Ground-Water Quality Investigation - Pavillion, Wyoming U.S. Environmental Protection Agency

Methods, Graphics, and Data Tables

November 8, 2011

Methods

Four sampling events (Phases I - IV) were conducted commencing in March 2009 and ending in April 2011. In March 2009 (Phase I), EPA collected samples from 35 domestic wells in the area of investigation, 2 post-reverse osmosis, and two 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 (ten previously sampled), 4 stock wells and two municipal wells; (2) a filter sample from a reverse osmosis system; (3) surface-water and sediment samples from five locations along Five-Mile Creek (a creek traversing the area of investigation); (4) gas and produced water/condensate samples (organic compounds only) from five production wells; and (5) ground-water samples from three 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 then prompted EPA to install two deep monitoring wells in June 2010 to differentiate potential deep versus shallow sources of ground-water contamination. Both wells were drilled to a depth of 305 m. Monitoring wells MW01 and MW02 were screened at 233 - 239 m and 293 -299 m bgs respectively. The expense of drilling deep wells with blowout prevention was a limiting factor in the number of monitoring wells installed. In September 2010 (Phase III), EPA collected gas samples from well casings of 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 deep monitoring wells to compare previous findings and expand the analyte list to include glycols, alcohols, and low molecular weight acids. Eight previously sampled domestic wells and three previously sampled stock/irrigation wells were also sampled at this time. The location of production wells, monitoring wells, and sampled domestic wells is illustrated in Fig. 1.

Monitoring wells were installed using mud rotary with drill-stem and annular-space borehole blowout prevention. Mud composition consisted of formation water, Quik-Gel high yield bentonite (Halliburton), and additives, including Penetrol nonionic wetting agent (Halliburton) and EZ-Mud Gold clay/shale stabilizer (Halliburton). All drilling additives were extracted in water (1:100 dilution) and analyzed for pH, inorganics, organics, glycols, and alcohols. The pH of samples varied between 6.6 and 11.2, potassium varied between 0.1 and 1.2 mg/L, chloride varied between not detected and 214 mg/L, ethanol and isopropanol detections were less than 90 µg/L, and acetone, tert-butyl alcohol (TBA), trimethylbenzenes, and glycols were not detected. Benzene, toluene, ethylbenzene, and xylenes (BTEX) were also non-detectable. The purpose of conducting these analyses was to ensure that the monitoring well results were not influenced by constituents in the additives. A mixture of water and Ouikrete commercial grade portland cement was used to seal the annular space above prepacked stainless steel screens using power-washed carbon steel tremie pipe. Wells were aggressively developed using standard methods (surging, bailing, air jetting). The monitoring wells were purged at least ten screen volumes prior to sampling. Cuttings were examined by manually washing drilling mud from rock fragments and recorded as a function of depth. Open-hole logging (caliper, density, resistivity, spontaneous potential, natural gamma) was conducted by Colog Inc., prior to placement of well construction materials. Deep

monitoring well construction is illustrated in **Fig. 2**. Both wells were screened in a white coarse-grained sandstone containing little or no shale similar to media targeted by local well drillers.

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 3.8 to 27 L/min. The rate of pumping was measured using a Model TM0050 in-line turbine flow meter with associated Model FM0208 flow monitor manufactured by Turbines, Inc. Drawdown during pumping was measured with a sonic water level sensor obtained from Eno Scientific, Inc. (model WS2010 PRO). The flow was split, with one portion going to waste and the other portion going to a flow cell equipped with a YSI 5600 multiparameter probe to track stabilization of pH (<0.02 standard units per minute), oxidation-reduction potential (<2 mV per minute), specific conductance (<1% per minute), dissolved oxygen (DO), and temperature.

Gas samples were collected from the casing of deep monitoring wells by connecting a 12.7 mm NPT stainless steel Swagelok® quick-connect body and a Swagelok® single-end shutoff stem to a 12.7 mm brass ball valve. The stem was connected to 6.35 mm internal diameter Tygon Masterflex tubing and a 0.5 liter Cali-5 Bond gas sampling bag equipped with a Leur-Fit ValveTM and a Leur-taper Quick-MateTM connector. A Masterflex E/S portable peristaltic pump was used to extract gas at 1 L/min. Samples were collected after stabilization (\pm 1%) of O₂, CO₂, and CH₄ readings on a GEM-2000 Plus CES-LANDTEC portable gas analyzer. During the Phase IV sample event, water from domestic wells was screened using a Thermo-Scientific TVA-1000B portable flame- and photo- ionization detector (FID/PID) and a 10 liter plexiglass sparge cell. Samples from domestic wells were routed through a closed (no contact with the atmosphere to avoid offgassing) sample train and collected in 0.5 liter Cali-5 Bond gas sample bags. Ultrapure N₂ gas was introduced into the bags and placed on a rotary shaker for one hour prior to headspace analysis on site using a portable gas chromatograph (GC) equipped with a thermal conductivity detector. Portable FID readings provided an immediate indication of methane in well water prior to GC analysis. Samples were also submitted to EPA's Office of Research and Development (ORD) laboratory in Ada, Oklahoma for analysis of dissolved gases.

Sampling chronology and analytical methods for all sampling events are summarized in **Supporting** Information (SI) Table 1. Analytical results from Phases I and II were made publically available in 2009 (1) and 2010 (2). Inorganic geochemical results for ground water (all phases) are summarized in SI Table 2. Organic and inorganic geochemical anomalies in deep ground-water monitoring wells (Phases III and IV) are summarized in SI Table 3. Aqueous analysis of light hydrocarbons, gas and headspace analysis of light hydrocarbons, and isotopic data for dissolved, gas phase, and headspace analysis are summarized in SI Tables Table 4a, 4b, and 4c, respectively (all phases). Quality assurance and control (QA/QC) measures for ground-water and gas sampling and analysis are summarized in SI Tables 5 to 16. Audits of Data Quality (ADOs) were conducted by a contractor (independent of this investigation) or an EPA OA Manager for all analyses conducted outside EPA's Contract Laboratory Program (CLP), with the exception of data collected during Phase I, which is still in progress. This included data from EPA's Region VIII laboratory in Golden, Colorado, EPA's Office of Research and Development Laboratory in Ada, Oklahoma, and Isotech Laboratories in Champaign, Illinois. A technical systems audit of Isotech Laboratories included an on-site visit by the independent contractor and EPA QA Manager. Two on-site field technical system audits were also conducted by the independent contractor and the EPA QA Manager to ensure compliance with the Category I (highest of four levels in EPA) Quality Assurance Project Plan established for this site for ground-water and gas sample collection.

