Investigation of Ground-Water Contamination near Pavillion, Wyoming Workgroup Meeting
November 30, 2011

Office of Research and Development
National Risk Management Research Laboratory,
Ground Water and Ecosystem Restoration Division, Ada, OK

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EPA/ORD/Ada, OK

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Site Background

- In early 2008, EPA received complaints from several domestic well owners near the town of Pavillion, Wyoming regarding sustained objectionable taste and odor problems in well water following hydraulic fracturing at nearby gas production wells.

- In response to these complaints, EPA initiated a comprehensive ground-water investigation in September 2008 under authority of the Comprehensive Environmental Response, Compensation, and Liability Act.

Domestic wells in the area of investigation overlie the Pavillion Gas Field which is one of several gas fields within the Wind River Basin - a large, complex, structural, asymmetric, deep sedimentary basin covering much of central Wyoming.
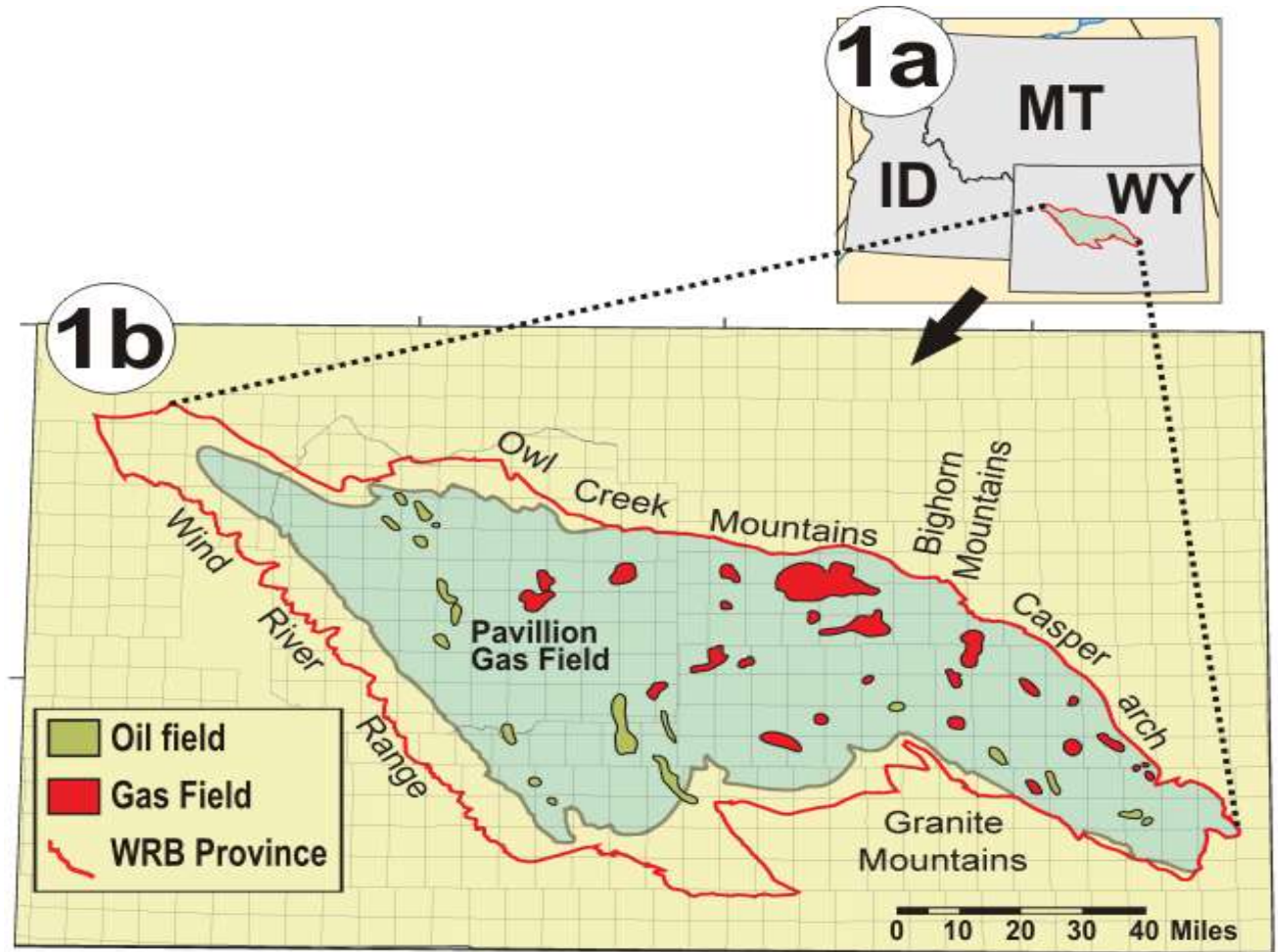

(a) Location of Wind River Basin in Wyoming. **(b)** Location of Pavillion Gas Field in the Wind River Basin. Figure from Johnson et al.2007

Chronology of production well completion at the Pavillion Gas Field
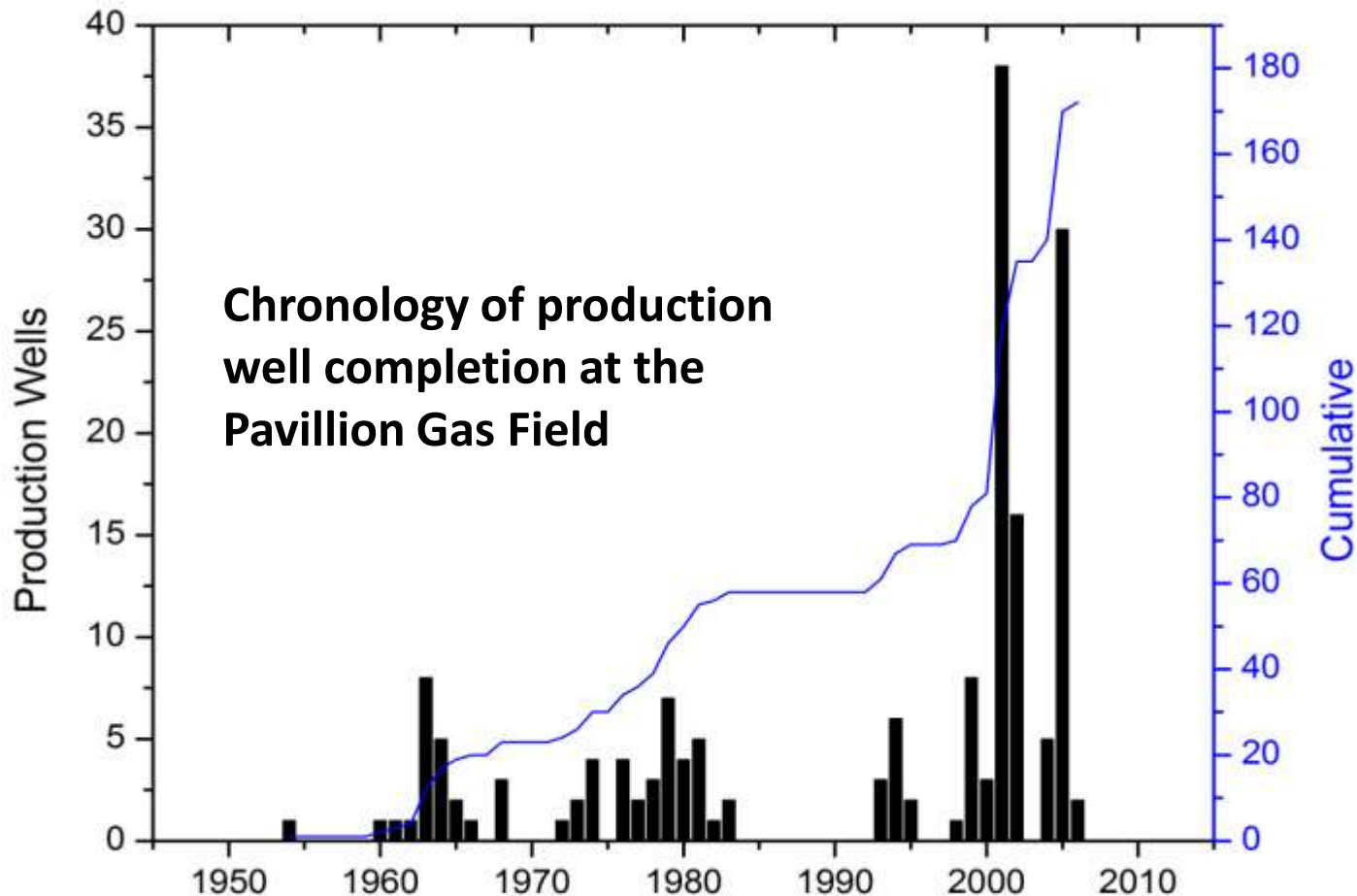
Oil and gas exploration wells were drilled in the 1950s. Commercial natural gas extraction in the field commenced in 1960 (Single 1969) with gas production well installation activity intensifying in the late 1990s through 2006. The field currently consists of approximately 169 vertical production wells. Ninety-seven production wells are designated as "Tribal Pavillion" and are regulated by the U.S. Bureau of Land Management (BLM). The remaining wells are designated as "Pavillion Fee" and are regulated by Wyoming Oil and Gas Conservation Commission (WOGCC). WOGCC provides information on line for both WOGCC and BLM regulated wells

Histograms summarizing depths of top of perforation interval of production wells, base of surface casing of production wells, and base of screened interval of domestic wells.
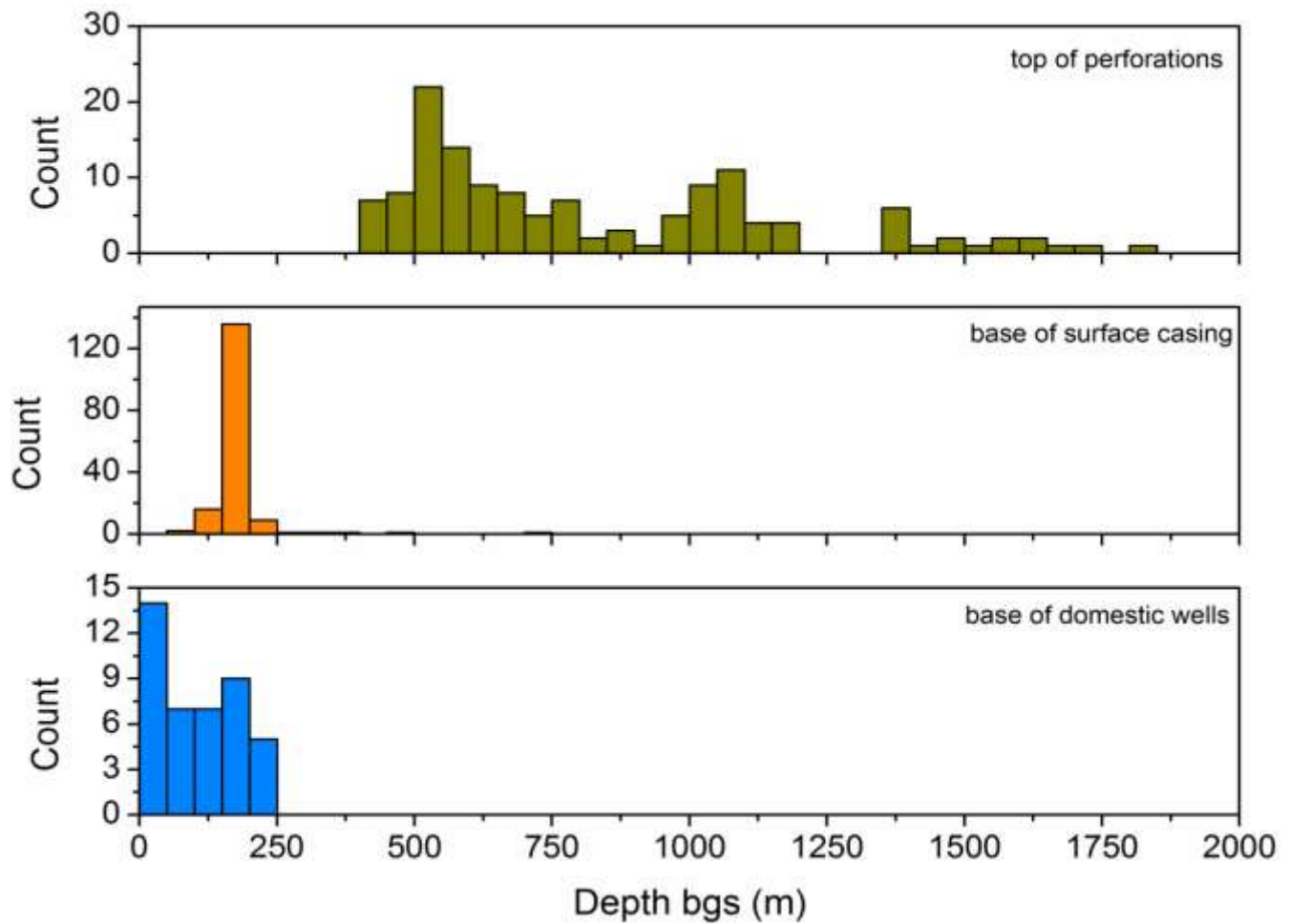
Records obtained on line from WOGCC indicate that hydraulic fracturing in gas production wells occurred as shallow as 372 m below ground surface (bgs) with associated surface casing in production wells as shallow as 110 m bgs. Records from the Wyoming State Engineer's Office and homeowners indicates that domestic wells (including stock wells) in the area of investigation are screened as deep as 245 m bgs. With the exception of two production wells, surface casing of gas production wells do not extend below the maximum depth of domestic wells in the area of investigation.

