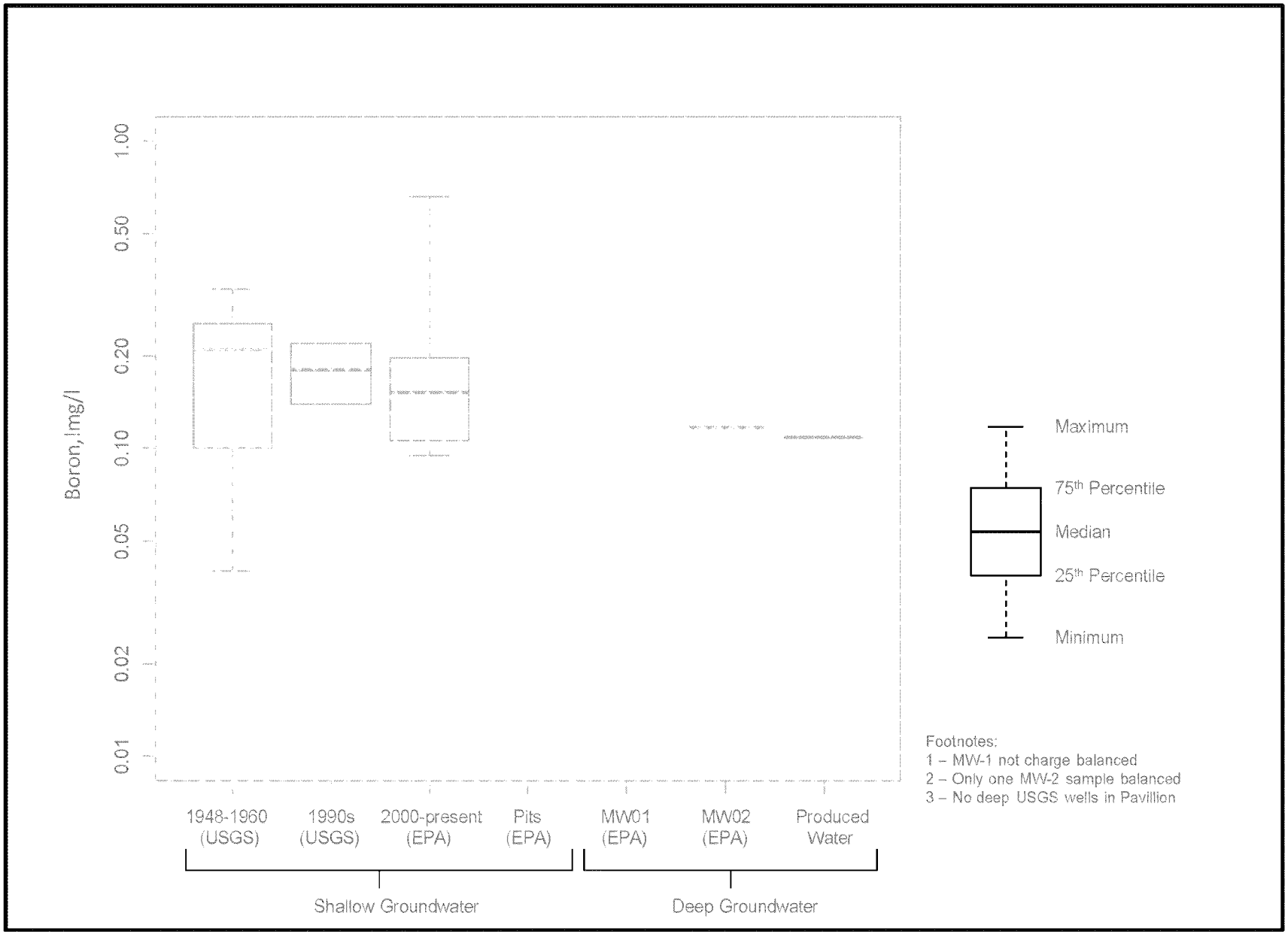

Figure 9 D#E(%&> ;43F*"3-78#)#/D#"#%J#%0*%)"()4#%3-4%! " #$%&' ()*"

TABLES

Table 1 Organic Compounds Reported in Domestic (PGDW) Wells *

	Analyte	Comment	Issues
1	1,1,2-Trichloro-1,2,2-trifluoroethane	Chlorofluorocarbon, detected in a single well	Unrelated to HF
2	1,3-Dimethyl adamantane	This compound was detected (with qualification) in concentrations up to 1.81 ug/l at 3 locations in phase II. All follow-up samples in Phase IV were similarly qualified. "1,3-dimethyl adamantane was also tentatively identified in at least one blank sample (Sample 1104026-04 (trip blank)) at 1.69 ug/l, a concentration higher than those in the Phase IV domestic wells samples (see page 147 of the Phase IV laboratory document).	Detections are not confirmed
3	2,4,5-Trichlorophenol	Qualified detection in 1 well in Phase II, no confirmation in later Phases	Detections are not confirmed
4	2,6-Dinitrotoluene	Qualified detection in 1 well in Phase II, no confirmation in later Phases	Detections are not confirmed
5	2-Chlorophenol	Qualified detection in 2 wells in Phase II, no confirmation in later Phases	Detections are not confirmed
6	2-Methylnaphthalene	Qualified detections in Phase II, but all Phase IV results were ND	Detections are not confirmed
7	4-Chloro-3-methylphenol	Qualified detections in 3 wells in Phase II, but all Phase IV results were ND	Detections are not confirmed
8	Acenaphthene	Qualified detections in 2 wells in Phase II, but all Phase IV results were ND	Detections are not confirmed
9	Acenaphthylene	Qualified detections in 1 well in Phase II, but all Phase IV results were ND	Detections are not confirmed
10	Acetate	One detection in Phase IV at 0.102 ug/l	Multiple possible sources from degradation of organic matter
11	Adamantane	Qualified detections in Phase II; a single detection in Phase IV, but also apepared in Phase III equipment blank	Detections are not confirmed
12	Aroclor-1016	One detection in Phase II, but no Phase IV follow-up	Detections are not confirmed; Unrelated to HF
13	Benzene	One detection in Phase II, flagged as J value	Detection not confirmed
14	Bis(2-ethylhexyl)phthalate	Detections in Phases I, II and IV; Most phase I and II results qualified; compounds occurs in Phase IV trip blank at concentration higher than most detections	Detections are not confirmed
15	Bis-(2-Ethylhexyl) Adipate	One detection in Phase IV at 1.64 ug/l	Detections are not confirmed
16	Butanes	Several detections in Phase II	Multiple possible sources
17	Butyl benzyl phthalate	Qualified detections in Phase II, but all Phase IV results were ND	Detections are not confirmed; Unrelated to HF
18	Caprolactam	Qualified Detections in Phase I and II, but no Phase IV follow-up	Detections are not confirmed; Unrelated to HF
19	Chloroform	One detection in Phase II, but all Phase IV results were ND	Detections are not confirmed; Unrelated to HF
20	Chloromethane	Qualified detections in Phase II, but all Phase IV results were ND	Detections are not confirmed; Unrelated to HF
21	Dimethylphthalate	Qualified detections in Phase I, but all Phase IV results were ND	Detections are not confirmed; Unrelated to HF
22	Di-n-butyl phthalate	Qualified detections in Phase II, but all Phase IV results were ND	Detections are not confirmed; Unrelated to HF
23	Di-n-octyl phthalate	One Qualified detections in Phase II, but all Phase IV results were ND	Detections are not confirmed; Unrelated to HF
24	Fluorene	Qualified detections in Phase II, but all Phase IV results were ND	Detections are not confirmed
25	Formate	One detection in Phase IV	Multiple possible sources from degradation of organic matter

Table 1 Organic Compounds Reported in Domestic (PGDW) Wells *

	Analyte	Comment	Issues
26	Heptanes	Detections in Phase II, but no follow up	Multiple possible sources
27	Hexanes	Detections in Phase II, but no follow up	Multiple possible sources
28	Methylene chloride	One detection in Phase II, but all Phase IV results were ND	Detections are not confirmed; Unrelated to HF
29	Naphthalene	Qualified detections in Phase II, but all Phase IV results were ND	Detections are not confirmed; multiple possible sources
30	Octanes	Detections in Phase II, but no follow up	Detections are not confirmed; multiple possible sources
31	Pentanes	Detections in Phase II, but no follow up	Detections are not confirmed; multiple possible sources
32	Phenol	Qualified detections in Phase II, but all Phase IV results were ND	Detections are not confirmed; multiple possible sources
33	Propanes	One detection in Phase II, but all Phase IV results were ND	Detections are not confirmed
34	Styrene	One detection in Phase II, but all Phase IV results were ND	Detections are not confirmed
35	Tetraethylene Glycol	All results are qualified ! see text	Detections are not confirmed
36	Toluene	Detections in Phase II and IV	Multiple posisble sources
37	Triethylene Glycol	All results are qualified ! see text	Detections are not confirmed
38	Tris (2 butoxyethyl) phosphate	Qualified detections in Phase II, but all Phase IV results were ND	Detections are not confirmed

*Excluding Pesticides

Table 2 Issues with Geochemical Data from Deep Groundwater Monitoring Wells (from Table 3 in EPA Draft Report)

Compound	MW01 Phase 3 10/6/2010	MW02 Phase 3 10/6/2010	MW01 Phase 4 4/20/2011	MW02 Phase 4 4/19/2011	Issues with Anaytical Results
pH	11.9	12.0	11.2	11.8	Elevated pH and K are potential artifacts of poor well construction, high turbidity and poor sampling methodology.
K, mg/L	54.9	39.5	24.7	43.6	
Cl, mg/L	23.3	466	23.1	457	Cl is a marker for deep produced waters, and may indicate that deep wells are drilled into non-commerical petroleum deposits.
CH_4, mg/L	16.0	19.0	17.9	18.8	CH_4 occurs naturally in the Wind River Basin; the observed CH_4 in these wells may reflect their screening within shallow gas-bearing zones.
Benzene	nd	246	nd	139	These compounds occur naturally within petroleum reservoirs and gas condensates (see analyses for PGPP04, PGPP05, PGPP06); GRO and DRO quantifications are suspect and represent a high bias; low-level toluene and total xylenes concentrations should be re-stated as non-detect due to blank contamination.
Toluene	0.75[d]	617	0.56	336	
Ethylbenzene	nd	67	nd	21.5	
Xylenes (total)	nd	750	0.89[d]	362	
1,2,4-Trimethylbenzene	nd	69.2	nd	18.5	
1,3,5-Trimethylbenzene	nd	35.5	nd	nd	
Diesel Range Organics	634	1440	924	4050	
Gasoline Range Organics	389	3710	592	2800	
Phenol	11.1	56.1	20.9	64.9	Possibly detected in PGPP06; phenols are anaerobic degradation products of benzene.
Naphthalene	nd	6.06	nd	6.10	Occurs naturally within petroleum reservoirs and gas condensates (see analyses for PGPP04, PGPP05, PGPP06).
Isopropanol	----	----	212	581	Non-standard methods were used for analysis, and these compounds were found in drilling fluids and cuttings.
Tert-Butyl Alcohol	----	----	nd	4470	
2-Butanone	----	----	nd	120	
Diethylene Glycol	----	----	226	1570	Glycol detections may have been influenced by contact with cement. Non-standard analytical methods were used that were neither official EPA methods nor subject to required peer review. Confirmation sampling (following well completion) and peer review of the method should be conducted.
Triethylene Glycol	----	----	46	310	
Tetraethylene Glycol	----	----	7.3[c,d]	27.2	
2-Butoxyethanol	----	----	nd	nd	
2-Butoxyethanol	nd	nd	12.7	nd	
Acetone	----	----	79.5	641	These compounds can be degradation products of naturally occurring organic compounds and do not by themselves indicate anthropogenic influence.
Benzoic Acid	212	244	457	209	
Acetate	----	----	8050	4310	
Formate	----	----	112	558	
Lactate	----	----	69	213	
Propionate	----	----	309	803	

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APPENDIX A

Text of Freedom of Information Act (FOIA) Request Submitted by S.S. Papadopulos & Associates to USEPA on February 7, 2012[1]

Specific Information Needed: Records Relating to R8 Pavillion Study and December 8, 2011 Draft Report as follows:

1) Field notes for all Pavillion well installation and sampling events directed by EPA, specifically including Phase I (March 2009), Phase II (January 2010), Phase III (October 2010), Phase IV (April, 2011),excluding Phase III and Phase IV flow-cell logs.

2) Information (field logs, analytical data and lab sheets) for 9 permanent soil gas probes installed in July 2010, and any temporary soil gas probes installed and sampled (referenced in Sections 3.2, 3.3 and 5.2b of the GWERD QAAP).

3) Water Sampling Information: Field notebooks and Excel spreadsheets for Phases III and IV (as referenced in Section 7.1b of the GWERD QAAP).

[1]The initial request, submitted via web-form, included a typographical error. The text presented here is the corrected version, as per e-mail correspondence and phone conversation with Michelle Marcu of USEPA on February 8, 2012.

APPENDIX B

Preliminary QA/QC Review of Chemical Data from the USEPA's December 2011 Draft Report Investigation of Groundwater Contamination near Pavillion, Wyoming

Prepared for:

S.S. Papadopulos and Associates, Inc.