Borehole geophysical logs, available online from the Wyoming Oil and Gas Conservation Commission (WOGCC), were utilized to map lithology in the area of investigation (**Fig 3a and 3b**). Depending upon the specific well, various combinations of natural gamma, resistivity, self-potential, density, and neutron porosity logs were utilized. Log resolution was sufficient to discern distinct layers of shale 1 m or greater

in thickness but not sufficient to differentiate coarse- medium-, and fine-grained sandstones nor sandstones containing various proportions of shale. Descriptions of cuttings logged during installation of deep monitoring wells and domestic wells obtained from a local driller were used for near surface description. Neither grain size nor proportions of shale in sandstone were differentiated in near surface sandstones to maintain consistency with descriptions from geophysical logs. Lithology in the area of investigation is highly variable and difficult to correlate from borehole to borehole, even for boreholes in close proximity to one another consistent with other observations in the Wind River Formation (3). Sandstone and shale layers appeared thin and of limited lateral extent consistent, again consistent with previous observations of lithology in the Wind River Formation (4,5).

Cement bond variable density logs (CBL/VDL), available for less than half of production wells, were obtained online from the WOGCC to evaluate well integrity. Sporadic bonding is defined as an interval having an amplitude (mV) greater than A_{80} (6) where

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

and A_{80} , A_0 , and A_{100} = amplitude at 80%, 0%, and 100% bond respectively. A_0 typically corresponds to amplitude in free pipe whereas A_{100} corresponds to the best-bonded interval on the CBL. CBL/VDLs provide an average volumetric assessment of the cement in the casing-to-formation annular space and are considered low resolution tools compared to ultrasonic imaging tool logs which provide a high-resolution 360° scan of the condition of the casing-to-cement bond (7). Acoustic imaging tools do not directly measure cement seal. All CBL/VDLs available from WOGCC reflect pre-hydraulic fracturing conditions.

References Cited

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- U.S. Environmental Protection Agency. 2010. Expanded Site Inspection Analytical Results Report, Pavillion Area Groundwater Investigation Site, August 30, 2010. <u>http://www.epa.gov/region8/superfund/wy/pavillion/</u>.
- 3. J. L. Osiensky, G. V. Winter, R. E. Williams, Ground Water 22, 298 (1984).
- E. L. Single, Wyoming Geological Association 21st Field Conference Guidebook, pp. 101-103 (1969).
- R. M. Flores, C. W. Keighin, Reservoir anisotropy and facies stratigraphic framework in the Paleocene Front Union Formation, western Wind River Basin, Wyoming, in Keefer, W.R., Metzger, W.J., and Godwin, L.H., eds., Oil and Gas and other Resources of the Wind River Basin Wyoming: Wyoming Geological Association Special Symposium, p. 121-141 (1993).
- 6. U.S. Environmental Protection Agency Region VIII, Ground Water Section Guidance No. 34 March 31, 1994.
- 7. K. Bybee, Journal of Petroleum Technology, 64 (2007).

GRAPHICS

(Figures)

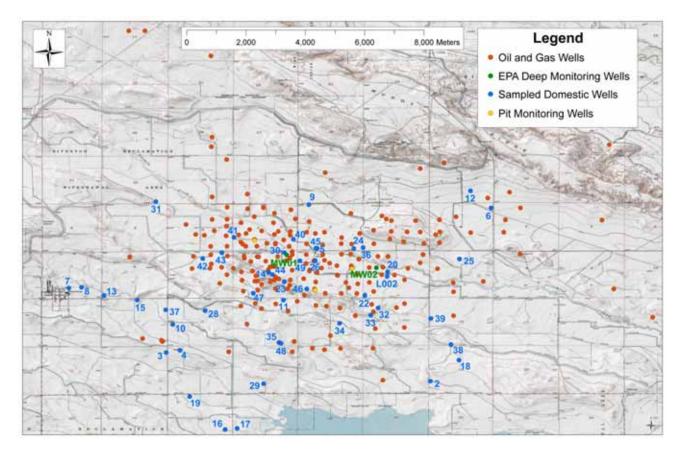


Fig. 1. Map illustrating location of oil and gas production wells, sampled PGDW series domestic wells (only numbers shown to conserve space), two deep monitoring wells and three shallow monitoring wells near pits. PGDW07 and 08 are municipal wells in the Town of Pavillion.

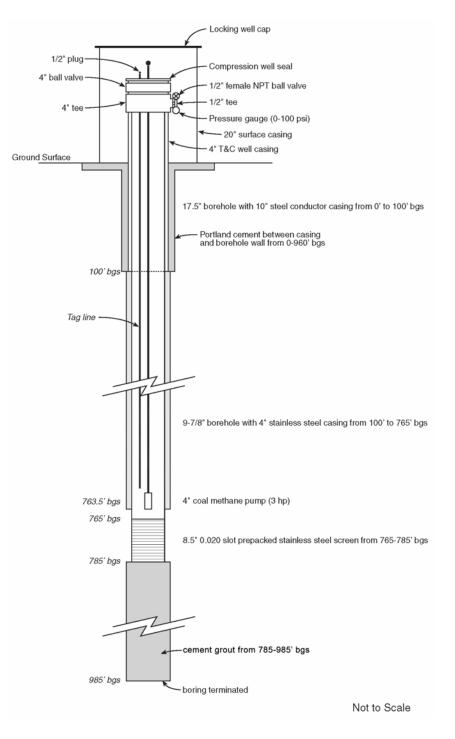


Fig. 2. Schematic illustrating construction of MW01.

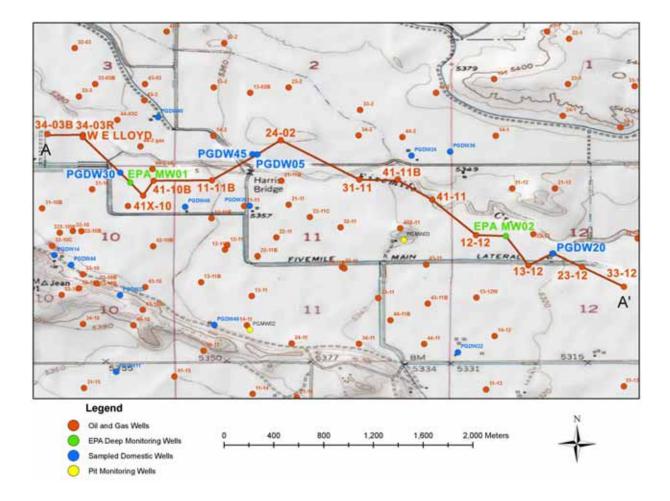


Fig. 3a. Map illustrating transect used to develop lithologic cross section and evaluation of CBL/VDLs.