Gas extraction occurs from both the lower Eocene Wind River Formation and underlying Paleocene Fort Union Formation.

The Wind River Formation extends from the surface to approximately 1036 m below ground surface (bgs). The Fort Union Formation ranges in thickness from 762 to 914 m in the area (Flores and Keighin 1993). The Waltman Shale Member in the Fort Union Formation is absent below the Pavillion Gas Field.

Gas trapping occurs in localized stratigraphic sandstone pinchouts on the crest and along flanks of a broad dome (Mueller 1989, Keefer and Johnson 1993).

The most productive zone of gas extraction in the Wind River Formation occurs at its base and is often targeted for gas extraction (Single 1969).
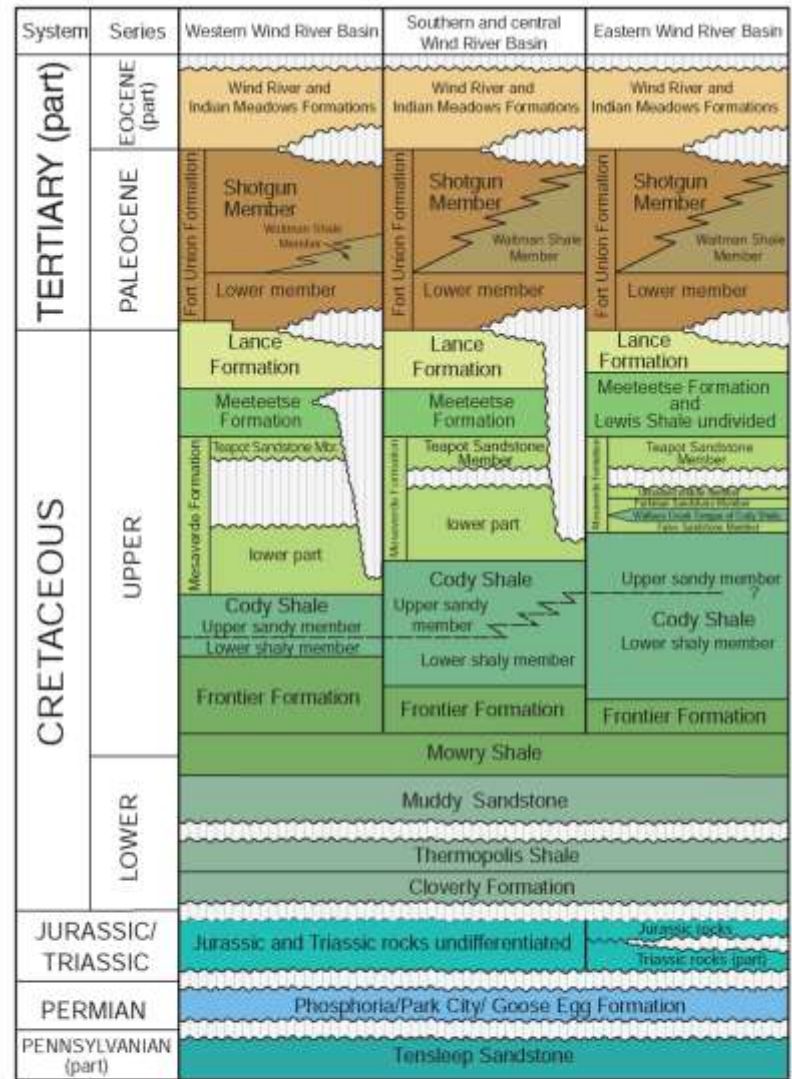
The Wind River Formation consists of laterally discontinuous interbedded layers of sandstones and shale with coarse-grained meandering stream channel deposits (Osiensky et al. 1984).

There is substantial vertical and lateral stratigraphic variation over short distances (Single 1969, Flores and Keighin 1993).

Individual productive sandstones generally vary in thickness from 1 to 21 m with permeability varying from 0.1 to 300 millidarcies and porosity ranging from 4 to 28 percent (Single 1969).
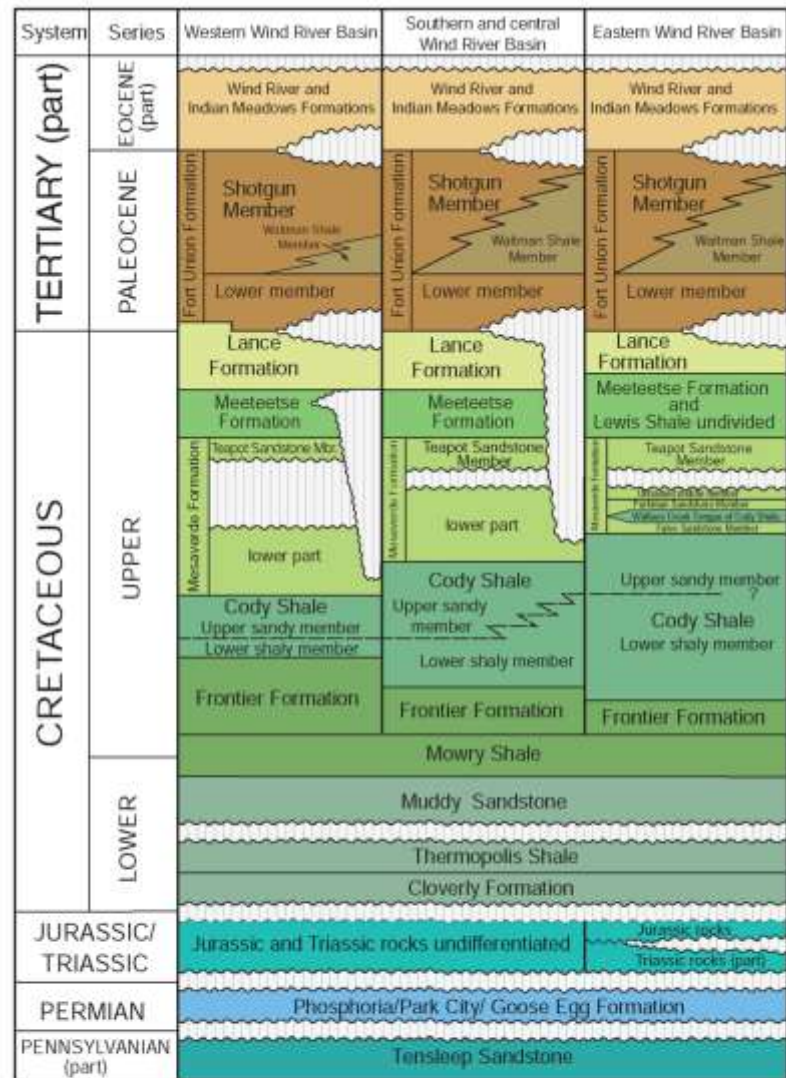
The Wind River Formation meets the definition of an Underground Source of Drinking Water (USDW) under the United States Code of Federal Regulations, Title 40, Section 144.3.

Fluids used for hydraulic fracturing were injected directly into the Wind River Formation.

- Ground water from the upper Wind River Formation is the principal source of domestic, municipal, and stock (ranching, agriculture) water in the Pavillion area (WY State Water Plan 2003).

- Water yields from wells in the upper Wind River Formation range up to 11,300 L/min with total dissolved-solids (TDS) concentrations ranging from 100 to 5,110 mg/L (WY State Water Plan 2003, Daddow 1996).

- The town of Pavillion has five municipal wells screened at depths ranging from 122 to 158 m bgs with average daily use estimated at 60,000 L/day (WY State Water Plan 2003).

Methods

Four sampling events (Phase I - IV) were conducted commencing in March 2009 and ending in April, 2011.

- In March, 2009 (Phase I), EPA collected aqueous samples from 35 domestic wells (including two samples from post reverse osmosis systems) in the area of investigation and 2 municipal wells in the town of Pavillion.

- Detection of methane and dissolved hydrocarbons in several domestic wells prompted collection of a second round of samples in January, 2010 (Phase II). During this phase, EPA collected: (1) ground-water samples from 17 domestic wells (10 previously sampled), 4 stock wells, and 2 municipal wells; (2) a filter sample from a reverse osmosis system; (3) surface-water and sediment samples from 5 locations along Five-Mile Creek (a creek traversing the area of investigation); (4) gas and produced water/condensate samples (organic compounds only) from 5 production wells; and (5) ground-water samples from 3 shallow monitoring wells and soil samples near the perimeter of three known pit locations.

Detection of elevated levels of methane and diesel range organics (DRO) in deep domestic wells located close to one or more gas production wells prompted EPA to install 2 deep monitoring wells in June 2010 to differentiate potential deep (hydraulic fracturing) versus shallow (e.g., pits) sources of ground-water contamination.

- In September 2010 (Phase III), EPA collected gas samples from well casing from MW01 and MW02. In October 2010, EPA collected ground-water samples from MW01 and MW02 in addition to a previously unsampled domestic well and two previously sampled domestic wells.

- Finally, in April 2011 (Phase IV), EPA resampled the 2 deep monitoring wells to compare previous findings and expand the analyte list to include glycols, alcohols, and low molecular weight acids. Eight previously sampled domestic wells and three previously sample stock/irrigation wells were also sampled at this time.

The expense of drilling deep wells while utilizing blowout prevention was the primary limiting factor in the number of monitoring wells installed.

EPA installed two deep monitoring wells using air (0 - 6 m bgs) and mud rotary (6 m bgs to target depth). Mud rotary was selected for installation of deep monitoring wells because it allowed the use of blowout prevention (BOP). Use of BOP was necessary during drilling given that a blowout occurred during installation of a domestic well at only 159 m bgs in December 2005 in the vicinity of PGDW05.

Mud composition consisted of formation water, municipal water from Riverton, WY transported on site by truck, Quik-Gel high yield bentonite and additives.

Mud and Additives

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

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

nd – not detected. ----- not measured. Drilling additives were extracted at the specified weight ratio into deionized water. † - Duplicate analysis. Blank sample is analysis of water used for the extraction of drilling additives. * Concentration above minimum detection limit, but below the level of quantification. The pH of mud during drilling varied between 8.0 and 9.0.

Since inorganic and organic concentration patterns measured in the drilling additives do not match patterns observed in the deep monitoring wells and because large volumes of ground water were extracted from the wells during development and prior to sampling, it is unlikely that ground-water chemistry was at all impacted by drilling additives.

Cuttings

Composite samples of cuttings were collected and sent to TestAmerica Laboratories in Denver, Colorado for Toxic Characteristic Leaching Procedure (TCLP). Samples were analyzed for TCLP volatile organic compounds (GC-MS) in accordance with EPA SW-846 Methods 1311/8260B, for TCLP semivolatile organic compounds (GC-MS) in accordance with EPA SW-846 Methods 1311/8270C, for TCLP metals in accordance with EPA SW-846 Methods 1311/6010B, for TCLP mercury in accordance with EPA SW-846 Methods 1311/7470A.