7944 Wisconsin Ave,
Bethesda, MD 20814

Prepared by:

QA/QC Solutions, LLC

7532 Champion Hill Rd. SE
Salem, Oregon 97306

February 22, 2012

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Acronyms and Abbreviations

ACF	advanced chemical fingerprinting
ATSDR	Agency for Toxic Substances and Disease Registry
CLP	Contract Laboratory Program
DQI	data quality indicator
DQO	data quality objective
DRO	diesel range organics
FSP	field sampling plan
GC/FID	gas chromatography/flame ionization detector
GC/PID	gas chromatography/photoionization detector
GC/MS	gas chromatography/mass spectrometry
GRO	gasoline range organics
HPLC/MS/MS	high-performance liquid chromatography/m ass spectrometry/ mass spectrometry
LCS	laboratory control sample
MS/MSD	matrix spike/matrix spike duplicate
MQO	measurement quality objective
PAH	polycyclic aromatic hydrocarbon
PQO	project quality objective
QA/QC	quality assurance and quality control
QAPP	quality assurance project plan
SIM	selected ion monitoring
SRM	standard reference material
SVOC	semivolatile organic compound
USEPA	U.S. Environmental Protection Agency
VOC	volatile organic compound

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1.0 Introduction

QA/QC Solutions, LLC has completed a preliminary quality assurance and quality control (QA/QC) review of the Draft Report prepared by the U.S. Environmental Protection Agency (USEPA) Draft, Investigation of Ground Water Contamination near Pavillion, Wyoming report (U.S. EPA 2011a) released on December 8, 2011 and supporting analytical data. All information reviewed was posted online by USEPA Region 8 at http://www.epa.gov/region8/superfund/wy/pavillion/.

The purpose of this preliminary QA/QC review was to determine if applicable laboratory QA/QC procedures were properly documented and if the overall quality of the data reported is sufficient to support its intended purpose(s). A more in-depth review was completed on the results reported for the gasoline range organics (GRO), diesel range organics (DRO), volatile organic compounds (VOCs), semivolatile organic compounds (SVOCs), alcohol compounds, and glycol compounds data. A list of documents reviewed and accessed to prepare the findings presented herein is presented in the References section. The findings of this preliminary QAQC review are summarized below.

2.0 Summary of Preliminary Findings

Several items of concern were identified during the preliminary QA/QC review of draft report and supporting analytical data and include the following:

1. All data reported by USEPA should be subjected to a thorough internal and independent third-party data verification, data validation, data quality assessment (DQA), and data usability evaluation prior to its use. Completion of these tasks will allow for a better understanding of the overall quality of the data; verify that all applicable QA/QC procedures were documented and completed; identify potential limitations (if any) of the data; and, to help determine, with a known degree of confidence, if the data are usable for their intended purpose(s). A brief summary of some of the elements regarding QA/QC processes and procedures, data verification, data validation, DQA, and data usability evaluation are provided in Attachment 1 for reference.

2. Interpretation of the data and all work products produced should be subjected to a thorough internal and external peer review prior to its release. The intent of completing peer review is, in part, to identify if there are technical problems or unanswered questions associated with the work completed and the subsequent documentation of such work. This is a process of "enhancing a scientific or technical work product so that the decision or position taken by the Agency, based on that product, has a sound, credible basis" (U.S. EPA 2000).

3. Complete documentation of all data collected during the investigation is not yet fully posted on the USEPA website. Until such time that all analytical data is made available, a thorough assessment of the overall quality of the data cannot be completed at this time.

4. The USEPA acknowledges that several of the analytical method standard operating procedures (SOPs) used to complete some chemical analyses are not official EPA approved methods nor were they subjected to the required peer review (U.S. EPA 2000, 2002a); see note below. These SOPs are probably capable of generating acceptable and repeatable data; however, the use of non-EPA approved methods, coupled with the lack of appropriate (and required) peer review, could possibly result in the reporting of potentially biased data. It should be noted, however, that the USEPA reported applicable QC measurement data that included method blanks, surrogate compound recoveries, matrix spike and matrix spike duplicate recoveries, results of standard

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reference material (SRM) analyses, and laboratory duplicate sample analyses. The results of these QC measurements were generally acceptable, indicating the methods used for analysis are capable of producing data of good quality. In addition, the USEPA should state why these SOPs have not been subjected to the peer review process.

> **Note:** The specific comment made by EPA in the applicable SOPs is as follows: "This Standard Operating Procedure has been prepared for the use of the Ground Water and Ecosystem Restoration Division (GWERD) of the U.S. Environmental Protection Agency and may not be specifically applicable to the activities of other organizations. **THIS IS NOT AN OFFICIAL EPA APPROVED METHOD.** This document has not been through the Agency's peer review process or ORD clearance process."

5. There is not sufficient information available to completely address the qualitative and quantitative concerns regarding the GRO and DRO analytical results reported. A detailed description of how the USEPA is defining, qualitatively identifying, and quantifying GRO and DRO should be provided. The data currently available does not permit an independent verification of the GRO and DRO: complete quantification lists are not provided that list all of the chromatographic peaks that were used for qualitative purposes and the area or peak counts of those chromatographic peaks that were summed for quantitative purposes. Without this information it is not possible to determine what chromatographic peaks were used for qualitative and quantitative purposes and the validity of the data reported.

> **Note:** GRO (i.e., TPH as gasoline) and DRO (as a diesel product) are multipeak response mixtures containing hundreds of compounds. The analytical methods usually sum all of the chromatographic peaks eluting with a specific carbon range, which may or may not be a petroleum based compound, or by pattern matching (i.e. fingerprinting) the sample chromatogram to a specific petroleum product standard (e.g., diesel fuel #2, kerosene, etc.) using selected chromatographic peaks.
>
> SW-846 Method 8015D (U.S. EPA 2011b) defines GRO as the range of alkanes from C6 to C10 and DRO as the range of alkanes from C10 to C28. The sum of the peak areas (or peak height if used) of all applicable chromatographic peaks eluting within these specified carbon ranges are used for quantitative purposes. The GRO and DRO analytical methods will result in the detection of many non-alkane and non-petroleum based compounds. Depending on the qualitative and quantitative criteria that were used, GRO or DRO then may be reported as a false positive or biased high because other compounds that may be present, such as naturally occurring organics, that elute within the applicable carbon ranges.

Additional concerns regarding the GRO and DRO data are summarized in other discussion points below.

6. The use of the terms GRO (or TPH as gasoline) and DRO (i.e., as diesel range organics) are commonly misinterpreted to mean that GRO is an automobile fuel (gasoline) and DRO is a diesel fuel (e.g., diesel #2 fuel). Further, potentially false positive or highly biased data may be reported when non-target compounds are also present. To minimize potential misinterpretation of the GRO and DRO data reported, it is suggested that data qualifiers be assigned to these data. The purpose of the data qualifiers is to provide data users with a very clear understanding of what the GRO and DRO data reported represent. For example a qualifier code could be used to let data users

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know that the chromatographic fingerprint of the sample resembles a petroleum product eluting in approximately correct carbon range, but elution pattern does not match the calibration standard. Another qualifier code could be used to indicate the chromatographic fingerprint of the sample does not resemble a petroleum product.

7. It was not evident in the data made available for review if the GRO analyses were completed using acid preserved to pH <2 samples or were they unpreserved. This should be clarified.

8. The results reported other selected chemical constituents such as VOCs and SVOCs do not provide sufficient qualitative evidence to support that GRO and DRO as a petroleum product may be present in most samples. A few examples are discussed below.

9. The presence of GRO (i.e., TPH as gasoline) is suspect in most samples, but appears to be present in a few samples. The determination that the presence of GRO is suspect is based on the findings there is a poor match of the sample chromatogram to the standard used for qualitative purposes and that common constituents found in gasoline (e.g., BTEX and additives such as MTBE) were not detected or were present at very a low concentration and not confirmed in the VOC analyses completed using gas chromatography/mass spectrometry (GC/MS) using SW-846 Method 8260B (U.S. EPA 2011b). For those samples in which the presence of TPH as gasoline is plausible, its presence is supported by the detection of BTEX and other additives by the GC/MS method; however, the results reported for TPH as gasoline likely exhibit a high bias due to inclusion of non-petroleum related compounds as a result of the general requirements specified by the method and briefly discussed above. A few examples to illustrate the comments above include the following:

   - For Phase I, data summaries and original instrument printouts for the GRO and VOC analyses were posted on the USEPA website.
   - For Phase II, no field blank data (e.g., trip blanks or field blanks) were reported along with the sample results. The highest concentrations of TPH as gasoline were reported in samples PGMW01 at 389 ug/L, PGMW01D at 322 ug/L, PGMW 2,210 ug/L, and PGMW03 at 1,060 ug/L. The corresponding VOC results by GC/MS using SW-846 Method 8260B (U.S. EPA 2011b) for these samples typically reported as detected benzene, ethylbenzene, and xylenes, 1,3,5-Trimethylbenzene, tert-Butylbenzene, adamantane, and 1,3-Dimethly adamantane; toluene was either not detected or was present at a very low concentration. The concentration of benzene was atypically elevated compared to the other aromatic VOCs, which does indicate the presence of an unweathered or weathered gasoline profile. Further data analysis is recommended.
   - TPH as gasoline was reported as detected in Sample MW01 in the Phase III investigation at 389 ug/L. BTEX (and other gasoline-related components) should be detected in the VOC analyses by GC/MS using SW-846 Method 8260B (U.S. EPA 2011b); however, only toluene was detected (as a false positive) at a very low concentration. Review of the corresponding VOC data shows that toluene was reported as detected at 0.750 ug/L in MW01 and was also detected at 0.160 ug/L in the field blank, 0.540 ug/L in the trip blank, and 0.160 ug/L in the equipment rinsate blank associated with this sample.

     In following data validation protocols using the !5 times rule for uncommon contaminants by using the highest concentration found in any blank and

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taking into account any dilution factors (U.S. EPA 2008), all toluene results reported as detected at a concentration of !2.7 ug/L in all samples associated with this trip blank should be restated as undetected (U) at the concentration reported (if greater than that found in the blank) or restated as undetected at the concentration found in the blank if the concentration in the sample was lower. VOCs were not reported as detected in the method blank.

After taking into account contribution of VOC due to blank contamination, it is evident that BTEX and other VOCs are not present in MW01 during Phase III and the presence of GRO (as gasoline) is unlikely. This type of example is found with several other samples.

- TPH as gasoline was reported as detected in Sample MW01 in the Phase IV investigation at 592 ug/L. BTEX (and other gasoline-related components) should be detected in the VOC analyses by GC/MS using SW-846 Method 8260B). Review of the corresponding VOC data shows that toluene at 0.560 ug/L, m,p-xylenes at 0.890 ug/L, 2-Hexanone at 0.370 ug/L, 4-methyl-2-pentanone at 2.60 ug/L, and acetone at 79.5 ug/L were reported as detected in MW01. In the two field blanks, m,p-xylene was detected at 0.690 ug/L and 0.700 ug/L, in addition to 2-Butanone at 0.640 ug/L and 0.820 ug/L, 2-Hexanone at 0.290 ug/L and 0.410 ug/L, acetone at 1.03 ug/L and 1.38 ug/L, and methacrylonitrile at 0.270 ug/L and not detected in second field blank. Chloromethane was the only VOC reported as detected in the trip blank at 1.04 ug/L. VOCs were not reported as detected in the method blank.

  Using the !5 times rule for uncommon contaminants and the !10 times rule for common contaminants with highest concentration found in any blank and taking into account any dilution factors (U.S. EPA 2008), the toluene results are considered acceptable because this VOC was not detected in the associated blanks. However, all associated samples results would be restated as undetected if the concentration was !3.5 ug/L for m,p-xylene, ! 2-Butanone at! !4.1 ug/L, 2-Hexanone at !.05 ug/L, and acetone at !13.8 ug/L. After taking into account contribution of VOC due to blank contamination, only toluene would be considered at present in MW01 during Phase IV and there is no an indication that GRO (as gasoline) is present.

- The reported detection of TPH as gasoline in MW02 during the Phase III and IV investigations appears to be representative of gasoline and supported by the VOC by GC/MS results.

10. At this time there is no indication if any of the samples analyzed for DRO were subjected to silica gel column cleanup (or any other cleanup procedures) for the analysis of DRO. Cleanup of sample extracts is often necessary to remove or minimize interferences caused by non-target analytes that may be present so that more reliable qualitative identification and more accurate quantification can be completed. Silica gel retains the polar, naturally occurring, compounds while the non-polar, petroleum-based hydrocarbons remain in the extract. Use of this cleanup allows for more reliable qualitative identification and quantification to minimize the reporting of potential positive or biased high data (e.g., reporting of concentrations that are actually lower than are quantified. Additional cleanup procedures, such as alumina, may also be used to further minimize non-target analyte interferences. The USEPA should state if the samples analyzed for DRO were or were not subjected to this cleanup procedures. In addition, all future analyses for

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DRO should be completed with and without the use of silica gel column cleanup in order to evaluate if non-target organic compounds of biogenic origin may be causing a positive bias.