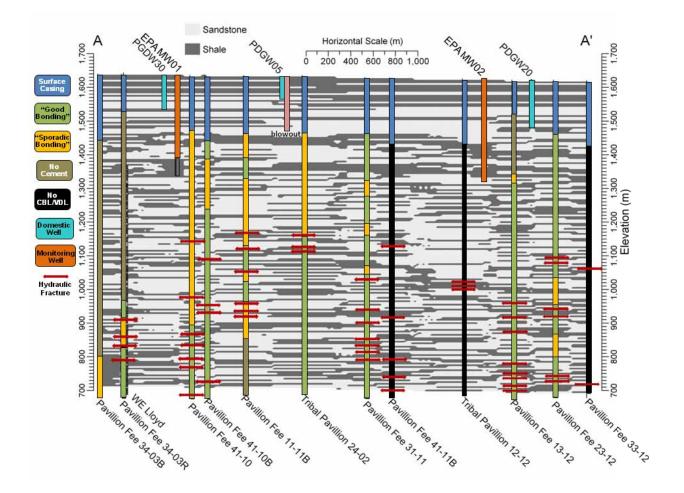
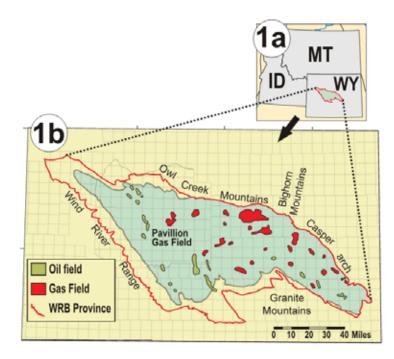
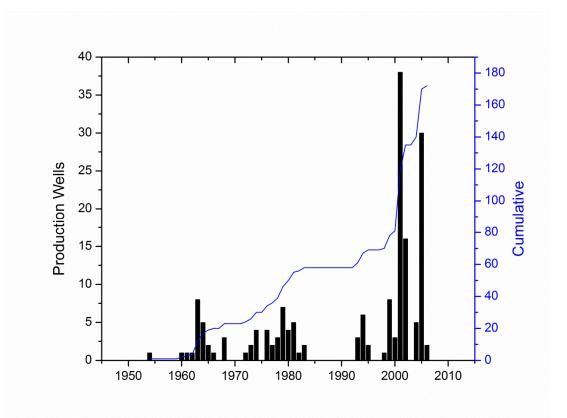


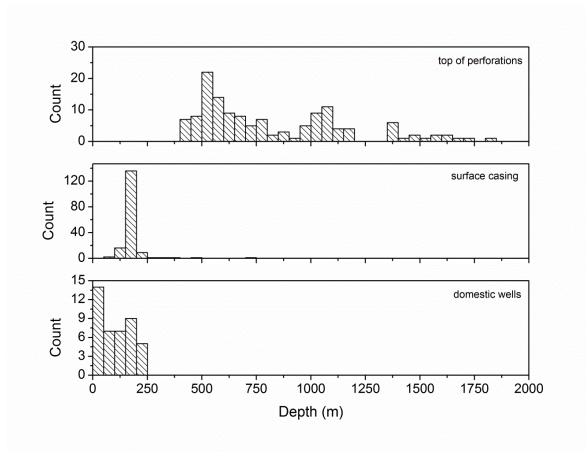
Fig. 3b. Lithologic cross-section along transect illustrating production wells (with evaluation of CBL/VDLs), domestic wells, and blowout location. Red arrows denote depths of hydraulic fracturing of unknown areal extent.



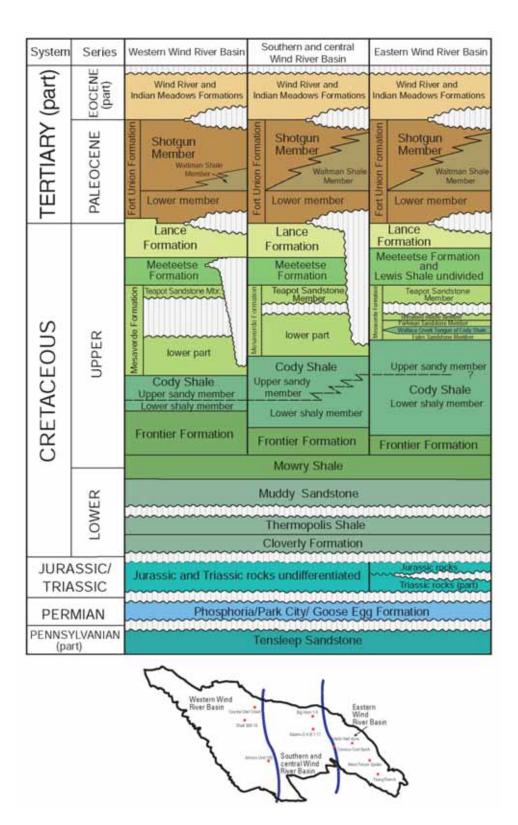
Location of Wind River Basin in Wyoming. (b) Location of Pavillion Gas Field in the Wind River Basin.



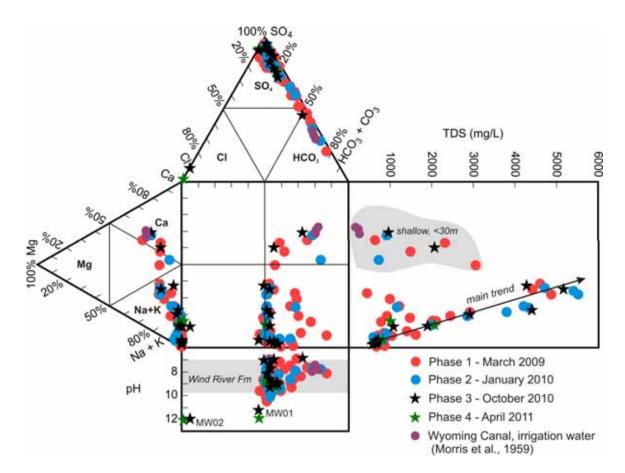
Chronology of production well completion at the Pavillion Gas Field



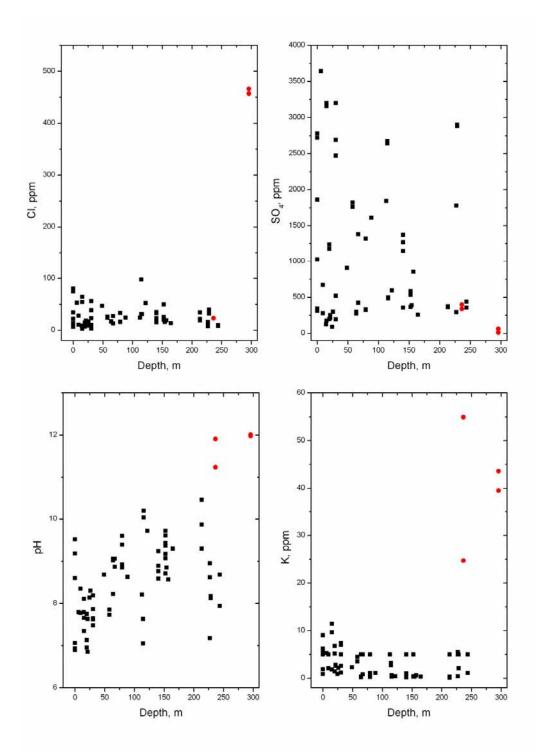
Histograms summarizing depths of top of perforation interval of production wells, base of surface casing of production wells, and base of screened interval of domestic wells.