Acetone, toluene, and m & p-xylene were detected in one sample at 6.9, 0.63, and 1.0 µg/L, respectively. Cuttings were disposed offsite in a landfill.

**No cuttings were place in boreholes.**

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

Examination of resistivity and cuttings indicated elevated resistivity at depths were white coarse-grained sandstone was observed. This relationship was utilized to place screens at both deep monitoring wells at the deepest observed interval of white coarse-grained sand During drilling, mud and cuttings were monitored in an open atmosphere with a TVA-1000B Thermo-Scientific portable flame- and photo-ionization detector (FID/PID) for health and safety monitoring.
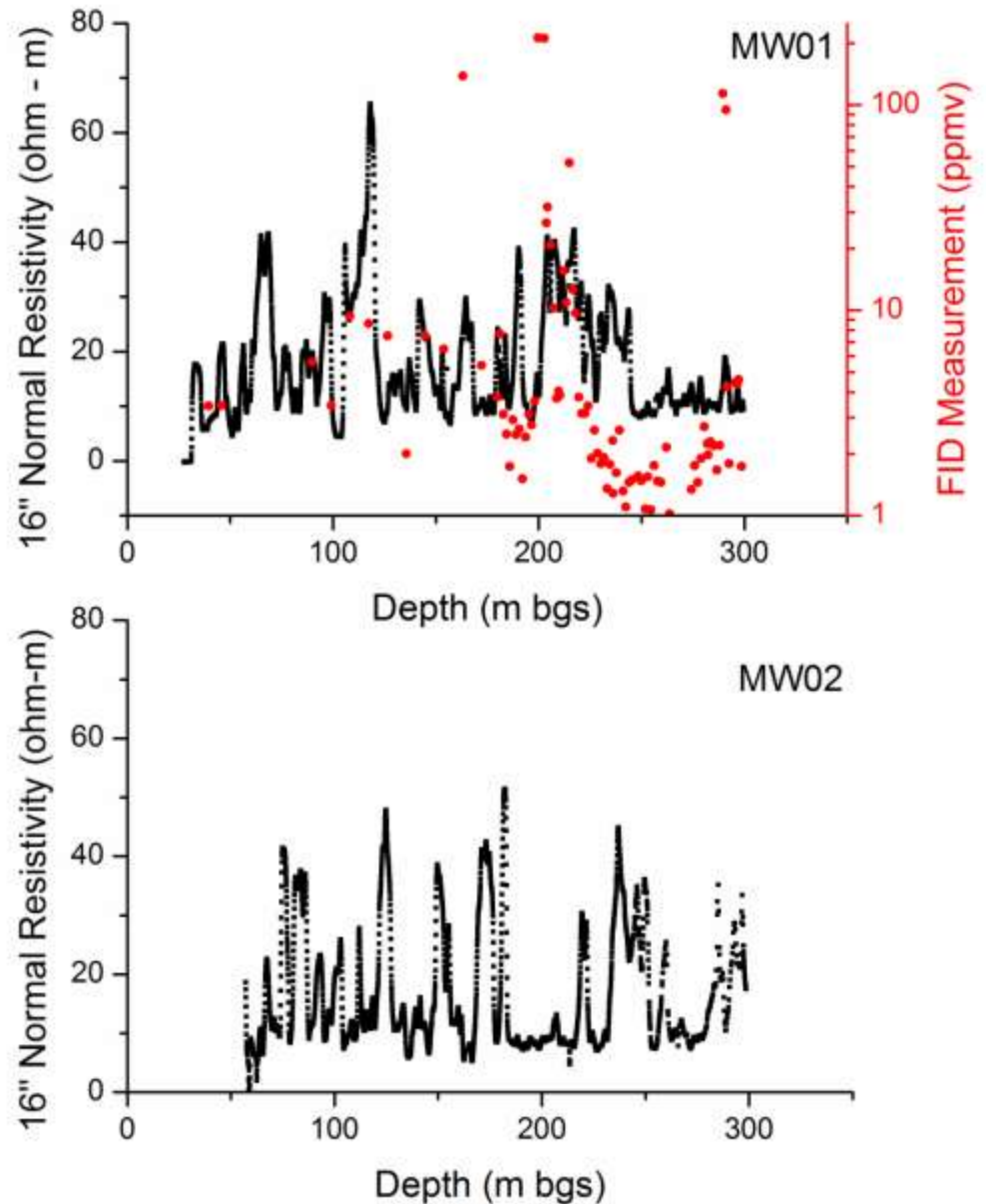
MW01
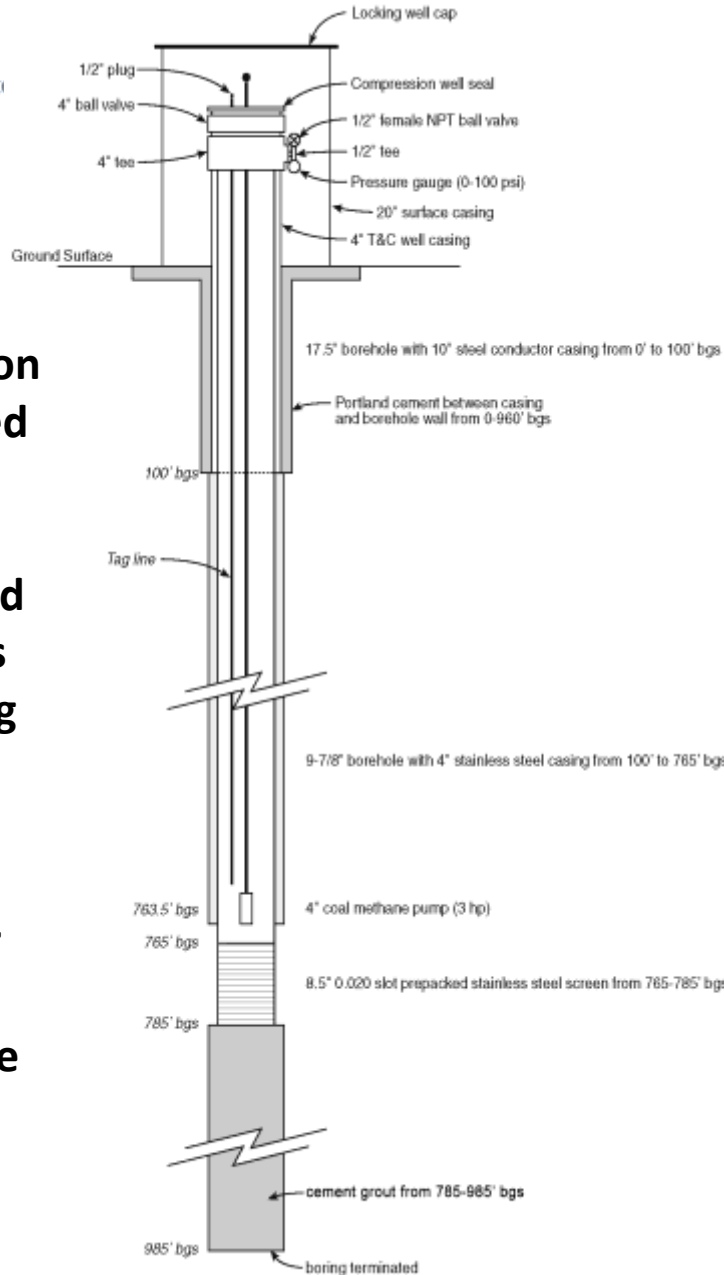
MW02
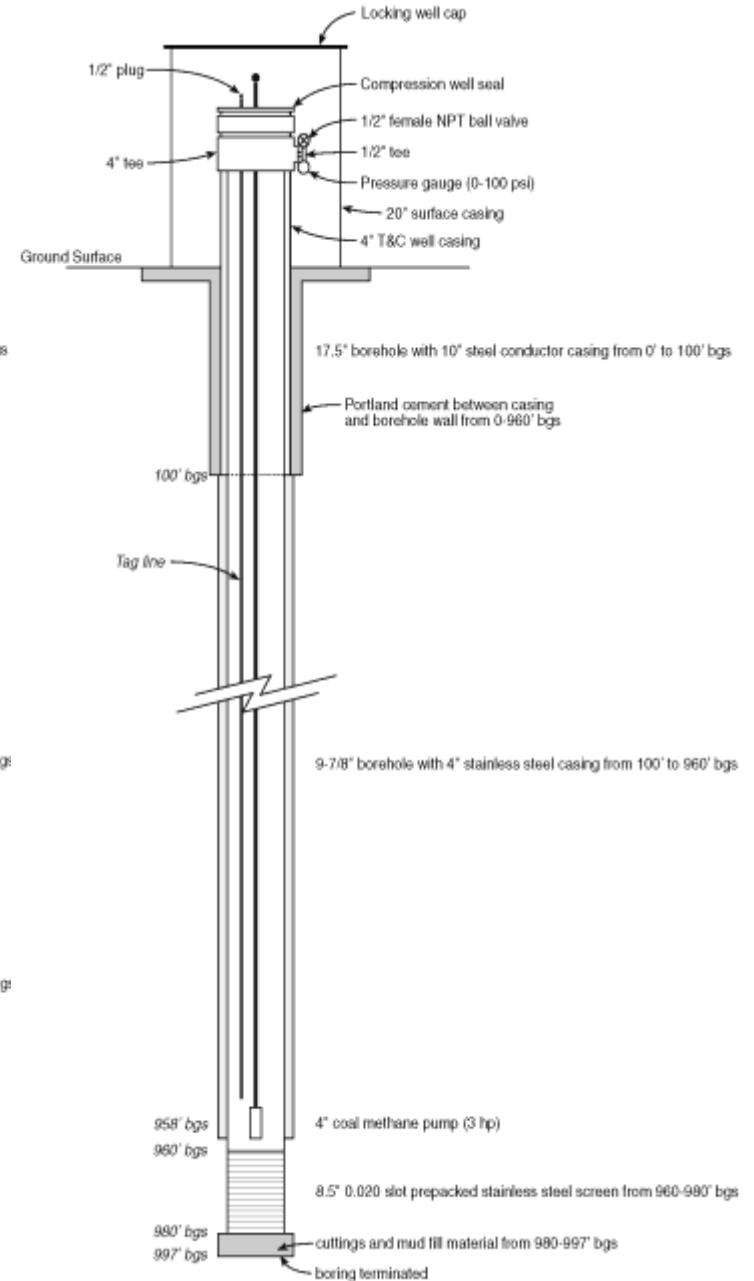
Jet Lube Well Guard hydrocarbon free lubricant used for drillstem.

No lubricants used to attach sections of casing or casing to screens.

Mounted (never touch soil) power washed screens, casing, and tremie pipe.

MW01
- Locking well cap
- 1/2" plug
- 4" ball valve
- 4" tee
- Compression well seal
- 1/2" female NPT ball valve
- 1/2" tee
- Pressure gauge (0-100 psi)
- 20" surface casing
- 4" T&C well casing
- Ground Surface
- 17.5" borehole with 10" steel conductor casing from 0' to 100' bgs
- Portland cement between casing and borehole wall from 0-960' bgs
- 100' bgs
- Tag line
- 9-7/8" borehole with 4" stainless steel casing from 100' to 765' bgs
- 763.5' bgs
- 765' bgs
- 4" coal methane pump (3 hp)
- 8.5" 0.020 slot prepacked stainless steel screen from 765-785' bgs
- 785' bgs
- cement grout from 785-985' bgs
- 985' bgs
- boring terminated
- Not to Scale

MW02
- Locking well cap
- 1/2" plug
- 4" tee
- Compression well seal
- 1/2" female NPT ball valve
- 1/2" tee
- Pressure gauge (0-100 psi)
- 20" surface casing
- 4" T&C well casing
- Ground Surface
- 17.5" borehole with 10" steel conductor casing from 0' to 100' bgs
- Portland cement between casing and borehole wall from 0-960' bgs
- 100' bgs
- Tag line
- 9-7/8" borehole with 4" stainless steel casing from 100' to 960' bgs
- 958' bgs
- 960' bgs
- 4" coal methane pump (3 hp)
- 8.5" 0.020 slot prepacked stainless steel screen from 960-980' bgs
- 980' bgs
- 997' bgs
- cuttings and mud fill material from 980-997' bgs
- boring terminated
- Not to Scale

The flow was split, with one portion going to waste and the other portion going to a flow-cell equipped with a YSI 5600 multiparameter probe to track stabilization of pH (<0.02 standard units per minute), oxidation-reduction potential (<2 mV per minute), specific conductance (<1% per minute), dissolved oxygen (DO), and temperature.