11. The presence of DRO (i.e., diesel range organics) is suspect in most samples, but appears to be present in a few samples. The determination that the presence of DRO is suspect is primarily based on the findings there is a poor match of the sample chromatogram to the standard used for qualitative purposes. The results reported for DRO likely exhibit a high bias due to inclusion of non-petroleum related compounds. A few examples to illustrate the comments above include the following:

    - In the Phase I investigation, DRO was reported as present in 13 of 15 samples were analyzed. Many samples had many chromatographic peaks, but none matched the diesel #2 standard used for calibration and quantification. Many of the samples did not have a characteristic fingerprint pattern to diesel range petroleum hydrocarbons. The chromatogram for Sample PGDW30, however, may be representative of mineral spirits, stoddard solvent, or other similar type petroleum hydrocarbon; the laboratory noted on this chromatogram "early diesel ?." Residual range oil product eluting after the DRO range may possibly be present in some samples (e.g., PGDW05). The chromatograms of other samples (e.g., the trap sample) are indicative of alkanes representative of plant waxes of likely terriginous origin.
    - In the Phase II investigation, DRO was reported as present in 28 of 35 samples were analyzed. The samples with the highest concentrations were PGMW01 at 638 ug/L from a 1:10 dilution, PGMW02 at 1,230 ug/L from a 1:10 dilution, PGMW03 at 62,100 ug/L from a 1:500 dilution, and PGMW04 at 4,830 ug/L from a 1:10 dilution. The chromatograms of these samples indicate a diesel-related fuel could possibly be present that elutes earlier than diesel #2, but can not be stated with certainty since other fuel products were not analyzed that could be used for comparison.

      While a fuel product could be present in the samples listed above, DRO was also reported as detected in the associated field blank at 26.5 ug/L. Therefore if these data were validated following guidance specified USEPA functional guidelines (U.S. EPA 2008), the results reported for PGMW01, PGMW02, and PGMW03 would be restated as undetected (U) because the concentrations prior to adjustment of the dilution factors were !5 times the concentration found in the field blank. The action limit would be 5 x 26.5 ug/L = 132.5 ug/L and the concentrations prior to adjustment of the dilution factor would be 63.8 ug/L for PGMW01, 123 ug/L for PGMW02, and 124.2 ug/L for PGMW03.
    - DRO was reported as detected in MW01 at 634 ug/L during the Phase III investigation and at 924 ug/L during the Phase IV investigation. For MW02 in the Phase III investigation, DRO was reported as detected at 1,440 ug/L and in the Phase IV investigation at 4,050 ug/L (and 4,200 ug/L in the duplicate sample). The DRO (as a petroleum product) detections are suspect in these samples because there is poor match with the diesel #2 standard and there were predominantly many early eluting peaks that are not indicative of a diesel-range fuel product that were used for both qualitative and quantitative purposes. There were a few chromatographic peaks within the

applicable carbon range, but the fingerprint did not appear to be that of an unweathered or weathered diesel fuel product.

- In Phase III, the SVOCs reported as detected in MW01 using GC/MS included phenol, benzyl alcohol, 3 & 4 methylphenol, benzoic acid, and bis(2-ethylhexyl) phthalate, all of which are not representative of a diesel product. The SVOCs by GC/MS reported as detected in MW02 included phenol, benzyl alcohol, 2-methylphenol 3 & 4 methylphenol, isophorone, 2,4-dimethylphenol, benzoic acid, naphthalene, 2-methylnaphthalene, 1-methylnaphtalene, and bis(2-ethylhexyl) phthalate.
- In Phase IV, the SVOCs reported as detected in MW01 using GC/MS included phenol, bis(2-chloroethyl)ether, benzyl alcohol, 3 & 4 methylphenol, benzoic acid, bis(2-ethylhexyl)adipate, and bis(2-ethylhexyl) phthalate, all of which are not representative of a diesel-range product. The SVOCs by GC/MS reported as detected in MW02 included phenol, 2-methylphenol 3 & 4 methylphenol, 2,4-dimethylphenol, benzoic acid, naphthalene, 2-methylnaphthalene, 1-methylnaphtalene, and bis(2-ethylhexyl) phthalate.

12. General information about fuels is provided in Attachment 2 for informational purposes.

13. Advance chemical fingerprinting (ACF) analytical methods should be considered to more definitively verify the absence and/or presence of GRO and DRO in all samples. Examples of ACF analyses would include such analyses for PIANO (i.e., Paraffins [straight-chain alkanes)], Isoparaffins [branched alkanes]. Aromatics, Naphthenes [cycloalkanes], and Olefins [alkenes]; aliphatic hydrocarbons (i.e., the normal alkanes from n-C_{10} to n-C_{32}, pristane, and phytane), and total resolved and unresolved complex mixtures by GC/FID; PAHs and alkylated PAHs by GC/MS operated in the selected ion monitoring mode (SIM); biomarker compounds such as steranes and terpanes by GC/MS SIM, and a full GC/MS scan for petroleum-related compounds (e.g., n-alkanes, isoalkanes, isoprenoids, alkylcyclohexanes, alkybenzenes, and bicyclanes within the C10 to C40 range).

14. The report stated the detection of glycols in several domestic well samples analyzed using a GC/FID technique were likely reported as false positive (see page 27 of the report). The USEPA further stated these glycol detections could not be confirmed using a liquid chromatography with tandem mass spectroscopy analysis (note: referenced as GC/MS/MS in the report). Per USEPA interpretation of the initial reporting of false positive glycol results, the confirmatory non-detected results should be used for interpretative purposes and not the GC/FID results.

    Notes: The USEPA report (see page 27) referenced the GC/FID technique used for the analysis of glycols as "EPA Standard Method 8015", but should be SW-846 Method 8015D. The USEPA report (see page 27) used the acronym GC/MS/MS, which is the acronym for gas chromatography/mass spectrometry/mass spectrometry; however, the text stated liquid chromatography with tandem mass spectroscopy. This discrepancy should be corrected.

    While the glycol analyses completed by HPLC/MS/MS during the Phase IV investigation were completed using a non-peer review method, the results of the quality control measurements are acceptable and these data are of generally good quality. These data tentatively indicate that glycol target compounds are present in MW01 and MW02 and there presence should be confirmed using other confirmatory techniques during future sample and analysis. In summary, results reported

using this analytical technique should be used for interpretive purposes rather than the GC/FID results.

15. The draft report states that some target compounds were present in associated blank water samples (e.g., method blanks, trip blanks, field blanks, and/or equipment rinsate banks). If the data were subjected to an appropriate degree of data validation, many results reported as detected would be restated as undetected (U) because the concentrations found in the samples were !5 times (used for uncommon contaminants) or !10 times (used for common contaminants such as acetone for VOC analyses and phthalate compounds for SVOC analyses; see U.S. EPA) the concentrations found in the associated blanks. The affected results would then either be restated as undetected (U) at the concentration found in the associated blank or at the concentration reported in the samples. Several examples of how blank contamination resulted in the reporting of false positives for VOCs, GRO, and DRO were discussed above.

16. The collection of samples and one field duplicate from only two monitoring wells (i.e., MW01 and MW02) during only two sampling events is not statistically significant. Results collected from MW01 and MW02 collected only two times is inadequate to support any conclusive interpretations of the data. In addition, there is no background or baseline data to compare the current data sets to for interpretative purposes. There are currently insufficient sample results for these two wells to support the decision-making process. More in-depth sampling and analysis needs to be completed to acquire sufficient data that will be statistically significant.

17. Data were reported for selected analyses completed on some of the drilling additives. It was noted that the results for the analysis for VOCs by head space GC/MS (see file name SampleResults_8OA778SF_SS6163_23993_07-21-11_Headspace.pdf on the USEPA website) were completed in July 2011 and after the Phase IV event. These data are from analyses completed using a concentrated preparation of the drilling additive(s) (e.g., AC [i.e., aqua clear], AC Lab Dup, Penetrol, and EZ Mud Gold) and water. There are also data reported for VOCs by head space GC/MS on two unknown samples that are labeled PAV 01, and PAV 02, which are not been described (or summarized) in the report. It is important to note that several alcohol compounds, BTEX, and other VOCs were reported as detected in PAV 01 and/or PAV 02, with some at elevated concentrations with the most significant detections in sample PAV 02. The significance of these data is unknown because no additional information has been provided in the report; therefore, additional information regarding samples PAV 01 and PAV 02 and their pertinence to the investigation is necessary.

This completes the preliminary summary of findings. Additional comments regarding the information reviewed are summarized in the sections below.

3.0 Specific Comments on EPA Draft Report

The comments provided below are based on the information present in the USEPA Draft, Investigation of Ground Water Contamination near Pavillion, Wyoming report (U.S. EPA 2011a).

Section 1.0: Site Background

No comments at this time.

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Section 2.0: Methods

Deep Monitoring Well Installation

Three of the six drilling additives were extracted in water (see page 5 and 6 of draft report). The following comments pertain the analyses that were completed of the drilling additives extracted in water:

- It is not clear if only one batch, or several batches, of drilling additive extractions with water were prepared for each of the determinations listed below. Clarification is requested.
- The source of the water that was used to conduct the extractions of the drilling additives should be specified. It does not appear that the formation water (i.e., the municipal drinking water from Riverton, WY) was tested for the chemical constituents completed on the drilling additives. Further clarification is requested. If any other water sources were used at any time, additional details are requested.
- A summary of results for the glycol analyses completed on the drilling additives has not been provided. A summary similar to those reported for the other analyses conducted should be provided. In addition, the method used to complete the analysis of glycols should be referenced and a copy of the applicable SOP used should be provided.
- Alternative method(s) should be found to extract and analyze the Dense Soda Ash, Quick-Gel, and Quik-Trol Gold drilling additives for organic chemicals of concern (e.g., VOCs, GRO, DRO, SVOCs, etc.) to make sure none of the target compounds of concern may be present.
- Analyses of a complete mixture of all of the drilling additives in the recommended formulation ratio should be extracted in water and analyzed for all chemicals of concern (e.g., inorganics, VOCs, GRO, DRO, SVOCs, etc.). This would be useful to evaluate all possible external sources of contamination.
- Drilling additives were extracted in water (see page 5 and 6 of draft report) and tested for the following constituents:
  - pH and conductivity (unspecified methods and dates of determination). All six additives (e.g., Aqua-Clear [AC], Penetrol, EZ-Mud Gold, Dense Soda Ash, Quik-Gel, and Quik-Trol Gold) were analyzed.
  - Chloride and sulfate using USEPA RSKSOP-214, Rev. 5 - Quality Control Procedures for General Parameters Analyses Using Lachat Flow Injection Analyses (FIA), Lachat FIA Method 10-117-07-1-B Determination of Chloride by Flow Injection Analysis Colorimetry (mercuric thiocyanate method - calibration range of 1 - 50 mg/L), and Lachat FIA Method 10-116-10-1-C Determination of Sulfate by Flow Injection Analysis (turbidimetric method - calibration range of 2 - 50 mg/L) on May 2011. All six additives (e.g., AC, Penetrol, EZ-Mud Gold, Dense Soda Ash, Quick-Gel, and Quik-Trol Gold) were analyzed.
  - Twenty-seven (27) elements using USEPA RSKSOP-213 Rev. 4 Standard Operating Procedure for Operation of Perkin Elmer Optima 3300DV ICP by inductively coupled plasma-optical emission spectroscopy (ICP-OES) on March 3, 2011. All six additives (e.g., AC, Penetrol, EZ-Mud Gold, Dense Soda Ash, Quick-Gel, and Quik-Trol Gold) were analyzed.

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- Selected volatile aromatic hydrocarbons (i.e., BTEX, acetone, tert-butyl alcohol, MTBE, 1,3,5-Trimethylbenzene, 1,2,4-Trimethylbenzene, and 1,23-Trimethylbenzene) using USEPA RSKSOP-122 Rev. 4 - Analysis of Volatile Aromatic Hydrocarbons by Purge & Trap Gas Chromatography Archon by gas chromatography with an unspecified detector on July 14-15, 2011. Only three of the six additives (e.g., AC, Penetrol, and EZ-Mud Gold) were analyzed.
- Thirty-nine (39) VOCs using USEPA RSKSOP-259/1 "Determination of Volatile Organic Compounds (Fuel Oxygenates, Aromatic and Chlorinated Hydrocarbons) In Water Using Automated Headspace Gas Chromatography/Mass Spectrometry on July 15-21, 2011. Only three of the six additives (e.g., AC, Penetrol, and EZ-Mud Gold) and two unknown samples (i.e., PAV 01 and PAV 02) were analyzed. A description of the PAV 01, and PAV 02 samples is required. It is not clear why other organic and inorganic analyses were not completed on these two samples and clarification is needed. A description of samples PAV 01 and PAV 02 and their pertinence to the investigation are necessary.
- Several forms of carbon (e.g. total organic carbon, total inorganic carbon, NPOC) using USEPA RSKSOP-102 rev. 5, Determination of Total Carbon, Total Organic Carbon, Dissolved Carbon, and Dissolved Organic Carbon in Water using the Dohrmann DC-80 Carbon Analyzer and RSKSOP-330 rev. 0 Determination of Various Fractions of Carbon in Aqueous Samples using the Shimadzu TOC-VCPH Analyzer on March 17-30, 2011. All six additives (e.g., AC, Penetrol, EZ-Mud Gold, Dense Soda Ash, Quick-Gel, and Quik-Trol Gold) were analyzed.
- Glycols were analyzed by an unspecified method on an unspecified date. Only three of the six additives (e.g., AC, Penetrol, and EZ-Mud Gold) were analyzed.
- Chemical characterization of the dense soda ash, Quik-Trol Gold, and Quik Gel were not completed apparently because "dissolved organic concentrations were low..." as stated in the USEPA report. Analyses of the dense soda ash, Quik-Trol Gold, and Quik Gel should be completed for all target organic compounds and all additives should be analyzed for SVOCs, GRO, and DRO.