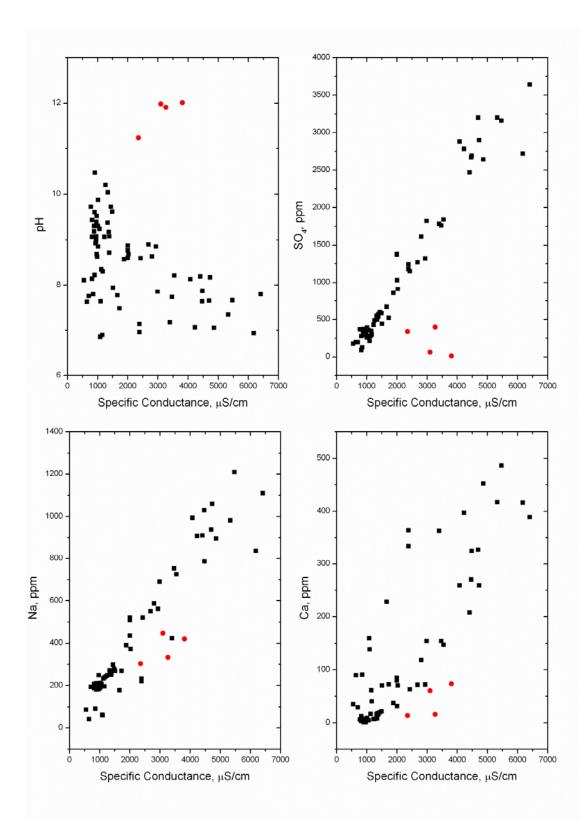
Generalized stratigraphic columns and correlations of Mississippian through Eocene strata in the Wind River Basin, Wyoming. The Pavillion Gas Field in located in the Western Wind River Basin.



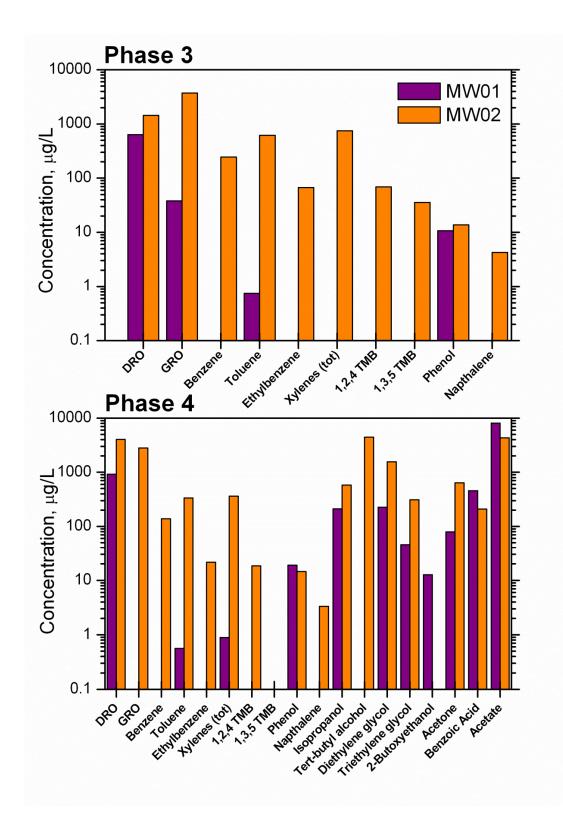
Durov diagram showing ground-water chemistry trends obtained in Phase I - IV sampling events and the composition of the irrigation water



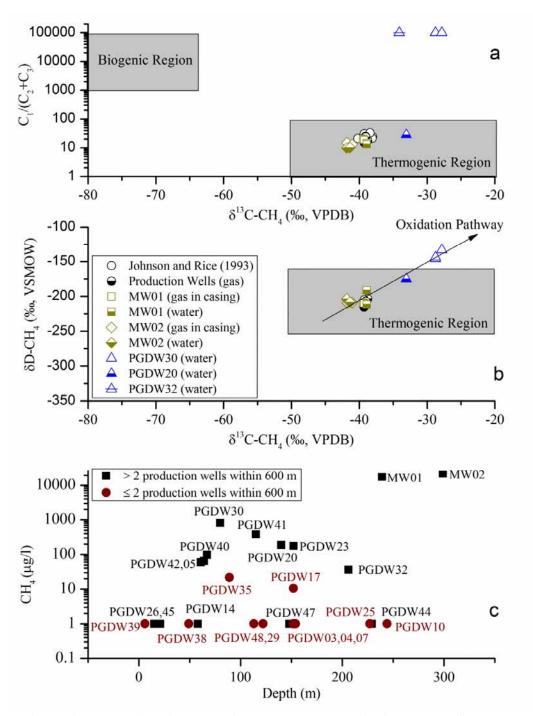
Depth trends of chloride, pH, sulfate, and potassium (filled black squares = domestic wells, filled red circles = monitoring wells).



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).



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



(a) Stable isotope ratios of carbon of methane versus ratio of methane (C₁) to ethane (C₂) and propane (C₃) in gas from production wells, monitoring wells, and domestic wells. Values of 100,000 are used to denote non detection of ethane and propane in samples. (b) Stable isotope ratios of carbon versus hydrogen of methane in gas from production wells (both literature and measured values), monitoring wells, and domestic wells. δD was not determined for PGDW32. Oxidation pathway (enrichment of ¹³C of remaining CH₄ with biodegradation) is illustrated. (c) Methane concentration in domestic and monitoring wells as a function of proximity to production wells and depth. Values of 1.0 were used for non-detection (detection limit 5 µg/L).

SUPPORTING INFORMATION

(Data Tables)

SI Table 1. Summary of subsurface sample locations, depth of sample collection, times (phases) of sampling, target analytes, laboratories utilized, and analytical methods