**Soil-Gas Sampling – Leak, Purge, and Gas Permeability Testing**

Ground-water in deep monitoring wells was sampled using dedicated explosion proof submersible pumps (10-cm Franklin Electric 3HP). Wells were purged at a flow rate of approximately 5 to 30 L/min. The rate of pumping was measured using a Model TM0050 in-line turbine flow meter with associated Model FM0208 flow monitor manufactured by Turbines, Inc. Drawdown during pumping was measured with a sonic water level sensor obtained from Eno Scientific, Inc. (Model WS2010 PRO).

Purge volumes prior to sampling ranged from about 200 to 450 L (Phase 3) and 1100 to 1250 L (Phase 4). Lower purge volumes in Phase 3 sampling were due to initial gas invasion into the screened intervals that caused cavitation and concern about prolonged pump operation. By the time of Phase 4 sampling, disruptive gas invasion was no longer observed and extended purging was possible.
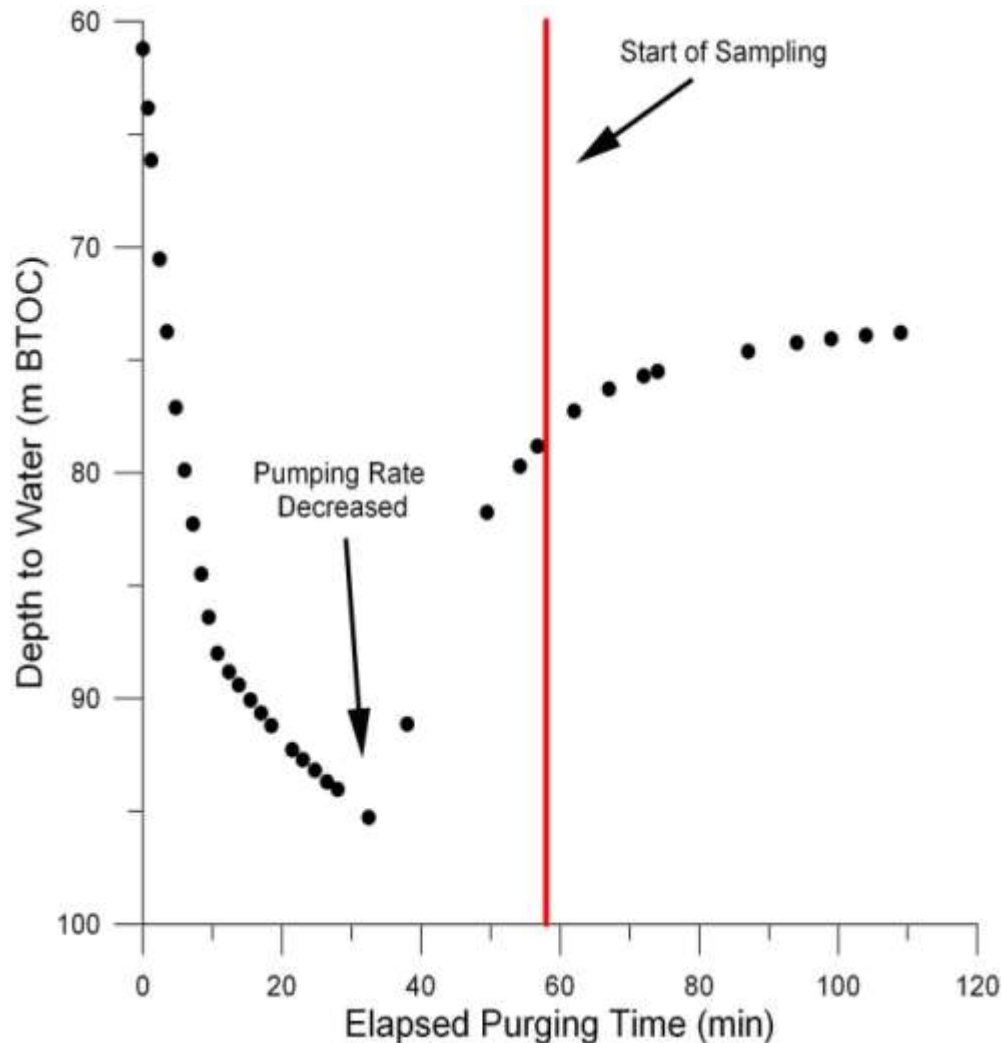
Variation of water level as a function of time in MW01 during Phase 4 well purging. The initial pumping rate was 24.2 L/min. After approximately 30 minutes of purging, the flow rate was decreased to 7.6 L/min. This reduced flow rate caused partial recovery of the water level and confirmation that formation water was being accessed.

An example of flow-cell readings through the purging of well MW02 is shown. The electrode readings show fairly rapid equilibration of pH and dissolved oxygen. Oxidation-reduction potential steadily decreased with the rate of change falling into the desired range (<2 mV per minute) by the end of purging. Specific conductance readings were typically variable, likely due to continuous off-gassing and bubble formation within the conductivity sensor. After field measurements stabilized, ground water was collected into sample bottles.
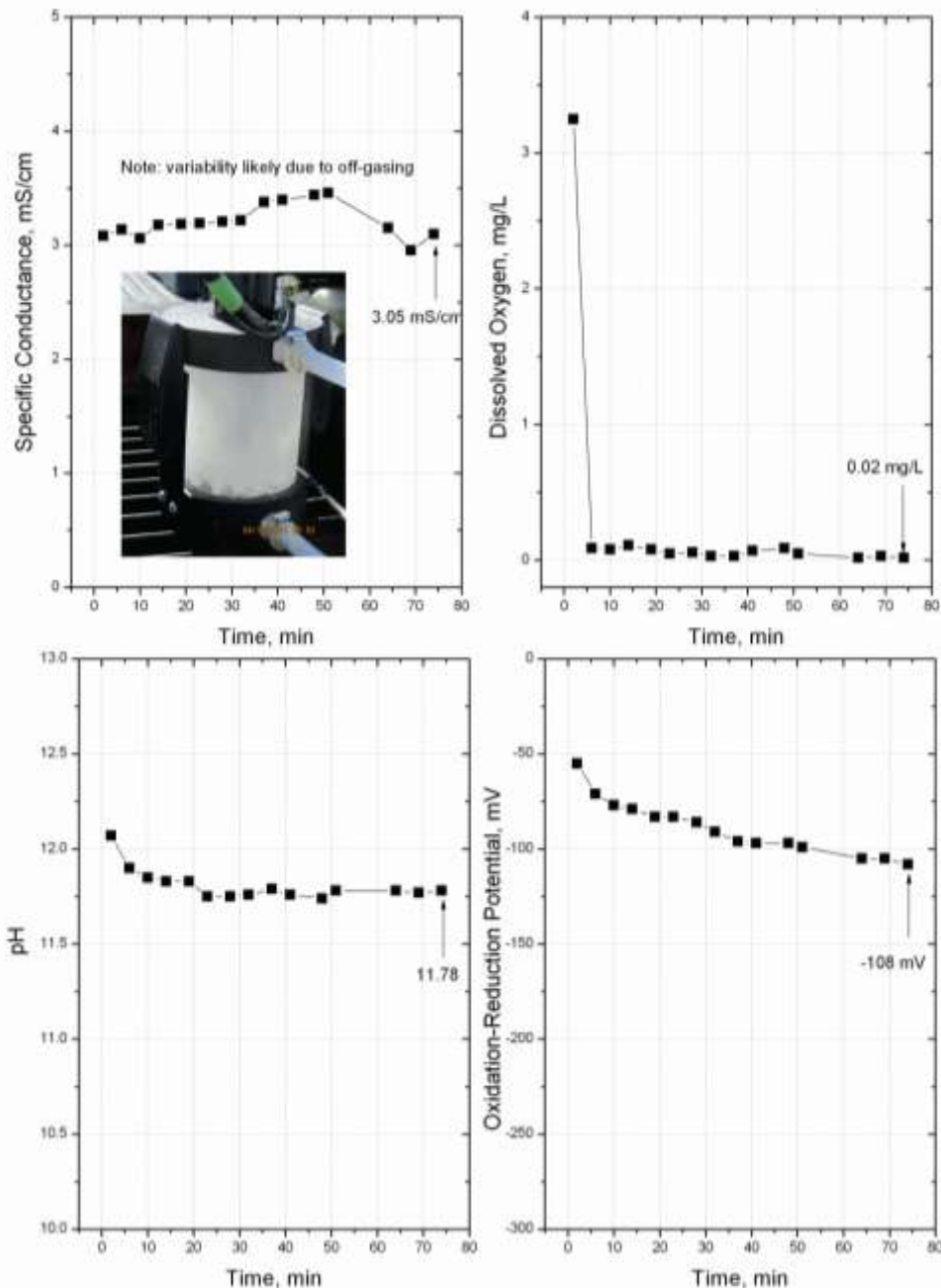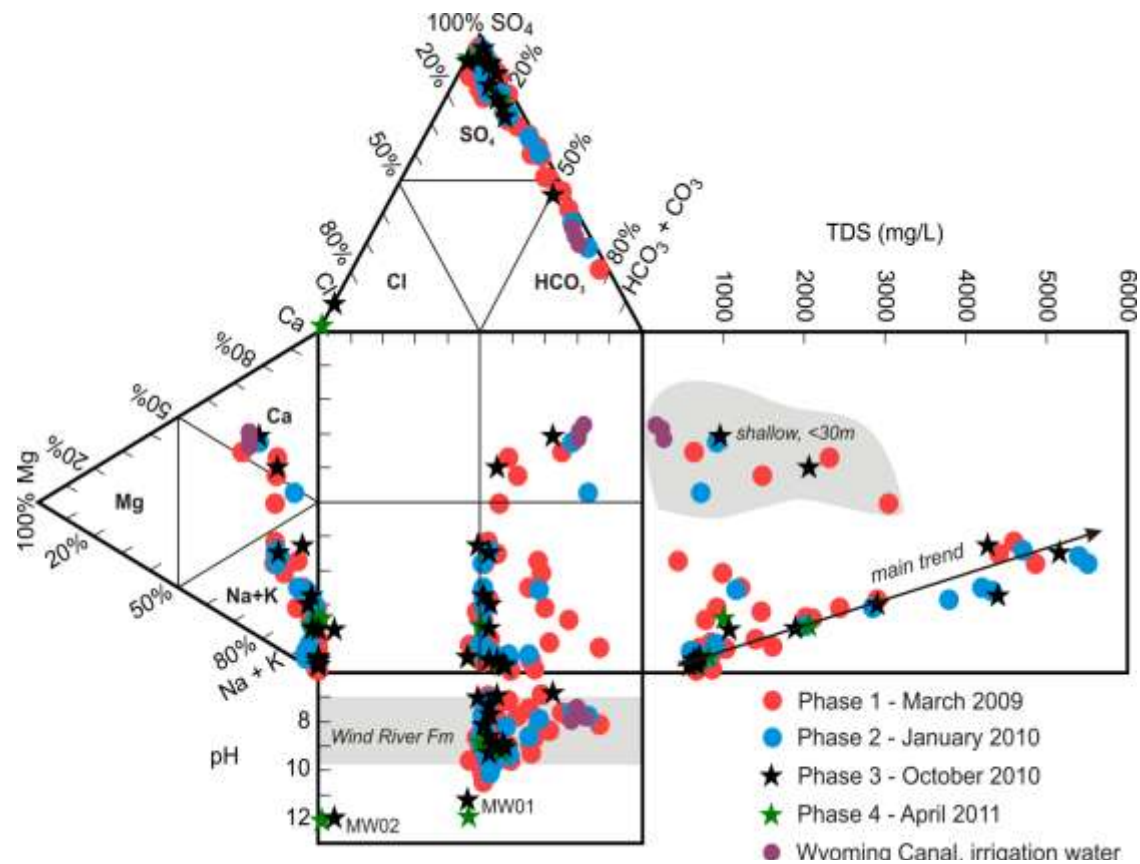
Shallow ground waters (< 31 m bgs) collected from drinking water wells and stock wells are near-neutral (pH 7.7 ± 0.4, n = 19) and display calcium-bicarbonate composition. Total dissolved solids concentrations are <6000 mg/L in all ground water samples. With depth, ground water becomes increasingly alkaline (pH 9.0 ± 1.0, n = 55), and with only one exception (MW02), is dominated by sodium and sulfate as the major cation/anion pair. This gradient in pH and water chemistry likely arises from the wide-scale surface application of irrigation water from the Wind River to support crop growth since irrigation water appears to represent an endmember composition. The chemical alteration from bicarbonate-type recharge water to sulfate-type ground water involves multiple water-rock interactions, including salt dissolution, carbonate mineralization, and exchange of divalent cations for sodium (Morris et al. 1959).
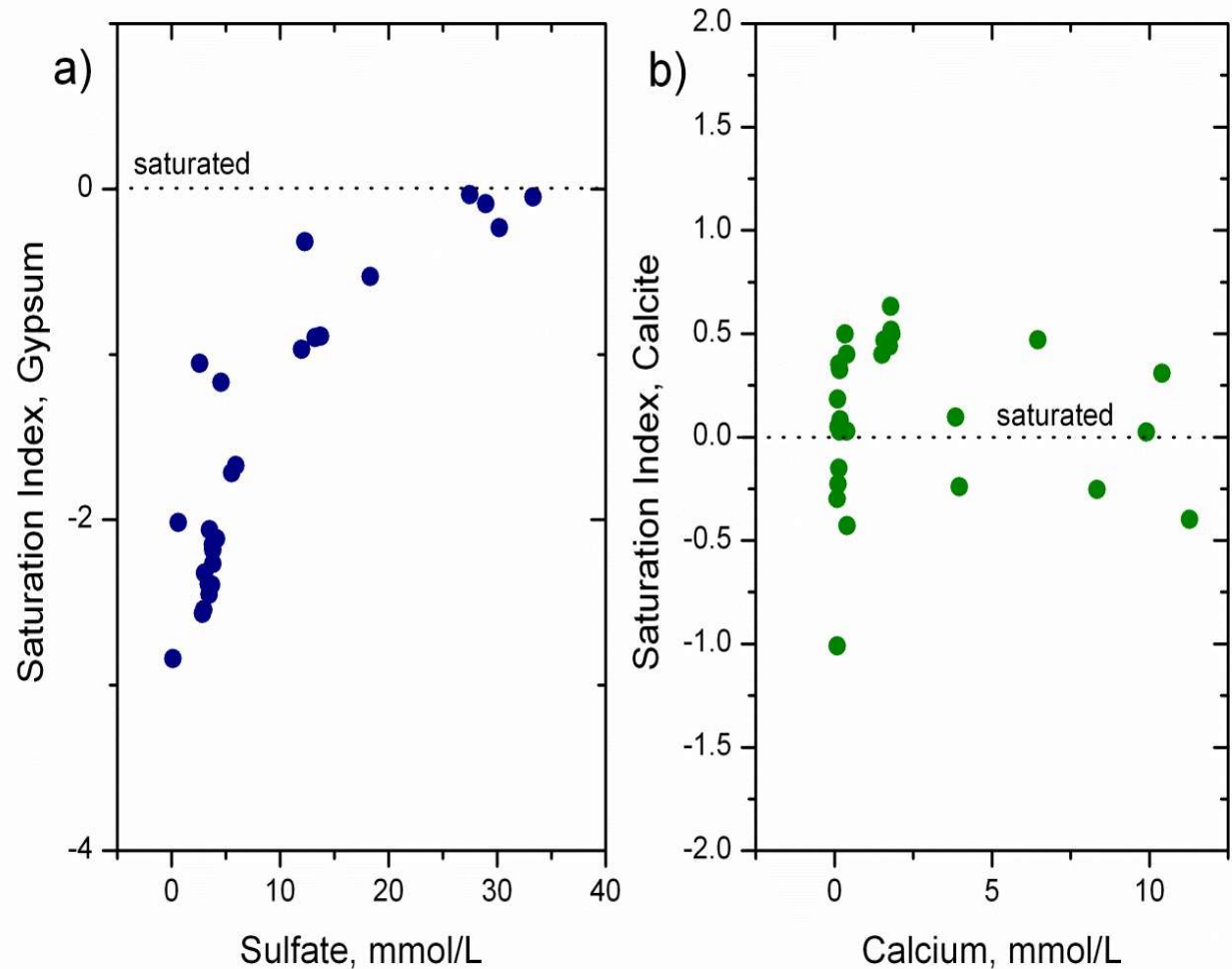
Saturation indices for **a)** gypsum versus sulfate concentration and **b)** calcite versus calcium concentration. Saturation Index is equal to the logarithm of the ratio of the ion activity product to the mineral solubility product. A Saturation Index of 0 corresponds to chemical equilibrium; values less than 0 and greater than 0 correspond to undersaturated and oversaturated conditions, respectively.