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

No comments at this time.

Section 3.0: Results and Discussion

Inorganic Geochemistry

The following comments are provided:

- The discussion on page 20, first full paragraph states the "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)." The following comments are provided:

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- If samples were aqueous, please explain how a solid unit (i.e., mg/kg) can be used? Was this a typo?
- It does not appear the assumption that 94% of the total alkalinity is hydroxide alkalinity been confirmed by completing analytical testing. USEPA should analyze for total alkalinity in the laboratory using a titration method such as SM 2320B, then using appropriate calculation to determine hydroxide alkalinity where hydroxide [OH–] alkalinity is present if phenolphthalein alkalinity is more than half the total alkalinity). The results obtained will assist with confirming the results obtained using the balance equation discussed in the report. Clarification is requested.
- It was suggested the elevated pH in MW01 and MW02 is due to addition of a strong base. Please provide more detailed evidence to support this assumption.

Organic Geochemistry

The following comments are provided:

- Many of the comments in this section are factually correct under very specific conditions, there is a lack of definitive sample-specific data to support the assumptions being made.
- USEPA states, "a wide variety of organic chemicals were detected in the monitoring wells…" The data have not been subjected to external peer review (e.g., verified and validated by an independent third-party), therefore, any definitive conclusions should to be made with care and be clearly stated in the report.
- USEPA states three glycol compounds were detected in several domestic wells, but then later dismisses these detections as likely false positives on page 27. As such, the reference to the detection of glycols should be removed or the interpretation they were reported as a false positive should be made in the first paragraph for accuracy. Further, all interpretations and assumptions made on the detection of glycols should be removed from the report. The detection of glycols in MW01 and MW02 reported using HPLC/MS/MS appear to be valid, but additional confirmatory analyses should be completed.
- USEPA states that "detections are more numerous and exhibit higher concentration in the deeper of the two monitoring wells…" is tentative at this time until all data are properly verified, validated, and qualified.
- USEPA states that due to breakdown of BTEX and glycols, that acetate and benzoic acid are "more enriched" the shallower of the two the monitoring wells, suggesting and upward/lateral migration with natural degradation and accumulation of daughter products (Corseuil et. al. 2011, Caldwell and Suflita 2000, Dwyer and Tiedje 1983)." It is factually correct that under very specific circumstances, the presence of acetate and benzoic may be the result of breakdown of such compounds as BTEX and glycols, however, no direct evidence has been presented at this time substantiating this breakdown pathway. The presence of benzoic acid and acetate could be due naturally occurring substances that may be present. Further explanation and supporting documentation should be provided to justify the reasons for the possible presence of benzoic acid and acetate.
- The USEPA states the detection of compounds associated with petroleum additives in groundwater would be "manifested as GRO, DRO, BTEX, naphthalenes, and trimethylbenzenes observed in deep monitoring wells." Until all data have been

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subjected to a rigorous data verification and data validation review, this statement may not be factually correct.

- ACF analytical methods should be considered to verify the absence and/or presence of GRO and DRO.
- The results reported for the glycols in Table 3 should be noted at being obtained for the HPLC/MS/MS method.
- The result's reported for GRO in samples MW01 and DRO in samples MW01 and MW02 reported in Table 3 should be qualified in some manner to indicate these data are not representative of gasoline or a diesel fuel.
- It is not clear if the information summarized in Table 4 is based on factual knowledge of the constituents present in the hydraulic fracturing fluid used at the Pavillion site or is from a search of the literature. The text referencing this table on page 23 is not clear. Further details documenting the source of information presented in Table 4 and if all of these chemicals were actually used at the site should be provide for clarity.
- The elimination of natural gas condensates as the possible source of BTEX (when, and if, it may be present) cannot be definitely ruled out at this time based on only two samples collected on two occasions from the two deep monitoring wells installed.
- The statement that GRO and DRO were detected in 23 of 28 domestic well samples may be incorrect (or biased) based on the limited review of the chromatographic data. Interpretation that is more detailed and qualification of the sample data should be completed. In addition, ACF analytical methods should be considered to verify the absence and/or presence of GRO and DRO.
- The statement that trace levels of exotic organic compounds present in some samples may not completely correct until a thorough data verification and validation review is completed.
- The comment that "foul odors associated with some domestic wells correlate with the detections of GRO and DRO" may be premature. As previously stated the presence of GRO and DRO is not definitive at this time until a thorough review of all sample chromatograms, VOC, and SVOC data is completed. There are other potential factors that can cause a foul odor and taste such as the presence of bacteria, high TDS, elevated concentrations of sulfide, and/or leaching of chemicals present in from well materials. Section 4.0: Conclusions

At this time it is premature to make any comments on this section until the document has been peer reviewed and corrections made to various sections based on comments from all reviewers.

4.0 Specific Comments on EPA Monitoring Well Drilling Information

Comments regarding the monitoring well drilling additive information presented in the report is discussed below.

4.1 Monitoring Well Drilling Additives Sample Results

The USEPA conducted some testing of the monitoring well drilling additives. The drilling additives were extracted in water (source not specified) in a higher concentrated mixture than recommended; see www.epa.gov/region8/superfund/wy/pavillion/docs.htm 1 and the file titled "Monitoring Well Drilling Additive Analysis, November 17, 2011 (PDF, 1 pg, 24K). Results for the analyses completed can be found at the same URL and include Sample Results ICP-OES, March 24, 2011 (PDF, 5 pp, 59K); Sample Results TC, TIC, TOC, NPOC, April 6, 2011 (PDF, 5 pp, 49K); Sample Results Headspace GPLC (chloride and sulfate), May 25, 2011 (PDF, 3 pp, 42K); Sample Results GCP&T OI, July 19, 2011 (PDF, 9 pp, 69K); Sample Results Headspace GC/MS, July 22, 2011 (PDF, 20 pp, 148K).

Of the analyses completed, the most notable results were reported for VOCs by head space GC/MS (see file name SampleResults_8OA778SF_SS6163_23993_07-21 -11_Headspace.pdf on the USEPA website). These analyses were completed in July 2011 after the Phase IV sampling event. The data reported are from a concentrated preparation of the drilling additive(s) and water from an unspecified source, and included preparation of AC [i.e., aqua clear], AC L ab Dup, Penetrol, and EZ Mud Gold. There are also data reported for two unknown samples (i.e., PAV 01 , and PAV 02) which has not been described (or summarized) in the report. Only selected analyses were completed on these additive samples (see Table 2 of USEPA report). Several alcohol compounds, BTEX, and other VOCs were reported as detected in PAV 01 and/or PAV 02, some at very high concentrati ons; the most significant detections are from the analysis of PAV 02. The significance of these data is unknown because no additional information has been provided regarding these two samples. A deseri ption of samples PAV 01 and PAV 02 and their pertinence to the investigation are necessary.

Organic chemical characterization of the dense soda ash, Quik Gel, and Quik-Trol Gold were not completed organic compounds because "dissolved orga nic concentrations were low..." as stated in the report. Analyses of the dense soda ash, Quik Gel, and Quik-Trol Gold should be completed for all target organic compounds and all additives should be analyzed for SVOCs, GRO, and DRO. In addition, a complete mixture of all additives should be prepared and analyzed for all constituents of concern.

5.0 Specific Comments on Analytical Methodology Used by Robert S. Kerr Laboratory (as posted on website)

The USEPA acknowledges that several of the analytic al method standard operating procedures (SOPs) that were used to complete some chemical analyses were not official EPA methods or were they subjected to required peer review.

USEPA noted in the SOPs listed below the following: "This Standard Operating Procedure has been prepared for the use of the Ground Water and Ecosys tem Restoration Division (GWERD) of the U.S. Environmental Protection Agency and may not be specifically applicable to the activities of other organizations. **THIS IS NOT AN OFFICIAL EPA APPROVED METHOD.** This document has not been through the Agency's peer review process or ORD clearance process."

The comment above is applicable to the following SOPs:

- RSKSOP112v6: SOP for Quantitative Analysis of Low Molecular Weight Acids in Aqueous Samples by HPLC, February 2011 (PDF, 22 pp, 95K).

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- RSKSOP175v5: SOP for Sample Preparation and Calculations for Dissolved Gas Analysis in Water Samples Using a GC Headspace Equilibration Technique, October 2010 (PDF, 33 pp, 297K).
- RSKSOP194v4: SOP for Gas Analysis by Micro Gas Chromatograph (Agilent Micro 3000), April 2010 (PDF, 13 pp, 65K).
- RSKSOP213v4: SOP for Operation of Perkin Elmer OPTIMA 3300 DV ICP-OES, September 2009 (PDF, 22 pp, 78K).
- RSKSOP214v5: SOP for Quality Control Procedures for General Parameters Analyses Using Lachat Flow Injection Analyses (FIA), March 2010 (PDF, 10 pp, 49K).
- RSKSOP257v3: SOP for Operation of Thermo Elemental PQ Excell ICP-MS, February 2011 (PDF, 16 pp, 80K).
- RSKSOP259v1: SOP for Determination of Volatile Organic Compounds (Fuel Oxygenates, Aromatic and Chlorinated Hydrocarbons) in Water Using Automated Headspace Gas Chromatography/Mass Spectrometry (Tekmar 7000 HS-Varian 2100T GC/MS System-Ion Trap Detector), November 2007 (PDF, 28 pp, 292K).
- RSKSOP276v3: SOP for Determination of Major Anions in Aqueous Samples Using Capillary Ion Electrophoresis with Indirect UV Detection and Empower 2 Software, April 2008 (PDF, 11 pp, 46K).
- RSKSOP296v1: SOP for Determination of Hydrogen and Oxygen Isotope Ratios in Water Samples Using a High Temperature Conversion Elemental Analyzer (TC/EA), a Continuous Flow Unit, and An Isotope Ratio Mass Spectrometer (IRMS), September 2010 (PDF, 8 pp, 48K).
- RSKSOP297v1: SOP for Metals Speciation Determination by LC/ICP-MS, August 2008 (PDF, 21 pp, 89K).
- RSKSOP298v1: SOP for Arsenic Speciation Determination by LC/ICP-MS with Anion Suppression and NaOH Mobile Phase, November 2009 (PDF, 21 pp, 452K).
- RSKSOP299v1: SOP for Determination of Volatile Organic Compounds (Fuel Oxygenates, Aromatic And Chlorinated Hydrocarbons) in Water Using Automated Headspace Gas Chromatography/Mass Spectrometry (Agilent 6890/5973 Quadrupole GC/MS System), March 2008 (PDF, 25 pp, 278K).
- RSKSOP313v1: SOP for Determination of R-123 Using the H25-IR Infrared Refrigerant Gas Leak Detector, May 2010 (PDF, 13 pp, 194K).
- RSKSOP314v1: SOP for Determination of Fixed Gases Using the GEM2000 and GEM2000 Plus Gas Analyzers & Extraction Monitors, May 2010 (PDF, 13 pp, 84K).
- RSKSOP320v1: SOP for Determination of Organic and Inorganic Vapors Using the TVA-1000B Toxic Vapor Analyzer, September 2010 (PDF, 18 pp, 211K).
- RSKSOP330: SOP for Determination of Various Fractions of Carbon in Aqueous Samples Using the Shimadzu TOC-VCPH Analyzer, March 2011 (PDF, 15 pp, 78K).

While the SOPs listed above may be capable of generating acceptable data, the results reported may be biased until they are subjected to a thorough technical review, are reproducible by commercial laboratories, and are officially approved. If any SOP is equivalent to EPA approved methods (e.g., SW-86 methods [U.S. EPA 2011b]), then this information, along with the similarities and differences between like methods, should be summarized.

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If a laboratory uses a nonstandard or unapproved method USEPA requires the data user to "provide method validation data to confirm that it will be adequate for the intended use of the data" (U.S. EPA 2002c). Information that should be reported with the data would include "determination of detection limits, quantitation limits, typical recoveries, and analytical precision and bias" (U.S. EPA 2002c). The evaluation of such data will "indicate the laboratory's ability to demonstrate control of the method and document the quality of the data obtained" (U.S. EPA 2002c). In addition, these SOPs listed above should be subjected to a thorough internal and external review and verified by using outside commercial analytical laboratories.

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This concludes the preliminary QA/QC review of the information documented in the USEPA *Draft, Investigation of Ground Water Contamination near Pavillion, Wyoming* report (U.S. EPA 2011b) and associated supporting information accessed online.

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ATTACHMENT 1

For data to be usable for its intended purpose(s), it must be of sufficient quality and quantity to know that the decisions that are made have an acceptable and known degree. A detailed discussion of these topics is beyond the scope or need of this preliminary data review; therefore, a brief summary of some of the elements regarding QA/QC processes and procedures, data verification, data validation, DQA, and data usability evaluation are provided below for consideration.

Brief Overview of QA/QC Processes and Procedures

There are essentially three "basic" components to be completed for any project, which lead to a specific end-product and/or decision. These are systematic planning, implementation and oversight, and data assessment. Each of these components is dependent on the others and each component must be completed every time in order to be confident that the right type and quality of the information obtained is usable for its intended purpose(s). Appropriate decisions (or end uses of the data) are made with an acceptable degree of confidence by knowing, in part, the following: 1) the purpose of the project was clearly stated; 2) appropriate DQOs were established; 3) proper types and numbers of samples were collected, that sampling locations were appropriate, and that correct sample collection techniques were used; 4) that appropriate analytical methods were used and the analyses were completed properly; 5) data verification and data validation were properly completed and that the overall quality of the data and its limitations were clearly documented); 6) the data sets were subjected to a proper DQA and data usability evaluation and the findings documented in a report; and, 7) confirming the findings and the decision(s) made were correct.