Sample	latitude	longitude	Depth (m bgs)	Туре	Media	major anions and alkalinity phase(lab)	Metals phase(lab)	Alcohols and VOCs phase(lab)	low molecular weight acids, glycols phase(lab)	SVOCs Pesticides PCBs, TICs phase(lab)	GRO, DRO, THE, TPH phase(lab)	Bacteria phase(lab)	fixed gases, C_1 - C_6 +, $\delta^{13}C$ and δD C_1 - C_4 DOC DIC, $\delta^{13}C$ DIC $\delta^{18}O$ and δD water phase(lab)
PGPP01 (Tribal Pavillion 14-10)	43.24578857	-108.6356735		PG	gas/ fluid			$II(R8^2)$		II(R8 ³)	II(R8 ⁴)		II(I ¹)
PGPP02	43.2486496	-108.6274796		PG	gas								$II(I^1)$
PGPP04 (Tribal Pavillion 24-02)	43.25984955	-108.6116409		PG	gas/ fluid			II(R8 ²)		II(R8 ³)	II(R8 ⁴)		$II(I^1)$
PGPP05 (Tribal Pavillion 33-10)	43.2486496	-108.6274796		PG	gas/ fluid			II(R8 ²)		II(R8 ³)	II(R8 ⁴)		$II(I^1)$
PGPP06 (Tribal Pavillion 14-2)	43.26016998	-108.6165009		PG	gas/ fluid			II(R8 ²)		II(R8 ³)	II(R8 ⁴)		$II(I^1)$
MW01	43.25682	-108.62185	233 - 239	MW	gas/ water	$\frac{\text{III}(\text{O}^1)}{\text{IV}(\text{O}^1)}$	III(S1) IV(S1)	III(R82,S2) $IV(R82,S3)$	IV(S ⁴ ,R3)	III(R8 ³) IV(R8 ³)	III(R8 ⁴) IV(R8 ⁴)		III(I ² ,I ⁵ ,O ² , S ⁵ ,S ⁶) IV(I ³ ,I ⁴ ,O ² , S ⁵ ,S ⁶)
MW02	43.25293	-108.59468	293 - 299	MW	gas/ water	$\frac{\text{III(O}^1)}{\text{IV(O}^1)}$	III(S1), IV(S1)	$\frac{\text{III}(\text{R8}^2,\text{S}^2)}{\text{IV}(\text{R8}^2,\text{S}^3)}$	IV(S ⁴ ,R3)	III(R8 ³) IV(R8 ³)	III(R8 ⁴), IV(R8 ⁴)		III(I ² ,I ⁵ ,O ² , S ⁵ ,S ⁶) IV(I ³ ,I ⁴ ,O ² , S ⁵ ,S ⁶)
PGMW01 (Pit 24-3#1)	43.26122665	-108.6316147	4.6	PGM	water	II(R8 ¹)	II(A4)	$II(A,R8^2)$		II(A,R8 ³)	II(E ² ,R8 ⁴)	II(E ¹)	II(R8 ⁵)
PGMW02 (Pit 14X-11#6)	43.24616241	-108.613205	4.6	PGM	water	II(R8 ¹)	II(A4)	$II(A,R8^2)$		II(A,R8 ³)	II(E ² ,R8 ⁴)	II(E ¹)	II(R8 ⁵)
PGMW03 (Pit 42X-11#4)	43.25263977	-108.6020584	4.6	PGM	water	II(R8 ¹)	II(A4)	$II(A,R8^2)$		II(A,R8 ³)	II(E ² ,R8 ⁴)	II(E ¹)	II(R8 ⁵)
PGSO01 (Pit 24-3)	43.26117325	-108.6316071	< 5	PGS	soil					II(R8 ³)	II(E ² ,R8 ⁴)		
PGSO02 (Pit 14X-11)	43.24636841	-108.6135254	< 5	PGS	soil					II(R8 ³)	II(E ² ,R8 ⁴)		
PGSO03 (Pit 42X-11)	43.2527504	-108.6022339	< 5	PGS	soil					II(R8 ³)	$II(E^2,R8^4)$		
PGDW01	unknown	unknown		DW	water	$I(R8^1)$	I(K)	I(L)		I(L,R8 ³)			
PGDW02	43.21848912	-108.5783117	15.2	DW	water	I(R8 ¹)	I(K)	I(L)		I(L,R8 ³)			
PGDW03	43.22721318	-108.6584107	152.4	DW	water	I(R8 ¹)	I(K), II(A4)	I(L) II(A,R8 ²)		I(L,R8 ³) II(A,R8 ³)	II(E ² ,R8 ⁴)	II(E ¹)	$II(I^1, R8^5)$
PGDW04	43.22790981	-108.6542063	152.4	DW	water	$I(R8^{1})$ $II(R8^{1})$	I(K), II(A4)	$I(L) \\ II(A,R8^2)$		I(L,R8 ³), II(A,R8 ³)	$I(E^2)$ $II(E^2,R8^4)$	$I(E^1) II(E^1)$	I(R8 ⁵) II(I,R8 ⁵)
PGDW05	43.25884666	-108.6126481	64.0	DW	water	I(R8), II(R8) IV(O ¹)	I(K) II(A4) IV(S ¹)	I(L) $II(A,R82)$ $IV(R82,S3)$	IV(S ⁴ ,R3)	I(L,R8 ³) II(A,R8 ³) IV(R8 ³)	$I(E^2)$ $II(E^2,R8^4)$	$I(E^1) II(E^1)$	I(R8 ⁵) II(R8 ⁵) IV(I ² ,O ² ,O ³ ,S ⁶)
PGDW06	43.27110813	-108.5599211	115.8	DW	water	I(R8 ¹)	I(K)	I(L)		I(L,R8 ³)			
PGDW07	43.24678442	-108.6879085	154.2	PGP	water	$I(R8^1)$	I(K)	I(L)		I(L,R8 ³)			I(R8 ⁵)