pH

pH values in MW01 and MW01 are highly alkaline (11.2-12.0), above the pH range observed in domestic wells (6.9-10), and above the pH range previously reported for the Wind River Formation (Plafcan et al. 1995, Daddow 1996). In the deep monitoring wells, up to 94% of the total alkalinity is contributed by hydroxide. The high pH measured in the deep monitoring wells was unusual and unexpected. Although ground water pH in these wells was >11, the total alkalinity was not particularly high (<500 mg/kg), and up to 94% of the total alkalinity was present as hydroxide Alkalinity contributed by carbonate/bicarbonate was less than the hydroxide component. In fact, inorganic carbon concentrations were so low in MW02 as to prevent the measurement of δ^{13}C of dissolved inorganic carbon. Presence of hydroxide alkalinity suggests strong base addition as the causative factor for elevated pH in the deep monitoring wells.

Depth trends of chloride, pH, sulfate, and potassium (filled black squares = domestic wells, filled red circles = monitoring wells).
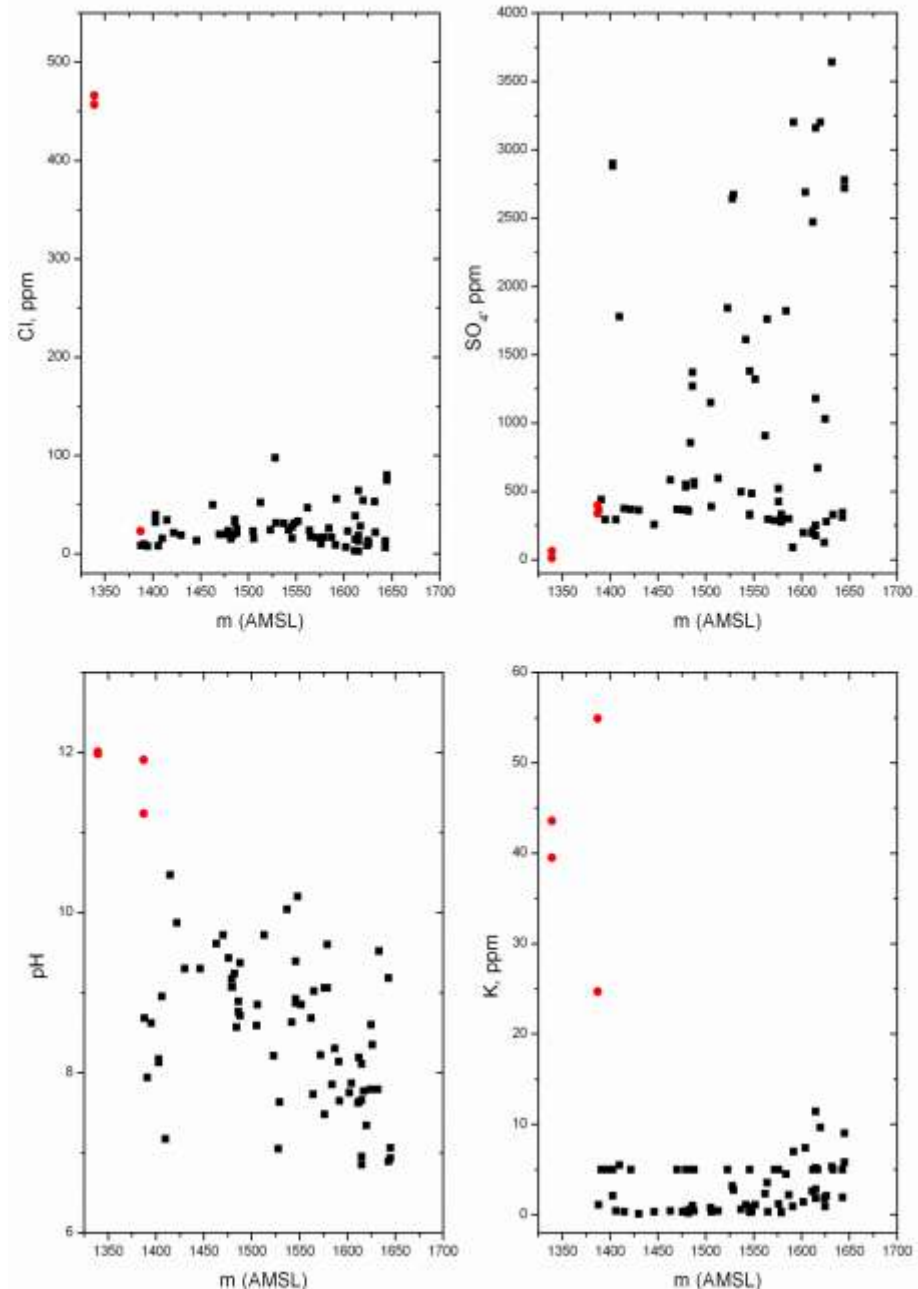
In order to gain additional insight, reaction path modeling was conducted to evaluate pH response to addition of strong base (KOH). Geochemical modeling was carried out by using ground water compositions for PGDW49, PGDW20, and PGDW32 (initial pH 7.3, 8.9, and 9.9, respectively). Modeled titration results are shown. pH is plotted versus the mass of KOH added per kg of solution. Model titration results vary as a function of ground water composition. Samples PGDW20 and PGDW32 have Na-SO$_4$-type compositions typical of deeper portions of the aquifer. In both of these cases, attainment of pH values between 11.2 and 12.0 requires small quantities of KOH addition (<250 mg KOH per kg of solution). Sample PGDW49 is elevated in Ca^{2+} and Mg^{2+}, lower in pH, and typical of shallower ground water compositions. In this case, significantly more KOH addition is required to attain pH values observed in the monitoring wells. The first derivative of the titration curve, or the buffer intensity, is shown. The buffer intensity indicates that ground water compositions like PGDW20 and PGDW32 inherently have little resistance to pH change up to about pH 12, at which point increased KOH additions are necessary to further increase pH. PGDW49 shows a broad peak on the buffer intensity diagram (pH 10 to 11) which reflects precipitation reactions to form calcium carbonate and magnesium hydroxide, reactions that consume hydroxide and therefore limit pH increases, until divalent cations are completely consumed. **The modeling results clearly show that ground water compositions typical of the Pavillion aquifer below 100 m (Na-SO$_4$-type) depth are especially vulnerable to the addition of strong base, with small KOH additions driving significant upward pH changes.**
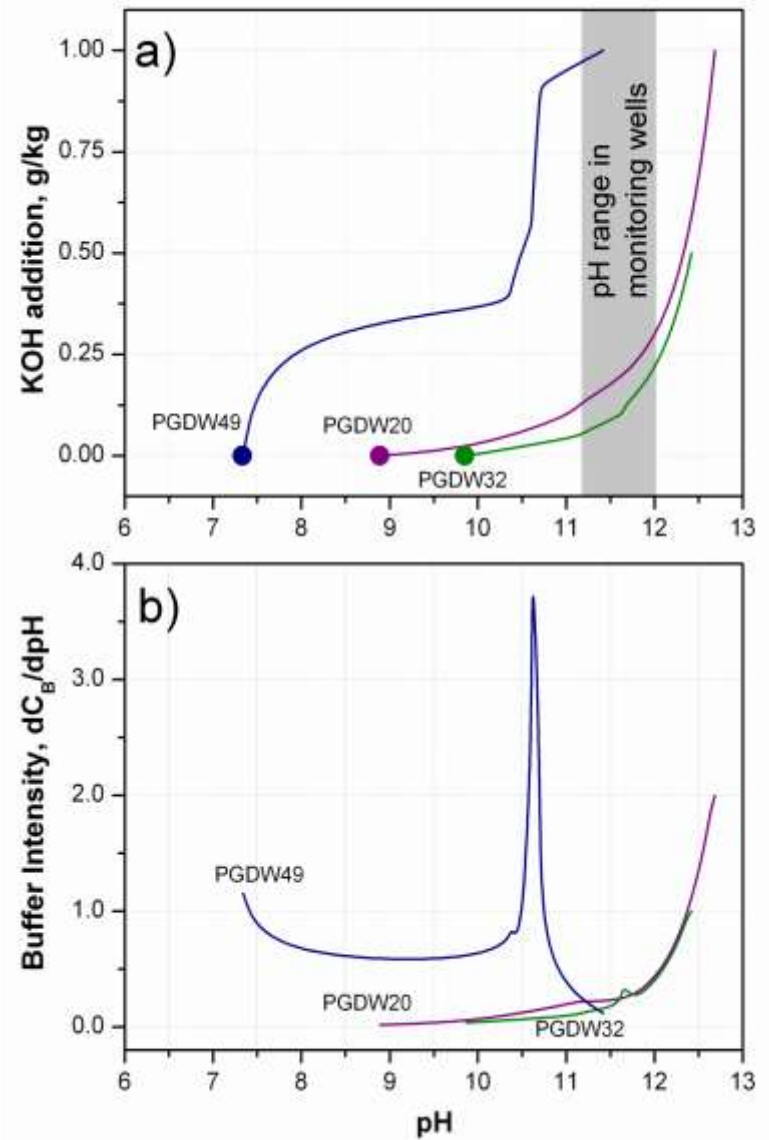
The geochemistry of ground water from the deep monitoring wells is distinctive from that in the domestic wells. Chloride enrichment in monitoring well MW02 is 18 times the mean chloride concentration (25.6 mg/L) observed in ground water from domestic wells. Chloride enrichment in this well is significant because regional anion trends tend to show increasing SO_4/Cl ratios with depth. The mean potassium concentration in domestic wells screened to 244 m bgs is 3 mg/L, with 99% of values <10 mg/L. Potassium enrichment in MW01 and MW02 is between 8.2 and 18.3 times the mean value of domestic wells.