Proper planning is essential – the overall objectives of the project should be clearly stated and understood by all team members (e.g., project mangers and staff, field sampling team members, applicable laboratory staff, and QA/QC personnel). Existing data should be thoroughly reviewed to assess its quality and usefulness, and to help identify data gaps that may need to be filled to meet project objectives. Logical and attainable DQOs (including project quality objectives [PQOs] and measurement quality objectives [MQOs]) should be established. Pertinent documents (e.g., the work plan, field sampling plan, and quality assurance project plan) should be prepared. Appropriate field sampling design (e.g., location, number, and type of samples) and sampling techniques should be determined. The most appropriate analytical methods should be selected to try to meet the established DQOs, PQOs, MQOs, reporting limit requirements, and data quality indicators (DQIs) (e.g., U.S. EPA 2005); DQIs would be end-point measurements for precision, accuracy, representativeness, comparability, completeness, and sensitivity.

Sound science and well-defined QA/QC processes and procedures should be used at all times to provide confidence, with a known degree of certainty, in the overall quality (or usefulness) and potential limitations of the data that is collected. Using data of poor quality and of insufficient quantity will result in making incorrect decisions and incurring unnecessary expenses. A brief description of QA/QC processes and procedures, data verification, data validation, DQA, and data usability evaluation is provided below.

Systematic Planning

Systematic planning is a process that follows "common sense," can be used in a graded approach, and is based on following the scientific method. Implementing this process is necessary to make sure an

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appropriate level of "checks and balances" have been defined and followed to be confident with an acceptable degree of uncertainty that the intended end-use goal(s) of a project have been met.

Some of the items required for the systematic planning process to be effective include, but are not limited to, the following:

- Establish appropriate, attainable, and well defined DQOs or PQOs following the 7-Step DQO process (U.S. EPA 2006a). This is the time to define the qualitative and quantitative objectives of the project (i.e., define the problem), define the appropriate type, quantity and quality of data that will be needed and to specify tolerable limits of potential decision errors that can be used that will permit answering specific questions and support the decisions that may be made.
- Make sure the sampling rationale and design are appropriate to meet the needs of the project.
- Develop logical performance criteria (i.e., the type, quantity, and quality of data that should be collected to meet the intended purpose(s) of the project.
- Define appropriate MQOs that will specify the quantitative acceptance criteria to be used to assess the overall quality of applicable DQIs (e.g., precision, accuracy, representativeness, completeness, comparability, and sensitivity).
- Prepare applicable technical documents such as a work plan, FSP, and QAPP.
- Define the type and level of technical QA/QC oversight and associated tasks (e.g., data verification, data validation, and DQA and usability evaluation) that will be completed to be able to assess and define the overall quality, limitations, and ultimate usability (reliability) of the data gathered.

Using the systematic planning approach results in establishing and defining appropriate management and scientific elements that result in a project's logical development, efficient use of time and money, transparency of intent and direction, soundness of project conclusions, and proper documentation to allow determination of appropriate level of peer review.

Data Verification, Data Validation, DQA, and Usability Assessment

Data verification is essentially a process for evaluating the completeness, correctness, consistency, and conformance (or compliance) of the data against the method, procedural, and/or contractual requirements that were established during the systematic planning stage. The specific details of how data verification is to be completed should be specified in documents such as the FSP and QAPP.

Data validation is basically an analyte- and sample-specific process that extends the evaluation of data beyond method, procedural, or contractual compliance (i.e., data verification) to determine the analytical quality of a specific data set. One of the primary purposes of data validation is to assess the overall quality of the data and to identify whether the results are meaningful, and valid. Data validation is a sampling and analytical process evaluation that includes evaluating compliance with methods, procedures, or contracts, and comparison with criteria based upon the quality objectives developed for the project. There are several USEPA guidance documents (e.g., U.S. EPA 1992, 2002b, 2008, 2010) that describe how to complete data validation should be referred to when completing this type of task. Some of the information that would be reviewed during data validation is summarized below.

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Example of Data Validation Procedures

Data validation procedures include evaluating the sample results and applicable quality control results reported by the laboratories. Non-CLP generated analytical data should be validated generally following the applicable guidance specified in such documents as:

- USEPA Contract Laboratory Program, national functional guidelines for superfund organic methods data review (U.S. EPA 2008).
- USEPA Contract Laboratory Program national functional guidelines for inorganic data superfund data review (U.S. EPA 2010).
- Guidance on Environmental Data Verification and Validation (U.S. EPA 2002b).
- In the context of method-specific, laboratory-established quality control requirements, and requirements specified in such documents as Field Sampling Plan (FSP) and/or QAPP, as applicable. Data validation procedures will need to be modified to accommodate QA/QC requirements for those analyses that are not specifically addressed by the applicable USEPA national functional guidelines or other guidance documents that may be used.

The results reported for the field, field quality control samples, and applicable quality control measurement data should be verified and validated, and should include a review of at least the following:

- Case narratives discussing analytical problems (if any) and procedures.
- Chain-of-custody documentation to verify completeness of the data set.
- Sample preparation logs or laboratory summary result forms to verify analytical holding times were met.
- Results for applicable instrument tuning, initial calibrations, and continuing calibration verification results to assess instrument performance.
- Results for applicable instrument blanks (i.e., initial calibration blanks and continuing calibration blanks), method blanks, trip blanks, and field blanks to determine whether an analyte reported as detected in any sample was the result of possible contamination introduced at the laboratory, during transport of samples, or during field sampling, respectively.
- Results for applicable internal standards performance to ensure that instrument sensitivity and response were stable during the analysis of the samples.
- Results for applicable method-specific quality control measurements (e.g., serial dilutions and interference check samples for metals analyses and dual column confirmation results for applicable organic compound analyses) to assess potential matrix interference effects.
- Results for applicable surrogate compound (or system monitoring compound for VOC analyses), laboratory control sample (LCS) (e.g., blank spike), duplicate LCS, matrix spike (MS), and matrix spike duplicate (MSD) recoveries to assess analytical accuracy.
- Results for applicable duplicate LCS and MSD analyses to assess analytical precision.

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- Results for the field duplicate samples to provide additional information in support of the quality assurance review.
- A review of instrument printouts (e.g., chromatogra ms, mass spectra, and quantification reports) to assess the validity of the qualitative analysis of the data to verify proper compound identifications have been made and to assess whether results may have been reported as a false negative or false positive.
- Verifying quantification of sample results and applicable quality control measurement (e.g., instrument calibrations; surroga te, MS/MSD, and LCS recoveries; and other applicable information for accuracy and precision) are accurate by recalculation.
- Review of all laboratory summaries of analytical results to verify completeness.

Performance based control limits established by the laboratory and control limits provided in the method protocols should be used to evaluate data quality and determine the need for qualification of affected results. Data qualifiers (e.g., J, UJ, U, R, NJ) should be assigned during validation when applicable QC measurement criteria are not met. The results of all verified and validated data should be documented and summarized in report or table.

DQA and usability evaluation (or assessment) is ess entially a scientific and statistical assessment of the data to determine if the overall objectives establi shed for the project have been met and if the data are of the right type, quality, and quantity to support their intended use(s) (U.S. EPA 2006b). This process is based on a fundamental premise that data quality is meaningful only when it relates to the intended use of the data and to help identify data deficiencies that may affect the interpretation and usability of th e data acquired. A "#$%&'&()! $##*##+*, (! &#! #&+-')! $, . ! evaluation of data based upon the results of data validation and verification for the decisions being made. In the usability step, reviewers assess whet her the process execution and resulting data meet quality objectives based on criteria established for the project and/or in the QAPP. DQA and usability evalu ation, in the strictest sense defined by USEPA (U.S. EPA 2006b), is completed using five steps and is an iterative process that involves the use of statist ical and graphical tools, for example, to determine if the data are of appropriate quality with a known degree of confidence (or uncertainty) and that the data can be used for its intended purpose(s). By completin g a DQA and usability evaluation, it can be determined with a greater degree of confidence if the overall objectives established for the project have been me t and if the data are of the right type, quality, a nd quantity to support their intended use(s)

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ATTACHMENT 2

GRO means Gasoline Range Organics and DRO means Diesel Range Organics. Does this mean that GRO results imply that gasoline (e.g. automotive gasoline) or that DRO results imply a diesel fuel product (such as fuel oil #1 or fuel oil #2) is present in the sample or does it mean something else? It is important to have clear understanding of what is meant by GRO and DRO. A brief discussion for information purposes is provided below.

Basic Introduction to "GRO" and "DRO"

Analyses for GRO and DRO were completed using SW-846 Method 8015D (U.S. EPA 2011b). This method states the following in Section 1.2.2:

> "GRO corresponds to the range of alkanes from C6 to C10 and covering a boiling point range of approximately 60#C – 170#C (Reference 6). DRO corresponds to the range of alkanes from C10 to C28 and covering a boiling point range of approximately 170#C – 430#C (Reference 6). The quantitative analyses of these fuel types are based on the procedures described in Sec. 11.11. The identification of specific fuel types may be complicated by environmental processes such as evaporation, biodegradation, or when more than one fuel type is present. Methods from other sources may be more appropriate for GRO and DRO, since these hydrocarbons are not regulated under RCRA. Consult State and local regulatory authorities for specific requirements."

Section 1.2.2 of this method clearly refers to fuel types, thus inferring a gasoline or diesel product. GRO is a qualitative and quantitative method for the analysis of volatile petroleum products (e.g., gasoline) that would include petroleum products such as aviation fuel, automotive gasoline(s), mineral spirits, stoddard solvent, naphtha, and natural gas condensates. DRO is a qualitative and quantitative method for semivolatile petroleum products (e.g., various diesel fuels) that would include petroleum products such as some jet fuels, kerosene, diesel fuels (e.g., diesel #1 and diesel #2).

Additional discussion of petroleum fuel products from other outside sources is summarized below for illustrative purposes.

Agency for Toxic Substances and Disease Registry (ATSDR)

ATSDR (ASTDR 1995) defines gasoline as the following:

> "Gasoline is a refined product of petroleum consisting of a mixture of hydrocarbons, additives, and blending agents. The composition of gasolines varies widely, depending on the crude oils used, the refinery processes available, the overall balance of product demand, and the product specifications. The typical composition of gasoline hydrocarbons (% volume) is as follows: 4-8% alkanes; 2-5% alkenes; 25-40% isoalkanes; 3-7% cycloalkanes; 1-4% cycloalkenes; and 20-50% total aromatics (0.5-2.5% benzene) (IARC 1989). Additives and blending agents are added to the hydrocarbon mixture to improve the performance and stability of gasoline (IARC 1989; Lane 1980). These compounds include anti-knock agents, anti-oxidants, metal deactivators, lead scavengers, anti-rust agents, anti-icing agents, upper-cylinder lubricants, detergents, and dyes (IARC 1989; Lane 1980). At the end of the production process, finished gasoline typically contains more than 150 separate compounds although as many as 1,000 compounds have been identified in some blends (Domask 1984; Mehlman 1990). Information regarding the chemical identity of gasoline is located in Table 3-1."

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ATSDR (ASTDR 1999) also defines types of "GRO" as follows:

"**Automotive Gasoline.** Automotive gasoline is a mixture of low-boiling hydrocarbon compounds suitable for use in spark-ignited internal combustion engines and having an octane rating of at least 60. Additives that have been used in gasoline include alkyl tertiary butyl ethers (e.g. MTBE), ethanol (ethyl alcohol), methanol (methyl alcohol), tetramethyl-lead, tetraethyl-lead, ethylene dichloride, and ethylene dibromide.

Other categories of compounds that may be added to gasoline include anti-knock agents, antioxidants, metal deactivators, lead scavengers, anti-rust agents, anti-icing agents, upper-cylinder lubricants, detergents, and dyes (ATSDR 1995a).

Automotive gasoline typically contains about 150 hydrocarbon compounds, though nearly 1,000 have been identified (ATSDR 1995a). The relative concentrations of the compounds vary considerably depending on the source of crude oil, refinery process, and product specifications. Typical hydrocarbon chain lengths range from C4 through C12 with a general hydrocarbon distribution consisting of 4-8% alkanes, 2-5% alkenes, 25-40% isoalkanes, 3-7% cycloalkanes, 1-4% cycloalkenes, and 20-50% aromatics (IARC 1989a). However, these proportions vary greatly. Unleaded gasolines may have higher proportions of aromatic hydrocarbons than leaded gasolines.

Table E-1.b (Appendix E) presents ranges and weight percentage means for a representative subset of the hydrocarbon compounds identified in gasoline. In cases where data are not available, the range and mean are left blank."