Sample	latitude	longitude	Depth (m bgs)	Туре	Media	major anions and alkalinity phase(lab)	Metals phase(lab)	Alcohols and VOCs phase(lab)	low molecular weight acids, glycols phase(lab)	SVOCs Pesticides PCBs, TICs phase(lab)	GRO, DRO, THE, TPH phase(lab)	Bacteria phase(lab)	fixed gases, C_1 - C_6 +, $\delta^{13}C$ and δD C_1 - C_4 DOC DIC, $\delta^{13}C$ DIC $\delta^{18}O$ and δD water phase(lab)
PGDW08	43.24697265	-108.6840567	157.0	PGP	water	$I(R8^1)$	I(K)	I(L)		$I(L,R8^3)$			
PGDW09	43.27211644	-108.615144	9.1	DW	water	$I(R8^1)$	I(K)	I(L)		$I(L, R8^{3})$			
PGDW10	43.23574855	-108.6563896	227.1	DW	water	$\frac{I(R8^{1})}{II(R8^{1})}$	I(K) II(A4)	I(L) II(A,R8 ²)		$I(L,R8^3)$ $II(A,R8^3)$	$I(E^2)$ $II(E^2,R8^4)$	II(E ¹)	$I(R8^{5})$ $II(I^{1},R8^{5})$
PGDW11	43.24312049	-108.6228628	227.1	DW	water	$I(R8^1)$	I(K)	I(L)		$I(L,R8^3)$			
PGDW12	43.27628927	-108.5661502	115.8	DW	water	$I(R8^1)$	I(K)	I(L)		$I(L,R8^3)$			
PGDW13	43.2444467	-108.6772771		DW	water	$I(R8^1)$	I(K)	I(L)		$I(L,R8^3)$			
PGDW14	43.25154027	-108.6273311	57.9	DW	water	I(R8 ¹)	I(K)	I(L), IV(R8 ² ,S ³)	IV(S ⁴ ,R3)	I(L,R8 ³)			$IV(O^3,S^6)$
PGDW15	43.24312129	-108.6671791	30.5	DW	water	$I(R8^1)$	I(K)	I(L)		$I(L,R8^3)$			
PGDW16	43.20381363	-108.6405183	161.5	DW	water	I(R8 ¹)	I(K)	I(L)		$I(L,R8^3)$			
PGDW17	43.20416653	-108.6368713	152.4	DW	water	$I(R8^1)$	I(K)	I(L)		$I(L,R8^3)$			I(R8 ⁵)
PGDW18	43.22491388	-108.569651	67.1	DW	water	$I(R8^1)$	I(K)	I(L)		$I(L,R8^3)$			
PGDW19	43.21382469	-108.651274	19.8	DW	water	$I(R8^1)$	I(K)	I(L)		$I(L,R8^3)$			
PGDW20	43.25166961	-108.5912756	140.2	DW	water	$I(R8^{1})$ $II(R8^{1})$ $III(O^{1})$ $IV(O^{1})$	I(K), II(A4) $III (S1)$ $IV(S1)$	I(L) II(A,R8 ²) III(R8 ² ,S ²) IV(R8 ² ,S ³)	IV(S ⁴ ,R3)	I(L,R8 ³), II(A,R8 ³) III(R8 ³) IV(R8 ³)	I(E ²) II(E ² ,R8 ⁴) III(R8 ⁴) IV(R8 ⁴)	$I(E^1) II(E^1)$	I(R8 ⁵) II(R8 ⁵) III(I ² , O ² , S ⁵ ,S ⁶) IV(I ² , O ² , S ⁵ ,S ⁶)
PGDW21	43.25167095	-108.5912762	140.2	DW	water	$I(R8^1)$	I(K)	I(L)		$I(L,R8^3)$			I(R8 ⁵)
PGDW22	43.24452934	-108.5981513		DW	water	$\frac{I(R8^{1})}{II(R8^{1})}$	I(K) II(A4)	I(L) II(A,R8 ²)		I(L,R8 ³), II(A,R8 ³)	$I(E^2)$ $II(E^2,R8^4)$	$I(E^1) II(E^1)$	I(R8 ⁵) II(R8 ⁵)
PGDW23	43.24866472	-108.6225943	152.4	DW	water	I(R8 ¹) II(R8 ¹)	I(K) II(A4)	I(L), II(A,R8 ²), IV(R8 ² ,S ³)	IV(S ⁴ ,R3)	I(L,R8 ³) II(A,R8 ³) IV(R8 ³)	$I(E^2)$ $II(E^2,R8^4)$	$I(E^1) II(E^1)$	I(R8 ⁵) II(I ¹ ,R8 ⁵) IV(S ⁶ ,S ⁶)
PGDW24	43.25877211	-108.6015059	30.5	DW	water	$I(R8^1)$	I(K)	I(L)		$I(L,R8^3)$			
PGDW25	43.25558722	-108.5694867	243.8	DW	water	$I(R8^{1})$ $II(R8^{1})$	I(K), II(A4)	I(L), II(A,R8 ²)		I(L,R8 ³), II(A,R8 ³)	II(E ² ,R8 ⁴)	II(E ¹)	$II(I^1, R8^5)$
PGDW26	43.25512275	-108.6132115	19.8	DW	water	$I(R8^{1}),$ $IV(O^{1})$	I(K)	I(L), IV(R8 ² , S ³)	IV(S ⁴ ,R3)	$\frac{I(L,R8^3)}{IV(R8^3)}$	IV(R8 ⁴)		$I(R8^5)$ $IV(I^2, O^2, O^3, S^6)$
PGDW28	43.23993143	-108.6465688	25.9	DW	water	$I(R8^1)$	I(K)	I(L)		I(L,R8 ³)			
PGDW29	43.21773909	-108.6288449	121.9	DW	water	$I(R8^1)$	I(K)	I(L)		$I(L,R8^3)$	$I(E^2)$		I(R8 ⁵)
PGDW30	43.25753218	-108.6225755	79.2	DW	water	$I(R8^{1})$ $II(R8^{1})$ $III(O^{1})$ $IV(O^{1})$	$I(K), II(A4)$ $III (S^1)$ $IV(S^1)$	I(L) II(A,R8 ²) III(R8 ² ,S ²) IV(R8 ² ,S ³)	IV(S ⁴ ,R3)	I(L,R8 ³), II(A,R8 ³) III(R8 ³) IV(R8 ³)	II(E2) $III(R84)$ $IV(R84)$	II(E ¹)	I(R8 ⁵) II(R8 ⁵) III(I ² , O ² , S ⁵ ,S ⁶) IV(I ² , O ² , S ⁵ ,S ⁶)
PGDW31	43.27302485	-108.6615302		DW	water	$I(R8^1)$	I(K)	I(L)		$I(L,R8^3)$			