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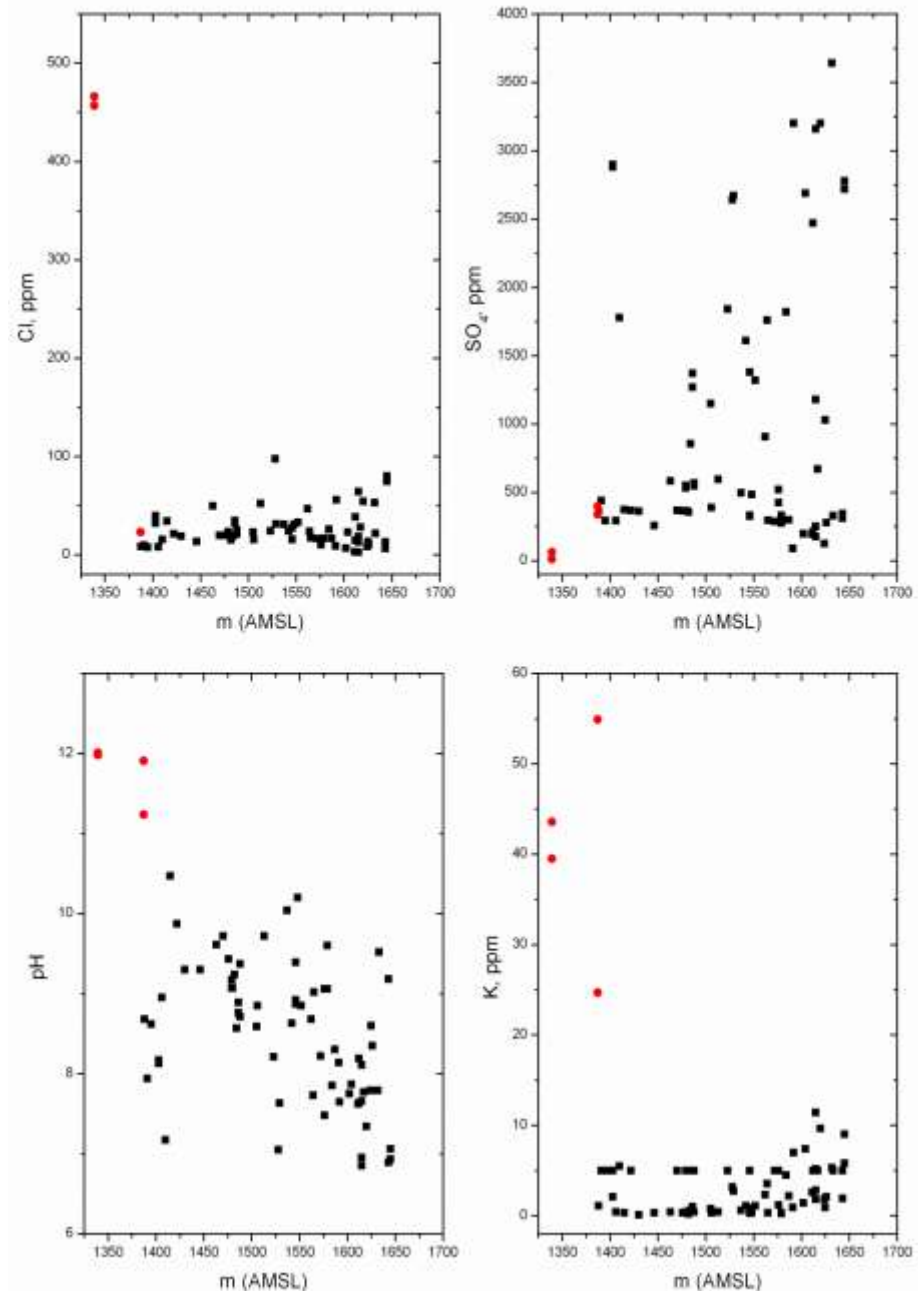
Concentrations trends versus specific conductivity. Note the monitoring wells show high pH and low sulfate, calcium, and sodium relative to the general trend observed in the domestic wells (filled black squares = domestic wells, filled red circles = monitoring wells).

The geochemistry of ground water from the deep monitoring wells is distinctive from that in the domestic wells.
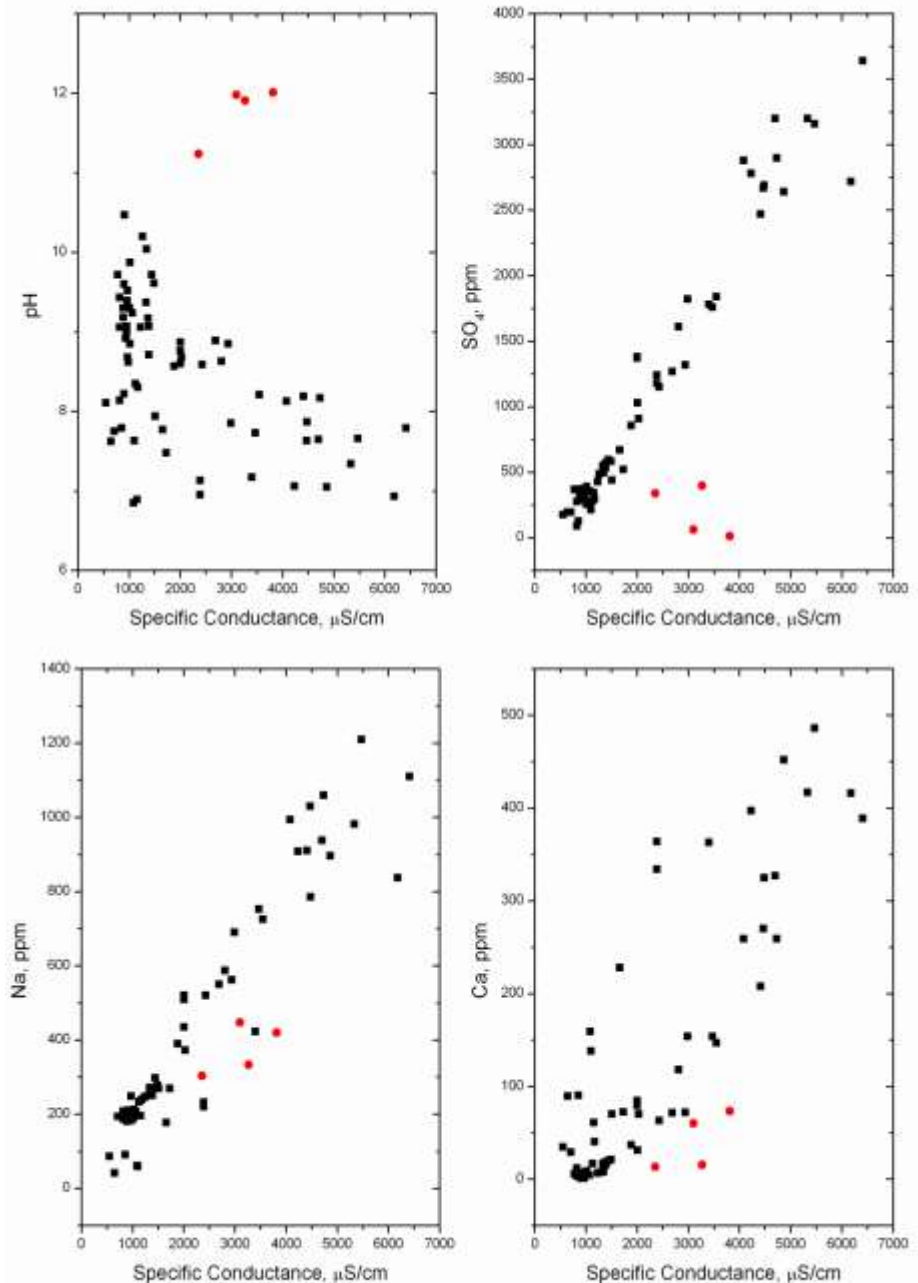
Organic Geochemistry

Organic Geochemical Anomalies

A wide variety of organic chemicals were detected in the monitoring wells including: GRO, DRO, BTEX, trimethylbenzenes, phenols, naphthalenes, acetone, isopropanol, tert-butyl alcohol, 2-butoxyethanol, 2-butanone, diethylene glycol, triethylene glycol, and tetraethylene glycol.

Detections of organic chemicals are more numerous and exhibit higher concentrations in the deeper of the two monitoring wells . This observation, along with trends in methane, potassium, chloride, and pH, suggest a deep source (>299 m bgs) of contamination.