"**Stoddard Solvent.** Stoddard solvent is a petroleum distillate widely used as a dry cleaning solvent and as a general cleaner and degreaser. It may also be used as a paint thinner, as a solvent in some types of photocopier toners, in some types of printing inks, and in some adhesives. Stoddard solvent is considered to be a form of mineral spirits, white spirits, and naphtha; however, not all forms of mineral spirits, white spirits, and naphtha are considered to be Stoddard solvent (ATSDR 1995b).\

Stoddard solvent consists of 30-50% linear and branched alkanes, 30-40% cycloalkanes, and 10-20% aromatic hydrocarbons. Its typical hydrocarbon chain ranges from C7 through C12 in length. Although a complete list of the individual compounds comprising Stoddard solvent is not available (Air Force 1989) some of the major components are presented in Table E-2.b (Appendix E). Alcohols, glycols, and ketones are not included in the composition, as few, if any, of these types of compounds would be expected to be present in Stoddard solvent (ATSDR 1995b). Possible contaminants may include lead (<1 ppm) and sulfur (3.5 ppm)."

"**Jet Fuel.** Jet fuels are light petroleum distillates that are available in several forms suitable for use in various types of jet engines. The exact compositions of jet fuels are established by the U.S. Air Force, using specifications that yield maximum performance by the aircraft. The major jet fuels used by the military are JP-4, JP-5, JP-6, JP-7, and JP-8. Briefly, JP-4 is a wide-cut fuel developed for broad availability in times of need. JP-6 is a higher cut than JP-4 and is characterized by fewer impurities. JP-5 is specially blended kerosene, and JP-7 is a high flash point special kerosene used in advanced supersonic aircraft. JP-8 is a kerosene modeled on Jet A-1 fuel (used in civilian aircraft). For this profile, JP-4 will be used as the prototype jet fuel due to its broad availability and extensive use.

Typical hydrocarbon chain lengths characterizing JP-4 range from C4 to C16. Aviation fuels consist primarily of straight and branched alkanes and cycloalkanes. Aromatic hydrocarbons are limited to 20-25% of the total mixture because they produce smoke when burned. A maximum of 5% alkenes are

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allowed in JP-4 (ATSDR 1995c). The approximate distribution by chemical class is: 32% straight alkanes, 31% branched alkanes, 16% cycloalkanes, and 21% aromatic hydrocarbons (ABB Environmental 1990). The typical hydrocarbon composition of JP-4 is presented in Table E-3.b (Appendix E)."

ATSDR (ASTDR 1999) defines types of "DRO" as follows:

"**Fuel Oil #1.** Fuel oil #1 is a petroleum distillate that is one of the most widely used of the fuel oil types. It is used in atomizing burners that spray fuel into a combustion chamber where the tiny droplets burn while in suspension. It is also used as a carrier for pesticides, as a weed killer, as a mold release agent in the ceramic and pottery industry, and in the cleaning industry. It is found in asphalt coatings, enamels, paints, thinners, and varnishes.

Fuel oil #1 is a light petroleum distillate (straight-run kerosene) consisting primarily of hydrocarbons in the range C9-C16 (ATSDR 19958). Fuel oil #1 is very similar in composition to diesel fuel oil #1: the primary difference is in the additives. The typical hydrocarbon composition of fuel oil #1 is presented in Table E-4.b (Appendix E)."

"**Fuel Oil #2.** Fuel oil #2 is a petroleum distillate that may be referred to as domestic or industrial. The domestic fuel oil #2 is usually lighter and straight-run refined; it is used primarily for home heating and to produce diesel fuel #2. Industrial distillate is the cracked type, or a blend of both. It is used in smelting furnaces, ceramic kilns, and packaged boilers (ABB Environmental 1990).

Fuel oil #2 is characterized by hydrocarbon chain lengths in the C11-C20 range, whereas diesel fuels predominantly contain a mixture of C10-C19 hydrocarbons (ATSDR 1995g). The composition consists of approximately 64% aliphatic hydrocarbons (straight chain alkanes and cycloalkanes), 1-2% unsaturated hydrocarbons (alkenes), and 35% aromatic hydrocarbons (including alkylbenzenes and 2-, 3-ring aromatics) (Air Force 1989). Fuel oil #2 contains less than 5% polycyclic aromatic hydrocarbons (IARC 1989b). The typical hydrocarbon composition of fuel oil #2 is presented in Table E-4.b (Appendix E)."

"**Fuel Oil #6.** Fuel oil #6 is also called Bunker C or residual. It is the residual from crude oil after the light oils, gasoline, naphtha, fuel oil #1, and fuel oil #2 have been fractioned off. Fuel oil #6 can be blended directly to heavy fuel oil or made into asphalt. It is limited to commercial and industrial uses where sufficient heat is available to fluidize the oil for pumping and combustion (ABB Environmental 1990)."

Washington Department of Ecology, Analytical Methods for Petroleum Hydrocarbons

The NWTPH method (Ecology 1997) uses the following explanation:

- "NWTPH-Gx is the qualitative and quantitative method (extended) for volatile ("gasoline") petroleum products in soil and water. Petroleum products applicable for this method include aviation and automotive gasolines, mineral spirits, stoddard solvent and naphtha."
- "NWTPH-Dx is the qualitative and quantitative method (extended) for semi-volatile ("diesel") petroleum products in soil and water. Petroleum products applicable for this include jet fuels, kerosene, diesel oils, hydraulic fluids, mineral oils, lubricating oils and fuel oils."

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As is evident from the descriptions provided, "GRO" and "DRO" includes several types of petroleum products. It is, therefore, critical that USEPA clarify what they are defining as GRO and DRO, what are the qualitative and quantitative procedures that were used, a description of the potential bias of this data (e.g., agreement or lack of agreement of sample data to the standards used for assessment), and other specific details..

Analysis of GRO and DRO

General Information

SW-846 Method 8015D is one method that can be used for the determination of ~C_5 to C_{12} gasoline range organics (GROs) and ~C_6 to C_{32} diesel range organics (DROs). Analysis for GRO is completed by purge and trap and analysis using a GC/PID and GC/FID. Analysis for DRO is based on a solvent extraction and analysis by GC/FID.

The calibration of GRO and DRO is markedly different from that for single-component analytes. In particular, the response used for calibration must represent the entire area of the chromatogram within the retention time range for the fuel type (GRO or DRO), including the unresolved complex mixture (UCM) that lies below the individual peaks (See Sec. 11.11 for information on calculating this area in SW-846 Method). SW-846 Method 8015D states in section 11.3.3.1, that for each fuel type, calibration standards should be prepared at a minimum of five different concentrations with one of the standards at a concentration at or below the quantitation limit necessary for the project. The concentrations of the other standards should be throughout the range of concentrations expected to be found in samples analyzed (or should define the working range of the detector).

SW-846 Method 8015D specifically states that "Whenever possible, the calibration should be performed using the specific fuel that is contaminating the site (e.g., a sample of the fuel remaining in the tank suspected of leaking). Where such samples are not available or not known, use recently purchased commercially-available fuel. A qualitative screening injection and GC run may be performed to identify unknown fuels." In section 11.4.2, SW-846 Method 8015D, the retention time range for GRO is defined using two specific gasoline components (i.e., 2-methylpentane and 1,2,4-trimethylbenzene). In section 11.4.3 of SW-846 Method 8015D, the retention time range for DRO is established from the retention times of the C10 and C 28 alkanes.

This method also states in Section 11.6.5 that "The identification of fuels, especially gasoline, is complicated by their inherent volatility. The early eluting compounds in fuels are obviously the most volatile and the most likely to have weathered unless the samples were taken immediately following a spill. The most highly volatile fraction of gasoline constitutes 50% of the total peak area of a gasoline chromatogram. This fraction is the least likely to be present in an environmental sample or may be present at only very low concentration in relation to the remainder of a gasoline chromatogram."

Potential Interferences

During analysis, matrix interferences that may be present can significantly bias the data. SW-846 Method 8015D states in section 4.4 (U.S. EPA 2011b) that "The flame ionization detector (FID) is a non-selective detector. There is a potential for many non-target compounds present in samples to interfere with this analysis. There is also the potential for analytes to be resolved poorly, especially in samples that contain many analytes. The data user should consider this and may wish to alter the target analyte list accordingly." The type and extent of matrix interference will vary considerably from one source to

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another depending upon the nature and diversity of the site being sampled and may include certain solvents, halogenated hydrocarbons and phthalate esters.

Cleanup of sample extracts is often necessary to remove or minimize interferences caused by the presence of non-target analytes in order to permit reliable qualitative identification of target analytes and accurate quantification of the concentration of the target analytes. Interferences may be from the presence of various natural and/or man-made organic chemicals also present in the matrix, during transport of the samples, and/or introduced at the laboratory during processing and analysis of the samples. Cleanup of samples analyzed for "DRO" is often a necessity, usually using silica gel. The purpose of the silica gel cleanup procedure is to remove as many non-petroleum hydrocarbon interferences (often of biogenic origin) that may be present in the sample. This cleanup step helps to minimize any potential positive bias (e.g., reporting of false positives and the reporting of concentrations that are actually lower than are quantified if cleanup has not been completed) that may be associated with the results reported. Additional cleanup procedures, such as alumina, may also be used to further minimize non-target analyte interferences.

Qualitative Identification and Quantification

Qualitative identification is typically based on comparison of the sample chromatograms to those of the standards used during analysis and is often referred to as "fingerprint matching." SW-846 Method 8015D is very specific concerning qualitative identification criteria that must be used for GRO and DRO analyses other than using retention time windows for the first and last eluting peaks within the GRO and DRO range. The method is clear in stating that calibration should be performed using the specific fuel that is contaminating the site.

Often, if gasoline is present in a sample, it will match the profile of the standard unless significant weathering has occurred, but generally the compounds eluting between toluene and naphthalene are usually present if the sample contains gasoline. It should be noted that if specific petroleum product identification cannot be made, an analyst usually should quantitate the samples using the calibration curve of the petroleum product that most closely resembles that of the sample. Other methods (Ecology 1997) state that if petroleum products cannot be identified quantification should be made with the gasoline calibration curve; however, "the term "gasoline range" hydrocarbons, or derivations of it, should not be used when reporting the petroleum values unless the analyst is unable to identify the petroleum product present."

The data reported by USEPA reference GRO as "TPH as gasoline" in all laboratory data summaries and used gasoline as the calibration standard. For the analysis of DRO, the USEPA reported the results as "diesel range organics" and based all quantifications using a diesel #2 product as the standard. A detailed description of how the USEPA is defining, qualitatively identifying, and quantifying GRO and DRO is requested.

ACF analytical methods should be considered to more definitively verify the absence and/or presence of GRO and DRO in all samples. Examples of ACF analyses would include such analyses for PIANO (i.e., Paraffins [straight-chain alkanes)], Isoparaffins [branched alkanes], Aromatics, Naphthenes [cycloalkanes], and Olefins [alkenes]; aliphatic hydrocarbons (i.e., the normal alkanes from n-C_{10} to n-C_{32}, pristane, and phytane), and total resolved and unresolved complex mixtures by GC/FID; PAHs and alkylated PAHs by GC/MS operated in the selected ion monitoring mode (SIM); biomarker compounds such as steranes and terpanes by GC/MS SIM, and a full GC/MS scan for petroleum-related compounds (e.g., n-alkanes, isoalkanes, isoprenoids, alkylcyclohexanes, alkybenzenes, and bicyclanes within the C10 to C40 range).

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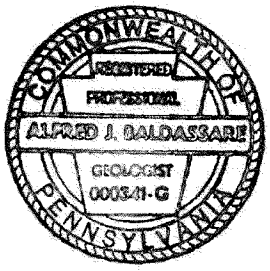
EPA Draft Report – December 2011
Investigation of Groundwater Contamination Near Pavillion, Wyoming

Prepared by:

Fred Baldassare, P.G.
Owner/Sr. Geoscientist

ECHELON
Applied Geoscience Consulting

March 27, 2012



EPAPAV0050458

Executive Summary

As a result of objectionable taste and odor complaints from groundwater in domestic water supply wells reported in early 2008 by homeowners near Pavillion, Wyoming, USEPA (EPA) completed a retrospective groundwater investigation of the area. The investigation revealed various VOC's, SVOC's, and methane among the contaminants in the groundwater. This report is relative only to EPA's draft interpretations and conclusions regarding methane/ethane in the groundwater.

The EPA investigation essentially concludes that thermogenic gas discovered in the groundwater has a similar stable carbon and hydrogen isotope composition of nearby operating gas wells, and therefore, the source of gas in the water supplies must be from area gas wells.

EPA's conclusions regarding the sources of methane/ethane in the groundwater are not supported by the data or their investigation as provided in the December 2011 draft Report. Specifically:

- EPA's draft conclusions are dismissive of important evidence that reveals 1) thermogenic methane occurs as a natural condition and secondarily 2) possibly the result of legacy gas well conditions for wells drilled in the field beginning in the 1950's.

- Isotope data suggests some oxidation of the gas in the shallow system; however, dissolved inorganic carbon (DIC) isotope data that do not corroborate this pathway are not discussed by EPA.

- EPA cites higher methane concentrations in groundwater at water wells in closer proximity to gas wells as a line of evidence indicating impact from area gas wells. This link is neither scientifically valid nor substantiated by EPA's investigation. Definition of the hydrogeological system and time series monitoring are necessary to interpret methane concentrations in an aquifer system.

- Details of gas well construction and completion critical to understanding the source of gas sampled from gas wells are not provided in the report. Without these details, links of gas well activity to alleged stray gas in the aquifer system are unsubstantiated.

- Three potential mechanisms of gas migration due to gas well activity are offered by EPA; however, pre-existing gas and, the potential for gas migration due to legacy conditions represent more viable sources of gas in the aquifer system yet are not discussed as potential sources.