Sample	latitude	longitude	Depth (m bgs)	Туре	Media	major anions and alkalinity	metals	Alcohols and VOCs	low molecular weight acids, glycols	SVOCs Pesticides PCBs, TICs	GRO, DRO, THE, TPH	Bacteria	fixed gases, C_1 - C_6 +, $\delta^{13}C$ and δD C_1 - C_4 DOC DIC, $\delta^{13}C$ DIC $\delta^{18}O$ and δD water
PGDW32	43.24075256	-108.5941561	205.7	DW	water	$I(R8^{1})$ $II(R8^{1})$ $IV(O^{1})$	$I(K),$ $II(A4),$ $IV(S^{1})$	$I(L)$ $II(A)$ $IV(R8^2,S^3)$	IV(S ⁴ ,R3)	I(L,R8 ³), II(A,R8 ³) IV(R8 ³)	II(E ² ,R8 ⁴) IV(R8 ⁴)	$II(E^1)$	I(R8 ⁵) II(R8 ⁵) IV(I ² , O ² , O ³ , S ⁶)
PGDW33	43.23855522	-108.5964146	9.1	DW	water	I(R8 ¹)	I(K)	I(L)		I(L,R8 ³)			
PGDW34	43.23605297	-108.6058086	30.5	DW	water	I(R8 ¹)	I(K)	I(L)		I(L,R8 ³)			
PGDW35	43.23021564	-108.6241763	88.4	DW	water	$I(R8^1)$	I(K)	I(L)		$I(L,R8^3)$			I(R8 ⁵)
PGDW36	43.25905726	-108.5987059	30.5	DW	water	$I(R8^1)$	I(K)	I(L)		I(L,R8 ³)	$I(E^2)$		
PGDW37	43.24016136	-108.6585376	24.4	DW	water	I(R8 ¹)	I(K)	I(L)		I(L,R8 ³)			
PGDW38	43.2296203	-108.572037	48.8	DW	water	$I(R8^1)$	I(K)	I(L)		I(L,R8 ³)	I(E ²)		I(R8 ⁵)
PGDW39	43.23750687	-108.5781708	6.1	DW	water	I(L) II(R8 ¹)	I(L), II(A4)	I(L), II(A,R8 ²)		I(L,R8 ³), II(A,R8 ³)		$II(E^1)$	
PGDW40	43.26156616	-108.6198273	67.1	DW	water	II(R8)	II(A4)	$II(A,R8^2)$		$II(A,R8^3)$	$II(E^2,R8^4)$	$II(E^1)$	$II(I^1, R8^5)$
PGDW41	43.262146	-108.6378479	114.6	DW	water	II(R8), IV(O ¹)	II(A4) IV(S ¹)	II(A,R8 ²) IV(R8 ² ,S ³)	IV(S ⁴ ,R3)	II(A,R8 ³) IV(R8 ³)	$II(E^2,R8^4),$ $IV(R8^4)$	II(E ¹)	II(I ¹ ,R8 ⁵) IV(I ² ,S ⁵ ,S ⁶)
PGDW42	43.25574493	-108.647316	61.0	DW	water	II(R8 ¹)	II(A4)	$II(A,R8^2)$		$II(A,R8^3)$	$II(E^2, R8^4)$	$II(E^1)$	II(I ¹ ,R8 ⁵)
PGDW43	43.25749207	-108.64151		DW	water	II(R8 ¹)	II(A4)	$II(A,R8^2)$		$II(A,R8^3)$	$II(E^2, R8^4)$	$II(E^1)$	$II(I^1, R8^5)$
PGDW44	43.25086975	-108.6261292	228.6	DW	water	II(R8)	II(A4)	II(A,R8 ²), IV(R8 ² ,S ³)	IV(S ⁴ ,R3)	II(A,R8 ³), IV(R8 ³)	$II(E^2,R8^4)$	II(E ¹)	II(R8 ⁵) IV(I ² ,O ³ ,S ⁶)
PGDW45	43.25888062	-108.6130142		DW	water	II(R8), IV(O ¹)	II(A4) IV(S ¹)	$\frac{II(A,R8^2)}{IV(R8^2,S^3)}$	IV(S ⁴ ,R3)	II(A,R8 ³) IV(R8 ³)	II(E2,R84), $IV(R84)$	II(E ¹)	$II(R8^5)$ $IV(I^2,O^2,O^3,S^6)$
PGDW46	43.24651337	-108.6157684	14.6	DW	water	II(R8 ¹)	II(A4)	$II(A,R8^2)$		$II(A,R8^3)$	$II(E^2, R8^4)$	$II(E^1)$	$II(I^1, R8^5)$
PGDW47	43.24520493	-108.6319885	147.5	DW	water	II(R8 ¹)	II(A4)	$II(A,R8^2)$		$II(A,R8^3)$	$II(E^2,R8^4)$	$II(E^1)$	$II(I^1, R8^5)$
PGDW48	43.2299881	-108.6235733		DW	water	II(R8 ¹)	II(A4)	$II(A,R8^2)$		$II(A,R8^3)$	$II(E^2, R8^4)$	$II(E^1)$	II(R8 ⁵)
PGDW49	43.25505829	-108.6178741		DW	water	II(R8 ¹)	II(A4)	II(A,R82) $IV(R82,S3)$		$II(A,R8^3)$ $IV(R8^3)$	II(E ² ,R8 ⁴)	II(E ¹)	$II(R8^5)$ $IV(I^2,O^3,S^6)$
PGPW01	43.24678802	-108.6879349	~ 154	PGP	water	II(R8 ¹)	II(A4)	II(A,R8 ²)		II(A,R8 ³)	$II(E^2,R8^4)$	$II(E^1)$	II(I ¹ ,R8 ⁵)
PGPW02	43.24697113	-108.6840515	~ 154	PGP	water	II(R8 ¹)	II(A4)	$II(A,R8^2)$		$II(A,R8^3)$	$II(E^2,R8^4)$	$II(E^1)$	$II(I^1, R8^5)$
LD-02	43.25167095	-108.5912762	185.9	DW	water	$III(O^1)$	$III(S^1)$	$III(S^2)$		III(R8 ³)			$III(I^2,O^2, S^5,S^6)$

Laboratories, Analytes, and Methods

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

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

E¹ - Energy Laboratories Inc., Billings, MT. Heterotrophic plate counts, iron reducing bacteria, sulfur reducing bacteria.

E² - Energy Laboratories Inc., Billings, MT. GRO, DRO, THE, and TPH.

 I^1 - Isotech Laboratories, Champaign, IL under contract by EnCana. Fixed gases and light hydrocarbons determined using ASTM D1945-03 in gas samples and headspace of aqueous samples. δ 13C and δ D for C₁ determined using gas stripping and IRMS in aqueous samples. δ 13C and δ D for C₁-C₄ determined using IRMS for gas samples.

 I^2 - Isotech Laboratories, Champaign, IL. Fixed gases and light hydrocarbons determined using ASTM D1945-03 in headspace of aqueous samples. δ 13C and δ D for C₁ and δ 13C for C₂ and C₃ determined using gas stripping and IRMS in aqueous samples. δ 13C DIC using gas stripping and IRMS.

 I^3 - Isotech Laboratories, Champaign, IL. Fixed gases and light hydrocarbons determined using ASTM D1945-03 in headspace of aqueous samples. $\delta I3C$ and δD for C_1 , $\delta^{13}C$ for C_2 - C_5 , and $\delta^{13}C$ for DIC gas stripping and IRMS in aqueous samples.

1⁴ - Isotech Laboratories, Champaign, IL. Fixed gases and light hydrocarbons determined using ASTM D1945-03 in gas samples. δ13C and δD for C₁ - C₃ using IRMS in gas samples.

 I^5 - Isotech Laboratories, Champaign, IL. Fixed gases and light hydrocarbons determined using ASTM D1945-03 in gas samples. $\delta 13C$ and δD for C_1 - C_3 using IRMS in gas samples. ^{14}C using AMS in gas samples.

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

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

O¹ - EPA, ORD, Ada, OK. SO₄, Cl, F, and Br determined using RSKSOP 276v3 and EPA Method 6500. NO₃ + NO₂ and NH₄ determined using RSKSOP 214v5 and EPA Method 350.1.

O² - EPA, ORD, Ada, OK. DIC and DOC determined using RSKSOP-330v0 and EPA Method 9060A.

O³ - EPA, ORD, Ada, OK. C₁ determined using RSKSOP 175v5 and Cali-5 gas sampling bags.

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

R8¹ - U.S. EPA Region 8 Laboratory, Golden, CO (fluoride, chloride, nitrite-N, nitrate-N, orthophosphate-P, and sulfate determined using EPA Method 300.0 and EPA Region SOP 310, alkalinity determined using EPA Method 310.0)

R8² - U.S. EPA Region 8 Laboratory, Golden, CO. VOCs determined using EPA Method 8260B.

R83 - U.S. EPA Region 8 Laboratory, Golden, CO. SVOCs determined using ORGM-515 r1.1 and EPA Method 8270D.

R84 - U.S. EPA Region 8 Laboratory, Golden, CO. GRO determined using ORGM-506 r1.0 and EPA Method 8015D. DRO determined using ORGM-508 r1.0 and EPA Method 8015D.

R85 - U.S. EPA Region 8 Laboratory, Golden, CO. Dissolved C1 in Phase I and dissolved C1-C3 in Phase II using EPA Method 524.2.

S¹ - Shaw Inc, Ada, OK in Phases III and IV. Metals and metals speciation determined using RSKSOP 213v4 and 257v2, or 332V0 and EPA Methods 200.7 and 6020.

S² - Shaw Inc, Ada, OK in Phases III and IV. Aromatics and chlorinated hydrocarbons determined using method RSKSOP-259v1 and EPA Method 5021A plus 8260C.

S³ - Shaw Inc, Ada, OK . Alcohols, aromatics, and chlorinated hydrocarbons determined using method RSKSOP-259v1.