Natural breakdown products of organic contaminants like BTEX and glycols include acetate and benzoic acid; these breakdown products are more enriched in the shallower of the two monitoring wells, suggesting upward/lateral migration with natural degradation and accumulation of daughter products.
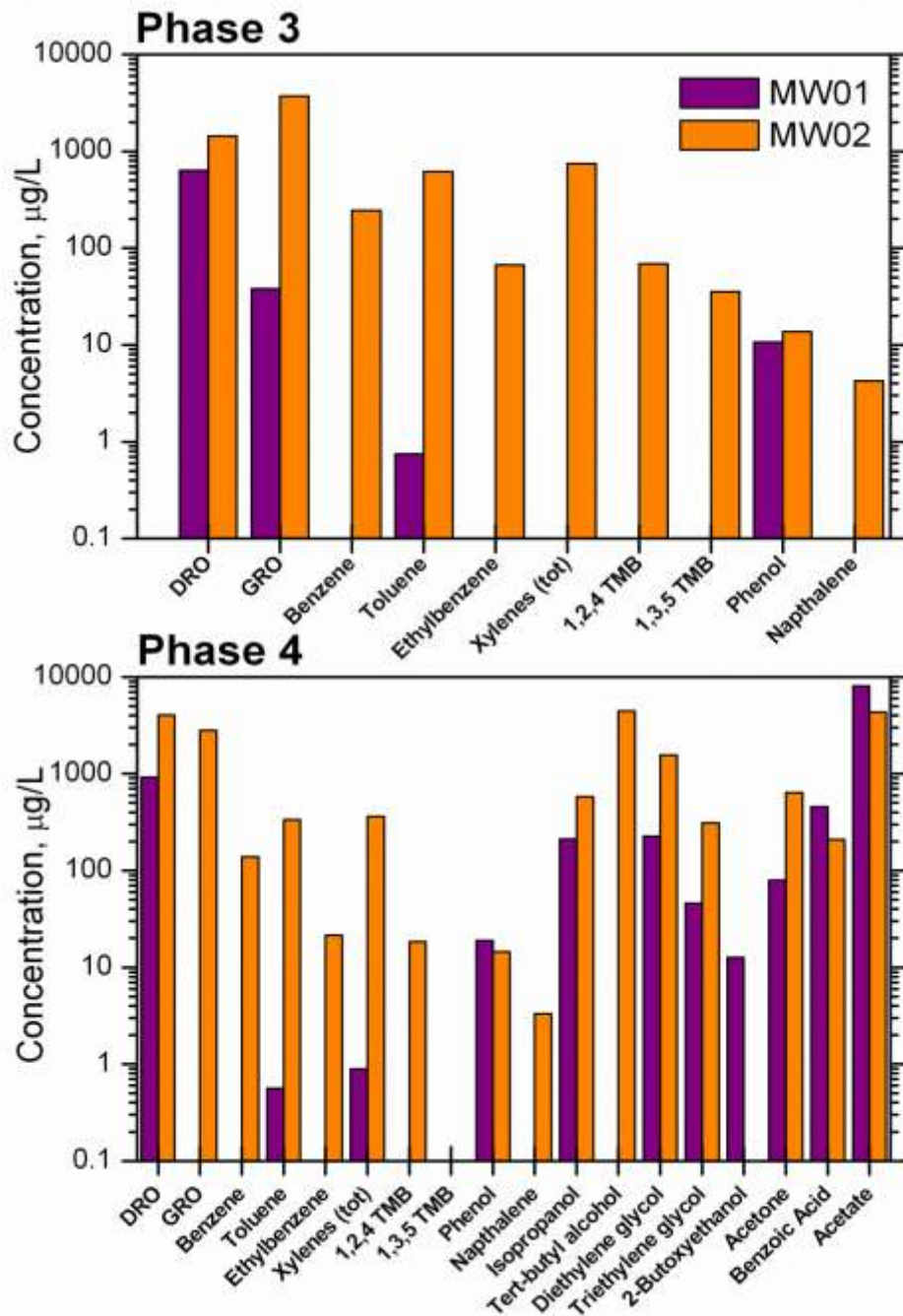
Geochemical Anomalies in deep ground-water monitoring wells.

† All values in ppb unless otherwise noted.
 ----- not analyzed
nd - not detected.
†† Includes phenol, 2,4-dimethylphenol, 2-methylphenol, 3&4 methylphenol.
 ††† Includes naphthalene, 1-methylnapthalene, and 2-methylnapthalene.
†††† Value below quantitation limit of 10 µg/L.
* 2-Butoxyethanol determined by HPLC-MS-MS.
** 2-Butoxyethanol determined by GC-MS.

Compound	MW01 Phase 3 10/6/2010	MW02 Phase 3 10/6/2010	MW01 Phase 4 4/20/2011	MW02 Phase 4 4/19/2011
pH	11.9	12.0	11.2	12.0
K, mg/L	54.9	39.5	24.7	43.6
Cl, mg/L	23.3	466	23.1	457
CH_4, mg/L	16.0	19.0	17.9	18.8
Benzene †	nd	246	nd	139
Toluene	0.75	617	0.56	336
Ethylbenzene	nd	67	ND	21.5
Xylenes (total)	ND	750	0.89	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	38	3710	nd	2800
Phenol ††	11.1	56.1	20.9	64.9
Napthalene †††	nd	6.06	nd	6.10
Isopropanol	-----	-----	212	581
Tert-Butyl Alcohol	-----	-----	nd	4470
Diethylene Glycol	-----	-----	226	1570
Triethylene Glycol	-----	-----	46	310
Tetraethylene Glycol	-----	-----	7.3 ††††	27.2
2-Butoxyethanol *	-----	-----	<10	<10
2-Butoxyethanol **	<0.25	<0.25	12.7	<0.10
Acetone	-----	-----	79.5	641
Benzoic Acid	212	244	457	209
Acetate	-----	-----	8050	4310
Formate	-----	-----	112	558
Lactate	-----	-----	69	213
Propionate	-----	-----	309	803

United States Environmental Protection Agency

Well completion reports obtained online from WOGCC and Material Safety and Data Sheets (MSDSs) obtained from the operator were reviewed to examine inorganic and organic compounds in additives used for hydraulic fracturing and similarity with detected elements and compounds in ground water.

- Well completion reports were limited to a subset of production wells and included dates of injection, injection depths, pressure, flow, and volume for slickwater and carbon dioxide foam fracture jobs.

- Some MSDSs list chemical formulation as proprietary (e.g., proprietary alcohols) or list a chemical family (e.g., blend of organic surfactants) rendering identification of constituents impossible.

- Inorganic additives are potential sources of elevated K, Cl, and OH in deep monitoring wells.

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

Compound/ Compound Class	Information from MSDSs and Well Completion Reports
pH	KOH was used in a crosslinker (<5%) and in a solvent (85-100%).
K	The formulation of fracture fluid provided for foam jobs typically consisted of CO_2, 6% KCl, 10% methanol, and "clean" fluid and "additives." Potassium metaborate was used in crosslinkers (5-10%, 30-60%). KOH was used in a crosslinker (<5%) and in a solvent (85-100%).
Cl	Ammonium chloride was used in crosslinker (1-27%).
BTEX	Aromatic solvent (typically BTEX mixture) was used in a breaker (<75%). Diesel oil (mixture of saturated and aromatic hydrocarbons including naphthalenes and alkylbenzenes) was used in a guar polymer slurry/liquid gel concentrate (30-60%) and in a solvent (60-100%). Petroleum raffinates (mixture of paraffinic, cycloparaffinic, olefinic, and aromatic hydrocarbons) was used in a breaker (<30-60%). Heavy aromatic petroleum naptha (mixture of paraffinic, cycloparaffinic and aromatic hydrocarbons) was used in surfactants (5-10%, 10-30%, 30-60%) and in a solvent (10-50%). Toluene was used in a flow enhancer (3-7%). Xylenes were used in a flow enhancer (40-70%) and a breaker (confidential percentage).
Trimethylbenzenes	1,2,4-trimethylbenzene was used in surfactants (0-1%). Diesel oil (mixture of saturated and aromatic hydrocarbons including naphthalenes and alkylbenzenes) was used in a guar polymer slurry/liquid gel concentrate (30-60%) and in a solvent (60-100%). Petroleum raffinates (mixture of paraffinic, cycloparaffinic, olefinic, and aromatic hydrocarbons) was used in a breaker (<30-60%). Heavy aromatic petroleum naptha (mixture of paraffinic, cycloparaffinic and aromatic hydrocarbons) was used in surfactants (5-10%, 10-30%, 30-60%) and in a solvent (10-50%).
DRO and GRO	Diesel oil (mixture of saturated and aromatic hydrocarbons including naphthalenes and alkylbenzenes) was used in a guar polymer slurry/liquid gel concentrate (30-60%) and in a solvent (60-100%). Petroleum raffinates (mixture of paraffinic, cycloparaffinic, olefinic, and aromatic hydrocarbons) was used in a breaker (<30-60%). Heavy aromatic petroleum naptha (mixture of paraffinic, cycloparaffinic and aromatic hydrocarbons) was used in surfactants (5-10%, 10-30%, 30-60%) and in a solvent (10-50%).
Napthalene	Naphthalene was used in surfactants (0-1, 5-10%) and a breaker (confidential percentage). Hydrotreated light petroleum distillates (mixture of C10-C14 naphthenes, iso- and n-paraffins) were used in a guar polymer slurry/liquid gel concentrate (40-60%). Diesel oil (mixture of saturated and aromatic hydrocarbons including naphthalenes and alkylbenzenes) was used in a guar polymer slurry/liquid gel concentrate (30-60%) and in a solvent (60-100%).
Isopropanol	Isopropanol was used in a biocide (20-40%), in a surfactant (30-60%), in breakers (<1%, 10-30%), and in foaming agents (<3%, 1-5%, 10-30%).
Tert-Butyl Alcohol	No MSDS listing. Breakdown product of methyl *tert*-butyl ether and *tert*-butyl hydroperoxide - found in gel breakers.
Glycols	Diethylene glycol was used in a foaming agent (5-10%) and in a solvent (0.1-5%). Triethylene glycol was used in a solvent (95-100%).
2-Butoxyethanol	2-butoxyethanol was used in a surfactant (10-30%), in foaming agents (<10%, <11%, <12%, 1-10%, 10-30%) and in solvents (15-40%, 60-100%). -
Acetone	Breakdown product of *tert*-butyl hydroperoxide - found in gel breakers. See discussion.
Benzoic Acid, Acetate, Formate, Lactate, Propionate, 2-Butanone, Phenols	Natural breakdown products of organic contaminants (e.g., BTEX, glycols, etc.).

Tert-butyl Alcohol (TBA)

- TBA is a synthetic compound.

- TBA is a biodegradation product of methyl *tert*-butyl ether (MTBE, synthetic chemical used as a fuel additive) under methanogenic conditions (e.g., Mormile et al. 1994, Bradley et al. 2001). TBA biodegradation is generally slow compared to the degradation of MTBE; this suggests that TBA could be present and persist even after complete MTBE removal from ground water systems impacted by fuel releases (Wilson et al. 2005). MTBE was not detected in either of the deep monitoring wells.

- TBA is a breakdown product of *tert*-butyl hydroperoxide (a gel breaker used in hydraulic fracturing; e.g., Hiatt et al. 1964). A second known pathway of TBA production is from the decomposition of the gel breaker *tert*-butyl hydroperoxide. Hiatt et al. (1964) found that decomposition of *tert*-butyl hydroperoxide yielded a 10-fold molar quantity of TBA, oxygen, *di-tert*-butyl peroxide, and acetone. Acetone was detected in MW02 during Phase 4 sampling at a concentration of 641 μg/L. Use of this breaker seems to be common in hydraulic fracturing formulations; however, available MSDSs lack clarity as to whether *tert*-butyl hydroperoxide was used in the Pavillion Gas Field for well stimulation.