EPAPAV0050459

Introduction

This report provides my review, and interpretations of the molecular results, the stable carbon and hydrogen isotope compositions of methane, ethane, propane and butanes for gas samples, and molecular results and stable carbon and hydrogen isotope compositions for methane, ethane, and dissolved inorganic carbon (DIC) for water samples as provided in the December 2011 USEPA Draft Report Investigation of Groundwater Contamination Near Pavillion, Wyoming. EPA analyzed groundwater for isotope geochemistry from thirty six water wells including two deep groundwater monitoring wells installed by EPA (MW-01, MW-02) screened at 233m to 239m (765'- 785') and 293m to 299m (960' – 980') respectively. All other private water supply wells were drilled to shallower depths ranging from 14.6m (~48') to 243.8m (~800').

My review and comments are restricted to the molecular and isotopic compositions for gas and water samples, and discussion on mechanism of gas migration. The dataset in the EPA report include samples collected before and during the investigation. The EPA study does not provide baseline methane/ethane concentration or isotope geochemistry. The isotope data reveal the methane detected in the groundwater and well head spaces for all wells are thermogenic in origin. Isotope compositions are plotted on interpretive isotope plots (Figures 1 & 2).

EPA initiated this investigation as a result of complaints in early 2008 by several private water well owners near the town of Pavillion, Wyoming alleging the onset of "...taste and odor" problems. EPA's investigation was initiated in September 2008 under the authority of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA).

Background

The area of investigation is described as a sparsely populated rural area east of the town of Pavillion, Wyoming. Domestic water wells overlie the Pavillion gas field, one of several gas fields within the Wind River Basin. Oil and gas exploration wells to this field were drilled in the 1950s. Natural gas production in the Pavillion gas field is reported to have commenced in 1960 with increased gas well drilling activity in the late 1990s – 2006. The field consists of approximately 169 vertical production wells. Natural gas production is from the Wind River Formation (Fm.), and deeper Fort Union Fm. The Wind River Fm. extends from the surface to approximately 3400 feet below grade surface (bgs). The most productive gas zone in the Wind River Fm. occurs at its base. The Fort Union Fm. ranges in thickness from 2500-3000' in the area. (USEPA, 2011)

It is reported that gas from the Wind River and Fort Union Fms. varies little in $\delta^{13}C$ for methane, ethane and propane with depth from the lower Eocene Wind River Fm. to deeper mature and post mature Upper Cretaceous source rocks. It is further stated that this suggests upward gas migration from deep source rocks. (Johnson and Rice 1993 and Johnson and Keighin 1998)

Groundwater from the Upper Wind River Fm. is identified as the principal potable water source in the Pavillion area. Total dissolved solids (TDS) concentrations in the groundwater are reported at concentrations ranging from 100-5,110 mg/l. (WY State Water Plan 2003, Daddow 1996).

EPAPAV0050460

EPA Draft Report findings for dissolved phase and gas phase geochemistry & transport mechanisms

1. EPA's investigation into the origin and source of natural gas in the Upper Wind River aquifer is retrospective. Their review of geophysical logs obtained online from the Wyoming Oil and Gas Conservation Commission (WOGCC) site reveals natural gas shows at 649, 682 and 826 ft. bgs. between the years of 1965-1973. As stated in the EPA draft report, this information provides evidence of natural gas in the groundwater at depths of domestic groundwater production prior to extensive commercial gas development in the Wind River Formation. Further, natural gas production began in the Pavillion field in 1960.

   Review Comments:
   There are no baseline methane/ethane concentrations or isotope data for groundwater from the Upper Wind River system. This is problematic as the evidence collected during EPA's investigation reveals the occurrence of natural gas in the aquifer system decades prior to their investigation. Further, pre-existing gas development beginning in 1960 represents a potential for gas migration due to legacy gas well conditions.

   The Upper Wind River Fm. is identified as both the aquifer for area domestic water supplies and deeper units as producing commercial volumes of natural gas. EPA briefly discusses the complexity of the aquifer system through analyses of geophysical logs by pointing out the lithology as highly variable and difficult to correlate well to well. Groundwater occurrence in the area is further characterized as complex with variability in location, elevation, and geologic unit. USGS reports (Daddow, 1996) more than 30 water-bearing formations in the Wind River Basin. Further, the Wind River Basin has a complicated structure created by uplifting, folding, and faulting.

   The complicated geologic setting of the Pavillion area provides a subsurface environment for upward gas migration through buoyancy-advective transport mechanisms as a natural condition during past periods of increased geologic activity. Legacy gas wells also provide a potential conduit for upward gas migration. It would, therefore, not be unexpected to have the occurrence of thermogenic methane in a shallow aquifer system above a petroliferous basin with migration as a natural condition or secondarily, due to legacy gas well conditions.

   EPA did not properly consider or evaluate the likely probability that methane in the Wind River aquifer system was a pre-existing condition.

2. EPA reports that elevated concentrations of dissolved methane detected in domestic water wells increases, in general, in water wells within proximity to gas production wells. It is also reported that methane was not detected in shallow water supply wells at depths < 164 feet regardless of proximity to natural gas production wells. The EPA draft report offers that methane concentrations are more elevated when there are > 2 production wells within ~1970 feet (horizontal distance) of water supplies.

   Review Comments:
   The basis for EPA's correlation of dissolved phase methane with proximity to natural gas production wells is questionable. Methane solubility in groundwater is, in large part, a function of hydraulic head pressure. In order to define spatial relationships between methane concentrations in the groundwater of domestic water supplies and the proximity to producing gas wells, it is necessary to define baseline conditions, and hydrostatic properties of the aquifer system including: 1) specific zones that yield

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groundwater to the domestic well, and 2) fluctuations in the hydrostatic head caused by daily use and seasonality. Additionally, groundwater yield for private water supply wells often varies well to well especially in fracture flow systems such as what occurs in the Wind River Fm. These variables directly affect the concentration of dissolved phase methane in the groundwater, and are necessary to define before spatial relationships between dissolved phase methane and proximity to gas wells can be linked. This testing must be over sufficient timeframe to observe trends (i.e., seasonal variations) in the data.

Dissolved phase methane concentrations in groundwater are reported at concentrations up to 19 mg/l. Table A3a. for EPA's draft report summarizes dissolved phase concentrations of light hydrocarbons. Groundwater data are provided for 1 to 3 sampling events for the 36 sampled water supplies. Significantly, only data from EPA's deeper monitoring wells (MW-01, MW-02) reveal methane concentrations above 1 mg/l. Data for the remaining 34 water supply wells reveal dissolved phase methane concentrations below 1 mg/l. Methane concentrations below 1 mg/l in an aquifer system in a petroliferous basin are more indicative of a baseline condition and not indicative of gas migration due to gas well activity.

Dissolved phase methane concentrations of the range reported during this investigation do not manifest in a manner that would be detectable by owners of private water supply wells, and therefore, could have been present for many years prior to recent gas well activity. The original complaints to EPA were taste and odor. Methane is colorless and odorless. EPA seemingly makes the unsubstantiated association of VOC and SVOC contamination in the aquifer with methane in the aquifer, all being sourced from area gas wells.

3. The EPA report states that gas in the water supplies is interpreted to be thermogenic in origin with some evidence of oxidation for groundwater samples in proximity to a December 2005 water well blowout where natural gas exited the borehole for 3 days.

   Review Comments:
   Details for the referenced water well blowout are not provided in the EPA report.

   Isotope compositions for groundwater supplies reveal a similar thermogenic origin for methane for area sampled gas wells. It is not uncommon for methane/ethane in shallow aquifer systems to be thermogenic in origin, and in the aquifer system due to source materials and migration pathways natural to the subsurface. This is especially true for formations that serve as the aquifer and as a natural gas producing formation such as the Upper Wind River Fm. Thermogenic gases in aquifer systems with similar isotopic compositions as gases from deeper producing formations is not, in of itself, evidence of gas migration. Recent studies reveal thermogenic gas in shallow aquifer systems overlying natural gas producing formations as a natural condition in other systems including the Northern Appalachian Basin. (Baldassare, et. al., 2012, in press).

   EPA identifies evidence of pre-existing methane in the groundwater and legacy gas wells in the field. This evidence, however, is seemingly dismissed as probable sources to the methane found in the groundwater.

4. EPA identifies three potential mechanisms for gas migration: 1) insufficient/inadequate cement outside of production casing. 2) fracture fluid excursion from thin discontinuous tight sandstone units into sandstone units of greater permeability. 3) the process of hydraulic fracturing created new fractures or

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enhanced the permeability of existing fractures, increasing connectivity of the fracture system.

Review Comments:
EPA acknowledges that the 3 mechanisms of stray gas migration to the aquifer are theoretical and that additional evidence is necessary to identify pathways. however, EPA provides no discussion or acknowledgement of the high probability that methane in the aquifer system could be the result of a natural condition or secondarily, due to well integrity problems associated with legacy wells.

5. Reference to the Duke study (Osborn, et. al., 2011) is identified as evidence that similar gas geochemistry and the potential for the 3 mechanisms of gas migration as well as the vertical chemical gradient observed during sampling of EPA installed wells MW01 and MW02. EPA reports on the Duke study that: "Isotopic data and other measurements for methane in drinking water were consistent with gas found in deep reservoirs such as the Marcellus and Utica shales."

Review Comments:
The Duke study related the occurrence and frequency of occurrence of thermogenic gas in private water supply wells as an indication that the methane/ethane in the aquifer came from natural gas production.

The frequency of thermogenic methane in aquifer systems in proximity to area gas wells requires definition of the hydrogeologic system, baseline methane concentrations, and time series data to evaluate variability. Neither the Duke study nor the EPA draft report defines these parameters. Further, recent research documenting baseline methane conditions from a significantly larger database (>1900 samples) than what was utilized for the Duke study reveals thermogenic gas as a natural condition in many areas of the north eastern Appalachian basin (Table 1). Significantly, a more detailed review of the geochemistry at the site specific level also reveals a complex thermal and migration history with gas mixtures and partial isotope reversals ($!^{13}C_1 > !^{13}C_2$) and thermally mature gases documented in some areas throughout the stratigraphic section above the Marcellus Formation. The study results revealing the origin of thermogenic gas in the shallow aquifer system and the complexity in gas geochemistry of the north eastern Appalachian basin provides an applicable analog to the Pavillion area investigation.

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Quaternary and Upper Devonian strata in the upper 610 m (2,000 ft) MGL isotope data					
Isotope	Mean (‰)	# Data Pts.	Std. Dev.		
d13C1	-42.12	134	5.69		
d13C2	-40.57	112	2.43		
dDC1	-228.26	76	34.91		
Middle Devonian strata, (includes the Marcellus Fm.) at a depth > 1,524m (5,000 ft) MGL isotope data					
Isotope	Mean (‰)	# Data Pts.	Std. Dev.		
d13C1	-32.87	1519	3.64		
d13C2	-38.64	1484	2.89		
dDC1	-163.45	1386	8.67		
Quaternary and Upper Devonian, gas and water samples from baseline groundwater testing programs					
Isotope	Mean (‰)	# Data Pts.	Std. Dev.		
d13C1	-45.23	67	16.02		
d13C2	-35.02	13	6.86		
dDC1	-212.19	67	43.98		

Table 1: $!^{13}C_1$, $!^{13}C_2$, $!DC_1$ compositions for mudgas (MGL) data and baseline groundwater samples in N.E. Appalachian Basin

6. Samples for dissolved inorganic carbon (DIC) were collected and analyzed for this investigation. DIC provides another parameter to constrain biodegradation of methane in the aquifer. The DIC results are not discussed in the EPA draft report.

   Review Comments:
   DIC concentrations represent the combination of $CO_3^{--}+HCO_3^{-}+CO_2$ dissolved in water. DIC are best interpreted by defining baseline conditions in the aquifer. Methane degradation is evidenced when the isotope of methane becomes enriched in 13C and the DIC becomes lighter. Although baseline DIC is absent from the dataset, the DIC concentrations for the domestic water wells that reveal oxidation of the carbon isotopes (PGDW 20, PGDW 30, PGDW 32) are not fully substantiated by the DIC of the PGDW 30, PGDW 32 water wells. (Figure 3) EPA should explain and further evaluate DIC results in the context of their conclusions.

7. The isotope data reveals the natural gas in the Wind River and Fort Union Formations is from the same source rocks.

   Review Comments:
   The protocol for gas sample collection from investigated gas wells is not reported or identified in the QAPP. Well construction/completion details, and casing pressure of gas wells sampled are not provided. In order to constrain stray gas to a potential point source (such as a gas well), it is imperative that the mechanical dimensions of the point source are defined. It is not clear if different producing intervals occur in gas wells drilled to the Wind River and Fort Union Fms., or if gas samples were collected from specific casing intervals. Analyses of natural gas from different gas producing intervals may reveal differences in gas origin.

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Investigations to determine gas origin in an aquifer overlying a known natural producing formation requires baseline data collection. The EPA investigation is retrospective and does not provide the necessary data to constrain the origin of gas in the aquifer.

Conclusions

The EPA DRAFT Report represents a retrospective study. Methane in groundwater was not considered as a probable baseline condition by the EPA though existing information reveals it was likely present in the groundwater prior to the reported complaints. Information obtained from the WOGCC reveals methane as a pre-existing condition in the area. An aquifer that overlies a known natural gas field and the potential for gas migration due to historical natural gas well development provide potential sources for methane detected in the domestic water supply wells.

EPA's investigation detected concentrations of methane in domestic water wells at concentrations below 1 mg/l. Methane is colorless and odorless and at concentrations below 1 mg/l would not be detectable by private water supply owners. The EPA report acknowledges that multiple lines of evidence are necessary to identify the source(s) of stray gas in the groundwater; however, the specific mechanism of gas migration is not identified in the EPA investigation. It is speculated that 3 mechanisms of gas migration are possible; however, EPA does not acknowledge that methane detected in the investigated water supply wells could have been a pre-existing condition. In fact, dissolved phase methane concentrations below 1 mg/l are more indicative of a baseline condition than the result of gas well activity.

The molecular results and isotope geochemistry collected from domestic water supply wells during this investigation do not prove the gas is from contemporary unconventional gas production or has migrated as a result of contemporary unconventional gas drilling. Properly interpreted, isotope geochemistry provides empirical evidence of gas origin, but not the specific gas source. Other data types and lines of evidence are necessary to identify the specific source of stray gas. The lack of baseline data, evidence of pre-existing methane in the shallow system, methane concentrations more indicative of a baseline condition, and natural dynamics of a petroliferous system in close proximity to an aquifer system provides evidence that the methane/ethane in the groundwater for the area investigated near Pavillion, Wyoming was likely in the aquifer system prior to contemporary unconventional gas drilling activity and complaints by residents.

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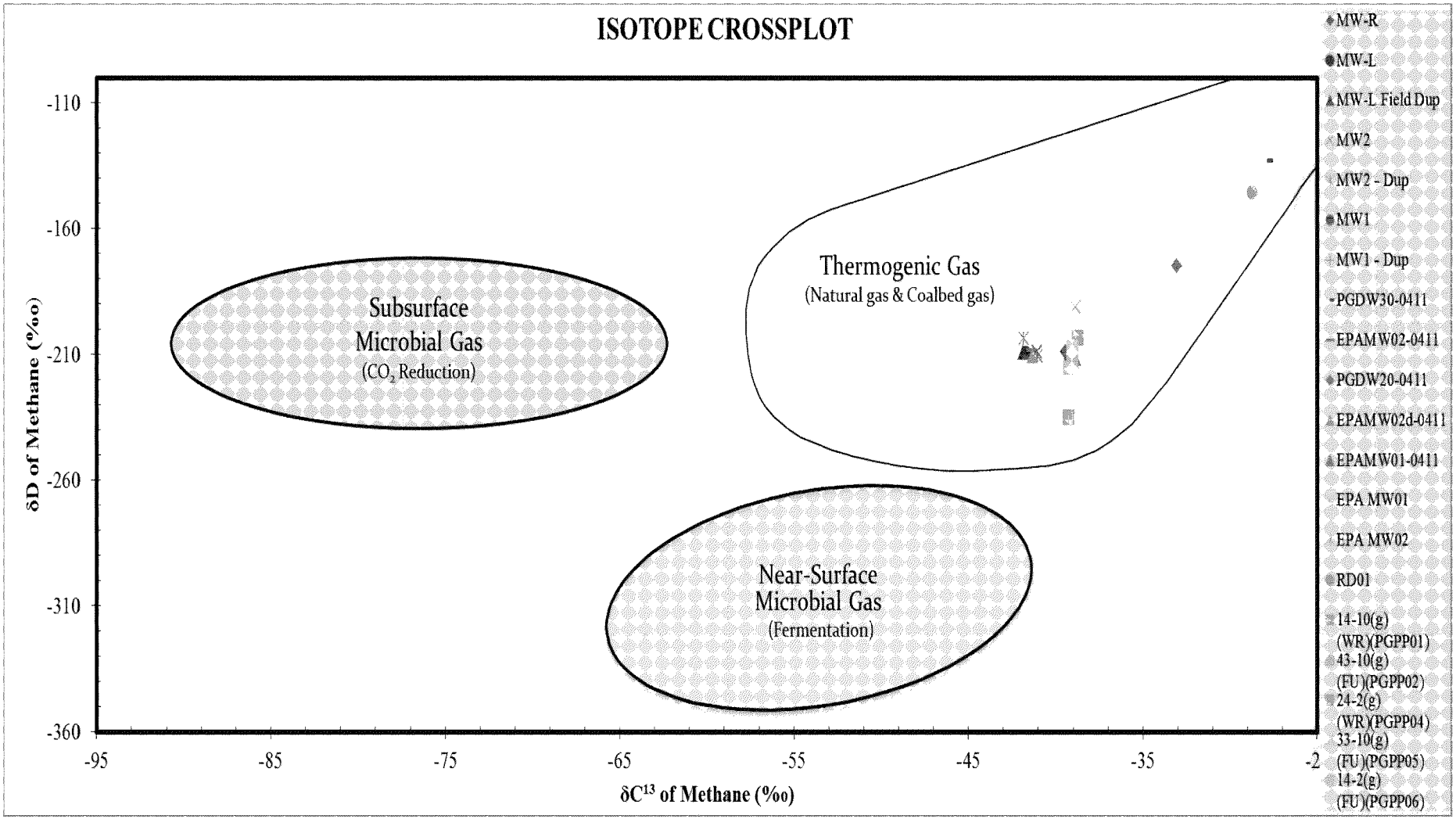

Figure1: Stable carbon & Hydrogen Isotope compositions for groundwater samples provided in EPA's DRAFT Report for Investigation of groundwater contamination near Pavillion, Wyoming

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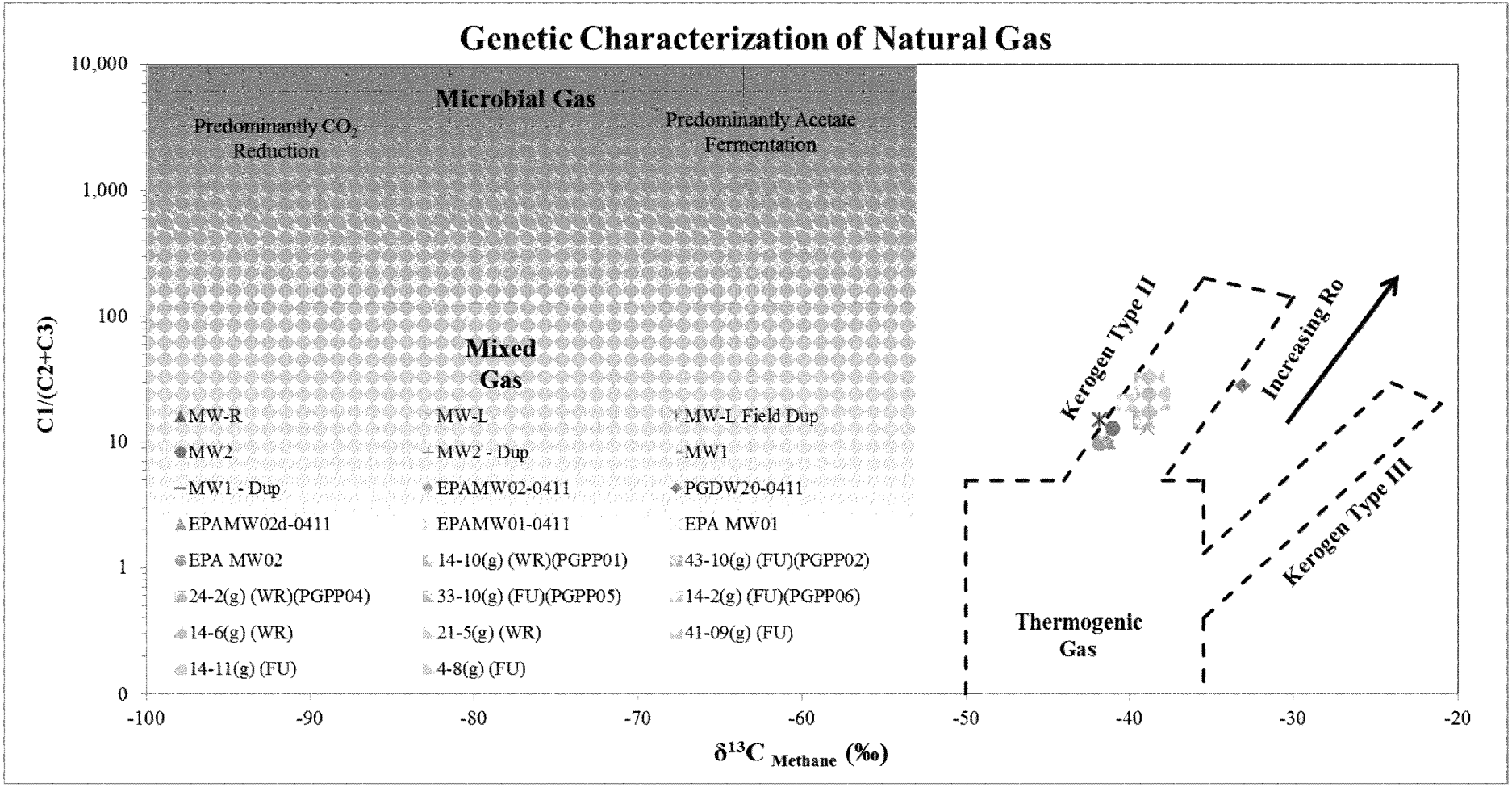

Figure 2: Genetic characterization of gas from natural gas wells and dissolved phase methane for groundwater samples provided in EPA's DRAFT Report for Investigation of groundwater contamination near Pavillion, Wyoming

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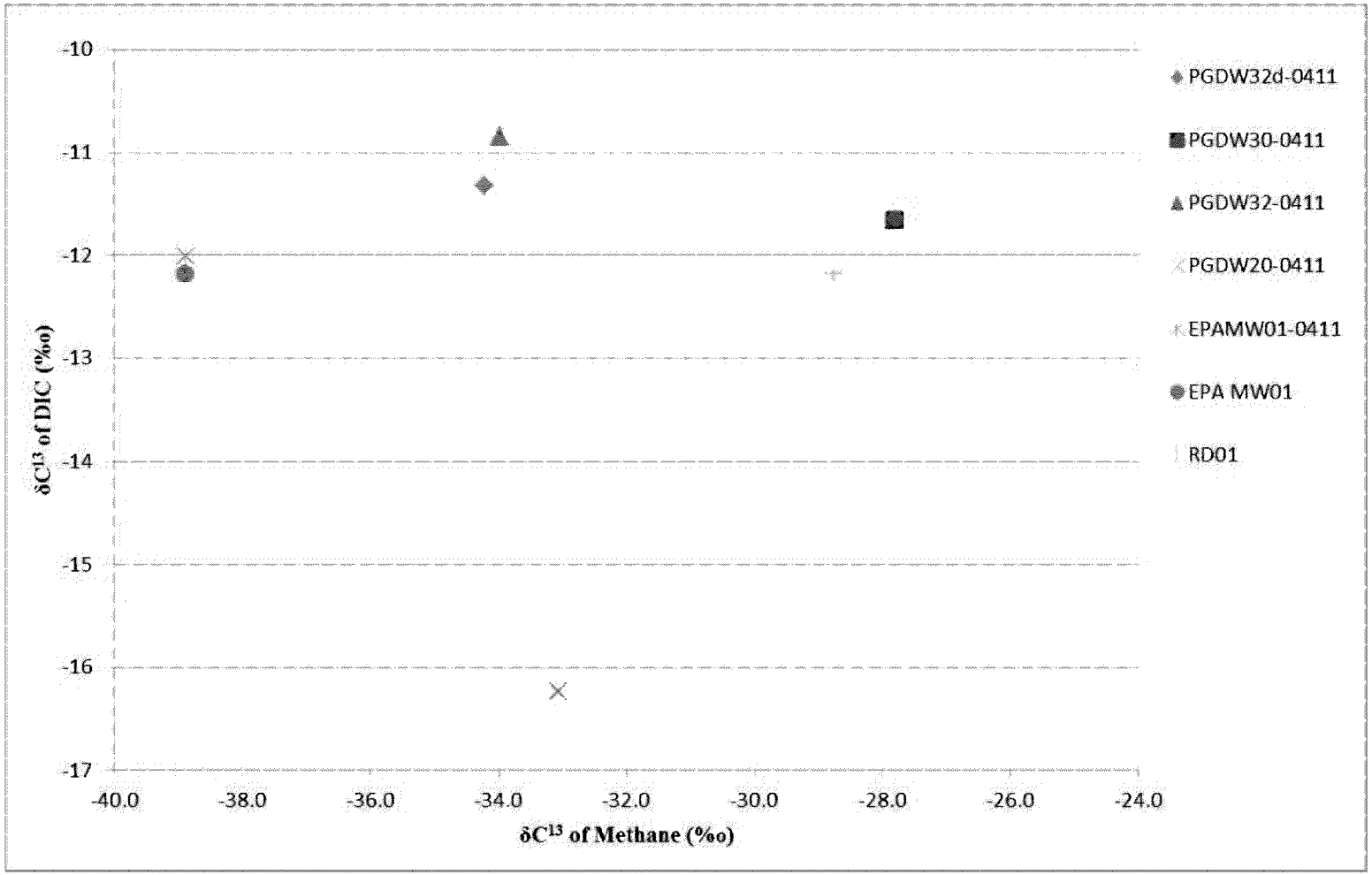

Figure 3: Correlation of DIC and ! 13C_1 for groundwater samples provided in EPA's DRAFT Report for Investigation of groundwater contamination near Pavillion, Wyoming

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