Gas Migration

Gas from the Fort Union and lower Wind River Formations varies little in δ^{13}C for methane, ethane, and propane with depth from the lower Eocene Wind River Formation to deeper mature and post-mature Upper Cretaceous source rocks suggesting upward gas migration (Johnson and Rice 1993, Johnson and Keighin 1998) from deep source rocks.
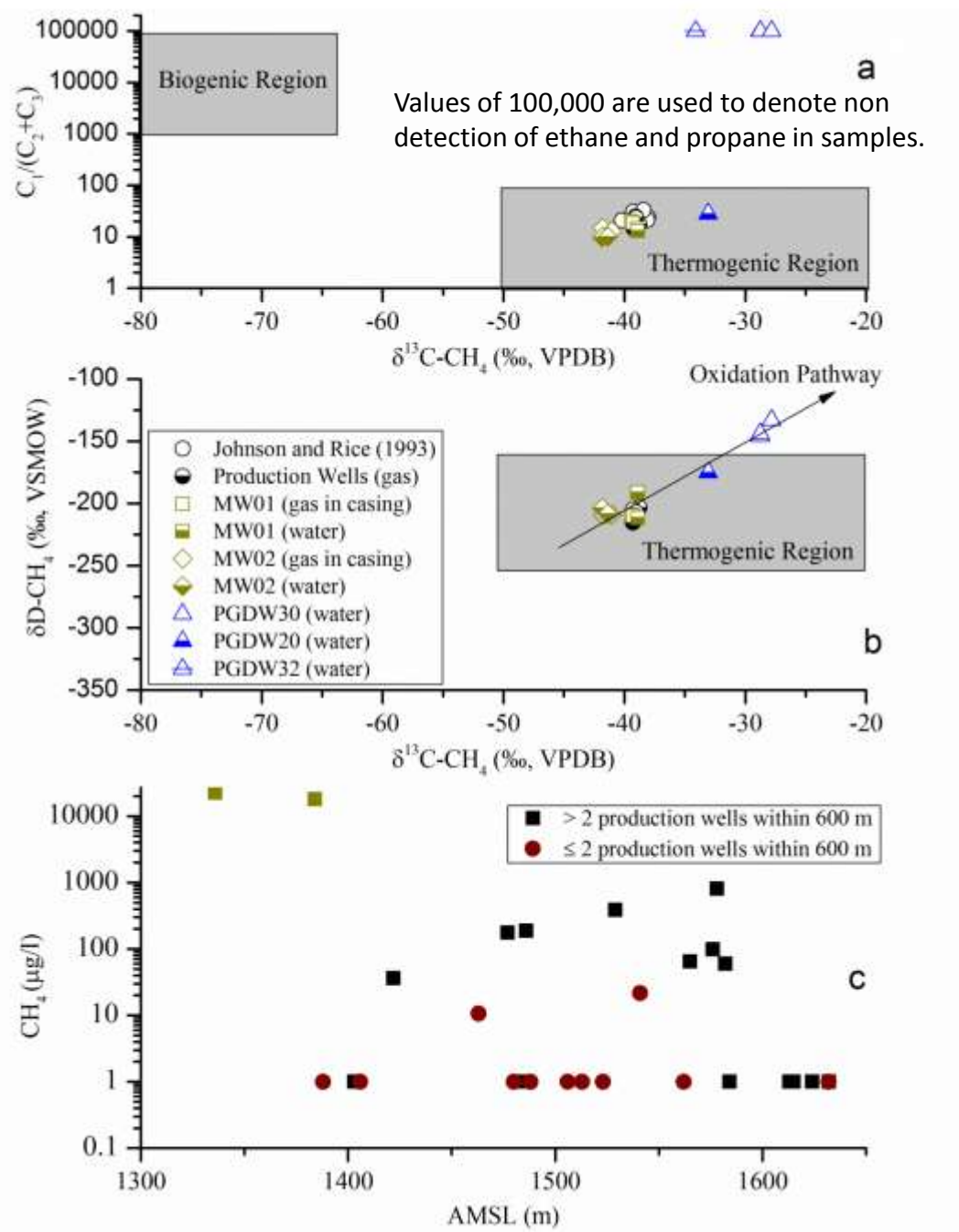
Lack of significant variation in δ^{13}C for light hydrocarbons limits the use of isotopic fingerprinting in evaluating enhanced gas migration from the Fort Union Formation to within 300 m of the surface. A substantial amount of additional compositional and isotopic data is available on the Wind River and Fort Union Formations but is classified as Confidential Business Information by the gas field operator.

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

Plots of $\delta^{13}C$-CH_4 versus δD -CH_4 and $\delta^{13}C$-CH_4 versus $C_1/(C_2 + C_3)$ indicate that light hydrocarbons in casing and dissolved gas in deep monitoring wells are similar to produced gas and have undergone little oxidation or biodegradation. These observations combined with radiocarbon analysis of CH_4 (< 0.2% percent modern carbon) obtained from gas in casing of both MW01 and MW02 indicates that methane in deep monitoring wells is of thermogenic origin.

Gas in domestic wells is oxidized thermogenic gas (enrichment of ^{13}C of remaining CH_4 with biodegradation). This observation is consistent with a pattern of dispersion and degradation with upward migration observed for organic compounds.

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

Values of 100,000 are used to denote non detection of ethane and propane in samples.

Elevated levels of dissolved methane in domestic wells generally increase with proximity to gas production wells . Methane was not detected in shallow domestic wells (e.g., < 50 m) regardless of proximity to production wells . All domestic wells with the exception of PGDW25 with 2 or less production wells within 600 m are located on the periphery of the gas field. PGDW25 is located within 1600 m of 15 gas production wells.

A review of open-hole geophysical logs obtained from the WOGCC internet site indicates the presence of gas-filled porosity at three locations at 198, 208, and 252 m bgs between the years 1965 - 1973 suggesting the presence of natural gas in ground water at depths used for domestic water supply prior to extensive commercial development. However, a review of 10 mud-gas logs recorded in the mid-1970s and early 1980s obtained on line from WOGCC, do not indicate gas shows within 300 m of the surface at any location.
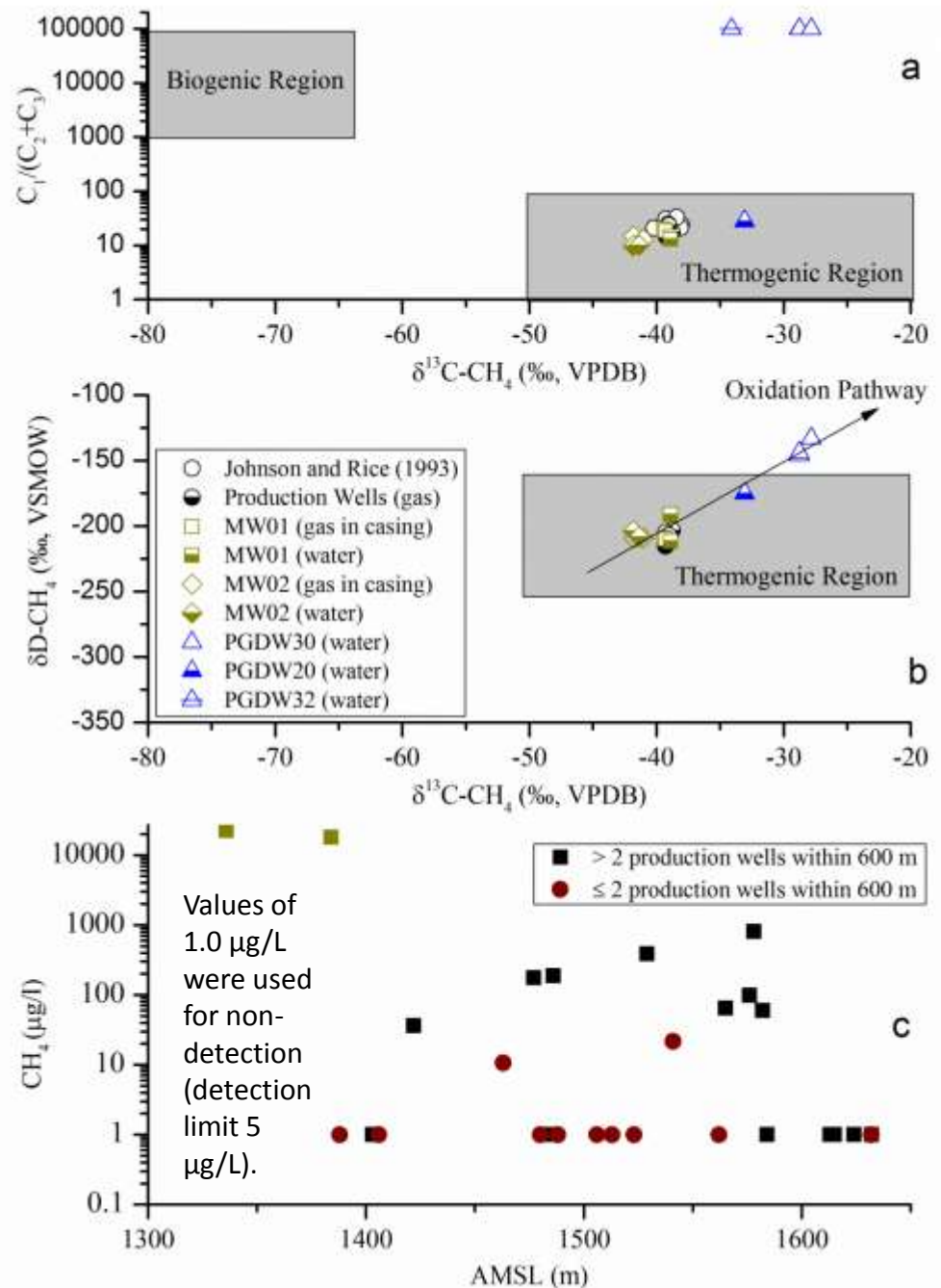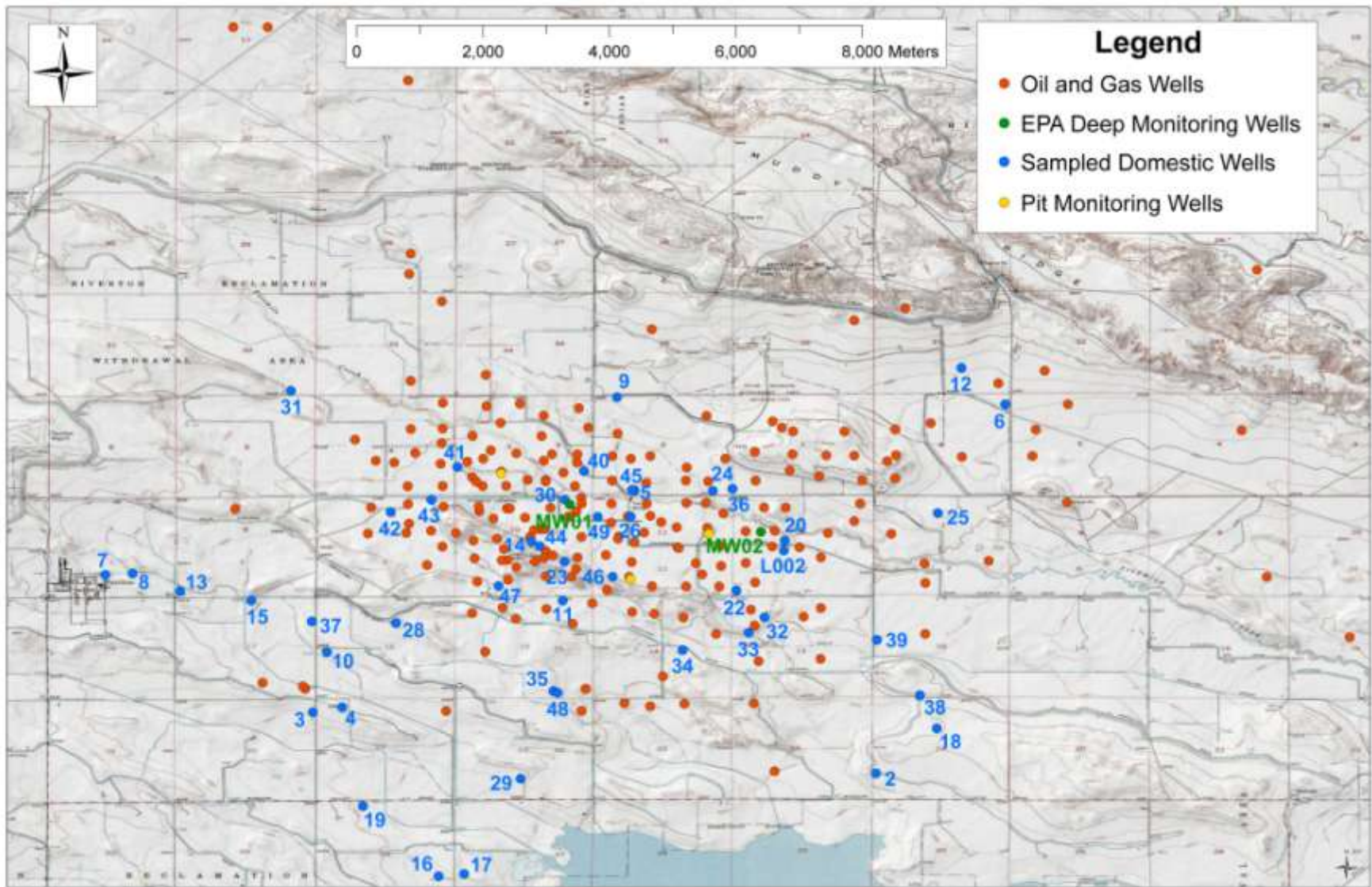
Map illustrating location of oil and gas production wells, sampled PGDWxx series domestic wells (only numbers shown to conserve space), two deep monitoring wells, and three shallow monitoring wells near pits. PGDW07 and PGDW08 are municipal wells in the town of Pavillion.

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Legend
- Oil and Gas Wells
- EPA Deep Monitoring Wells
- Sampled Domestic Wells
- Pit Monitoring Wells

0   400   800   1,200   1,600   2,000 Meters

N

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