S⁴ - Shaw Inc, Ada, OK. Low molecular weight acids determined using RSKSOP-112v6 .

S⁵ - Shaw Inc, Ada, OK. Dissolved gases C₁-C₄ determined using RSKSOP 194v4 and 175v5.

S⁶ - Shaw Inc, Ada, OK. Hydrogen and oxygen isotope ratios of water determined using RSKSOP-296v0.

Abbreviations

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

Analytical Methods

Isotech SOP100v0. Offline hydrocarbon gas preparation system, Gamma Bench, 12/27/2010.

Isotech SOP101v0. Offline gas preparation system, Alpha Bench, 10/21/2003.

Isotech SOP103v0. Delta Plus mass spectrometer, dual inlet analysis of δD, 2/22/2010.

Isotech SOP104. Delta S mass spectrometer, dual inlet analysis of δ^{13} C, in preparation.

Isotech SOP112v2. ¹³C/¹²C Determination of DIC, 05/26/2011.

ORGM-506 r1.0 - Region 8 SOP

ORGM-508 r1.0 - Region 8 SOP

ORGM-515 r1.1 - Region 8 SOP

RSKSOP-112v6 - Standard Operating Procedure for Quantitative Analysis of Low Molecular Weight Acids in Aqueous Samples by HPLC, 22 p.

RSKSOP-175v5 - Sample Preparation and Calculations for Dissolved Gas Analysis in Water Samples Using a GC Headspace Equilibration Technique, 16 p.

RSKSOP-194v4 - Gas Analysis by Micro Gas Chromatographs (Agilent MIcro 3000), 13 p.

RSKSOP-213v4 - Standard operating procedure for operation of Perkin Elmer Optima 3300 DV ICP-OES, 21 p.

RSKSOP-214v5 - Quality control procedures for general parameters analysis using Lachat Flow Injection analysis (FIA), 10 p.

RSKSOP-259v1 - Determination of volatile organic compounds (fuel oxygenates, aromatic and chlorinated hydrocarbons) in water using automated headspace gas chromatography/mass spectrometry TEKMAR 7000 HS-Varian 2100T GC/MS system-ION trap detector, 28 p.

RSKSOP-257v2 - Standard operating procedure for elemental analysis by ICP-MS, 16 p.

RSKSOP-299v1 – Determination of Volatile Organic Compounds (Fuel Oxygenates, Aromatic and Chlorinated Hydrocarbons) in Water Using Automated Headspace Gas Chromatography/Mass Spectrometry (Agilent 6890/5973 Quadruple GC/MS System), 25 p.

RSKSOP-276v3 - Determination of major anions in aqueous samples using capillary ion electrophoresis with indirect UV detection and Empower 2 software, 11 p.

RSKSOP-296v0 - Determination of hydrogen and oxygen isotope ratios in water samples using high temperature conversion elemental analyzer (TC/EA), a continuous flow unit, and an isotope ratio mass spectrometer (IRMS), 8 p.

RSKSOP-297v1 - Metals Speciation Determination by LC/ICP-MS, 21 p.

- RSKSOP-298v1 Arsenic Speciation Determination by LC/ICP-MS with Anion Suppression and NaOH Mobile Phase, 21 p.
- RSKSOP-313v1 Determination of R-123 using the H25-IR Infrared Refrigerant Gas Leak Detector, 12 p.

RSKSOP-314v1 - Determination of Fixed Gases using the GEM2000 and GEM2000 Plus Gas Analyzers & Extraction Monitors, 13 p.

RSKSOP-320v1 - Determination of Organic and Inorganic Vapors Using the TVA-1000B Toxic Vapor Analyzer, 18 p.

RSKSOP-330v0 - Determination of Various Fractions of Carbon in Aqueous Samples Using the Shimadzu TOC-VCPH Analyzer, 16 p.

U.S. EPA Method 200.7 - Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Spectrometry, Rev. 5, Jan 2001.

- U.S. EPA Method 300.0 Determination of Inorganic Anions by Ion Chromatography, Rev. 2.1, Aug. 1993.
- U.S. EPA method 310.1 Alkalinity (Titrimetric, pH 4.5), Rev. 1978.
- U.S. EPA Method 350.1 Determination of Ammonia Nitrogen by Semi-Automated Colorimetry, Rev. 2, Aug. 1993.
- U.S. EPA Method 5021A Volatile Organic Compounds in Various Sample Matrices Using Equilibrium Headspace Analysis, Rev. 1, June 2003.
- U.S. EPA Method 6020 Inductively Coupled Plasma-Mass Spectrometry, Rev. 1, Feb. 2007.
- U.S. EPA Method 6500 Dissolved Inorganic Anions in Aqueous Matrices by Capillary Electrophoresis, Rev. 0, Feb. 2007.
- U.S. EPA Method 8260C Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), Rev. 3, Aug. 2006.
- U.S. EPA Method 8015B Determination of Nonhalogenated Organics Using GC/FID, Rev. 2, Dec. 1996.
- U.S. EPA Method 8015D Nonhalogenated Organics Using GC/FID, Rev. 4, May 2003.
- U.S. EPA Method 8270D Determination of Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), Rev. 4, Feb. 2007.
- U.S. EPA Method 8000C Determinative Chromatographic Separations, Rev. 3, Mar. 2003.
- U.S. EPA Method 8260C Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), Rev. 3, Aug. 2006.
- U.S. EPA Method 8270D Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), Rev. 4, Feb. 2007.
- U.S. EPA Method 9060A Total Organic Carbon, Rev. 1, Nov. 2004.

Sample ID	T (°C)	рН	SC (µS/cm)	Alkalinity (mg/kg)	Na (ppm)	K (ppm)	Ca (ppm)	Mg (ppm)	Cl (ppm)	SO ₄ (ppm)	F (ppm)	NO ₃ (N) (ppm)
PGDW01				234	808	6.2	398	93.6	34.3	1860	0.4	6.2
PGDW02	13.4	8.11	551	108	86	1.8	34.8	5.3	2.6	175	0.7	< 0.5
PGDW03	11.1	9.37	1333	40	272	0.4	16.3	0.3	25.1	549	0.9	< 0.5
PGDW04	11.8	9.17	1370	29	270	0.4	18.0	0.1	21.6	551	0.9	< 0.5
PGDW05	12.0	9.02	956	93	192	0.3	3.6	0.1	17	295	0.9	< 0.5
PGDW06	13.8	10.20	1262	35	249	0.3	7.1	< 0.1	31	485	1.3	< 0.5
PGDW07	12.4	8.85	1016	61	213	0.3	8.9	0.1	15.7	390	1.2	< 0.5
PGDW08	12.4	8.57	1883	83	390	0.6	36.7	0.2	18.9	857	0.5	< 0.5
PGDW09	12.4	8.35	1128	254	233	2.1	16.6	4.1	10.5	279	2.4	3.2
PGDW10	12.2	8.95	948	147	204	0.4	6.1	0.1	8.0	293	0.9	< 0.5
PGDW11	13.1	7.17	3400	312	423	5.5	363	80.9	15.3	1780	0.2	1.3
PGDW12	12.4	10.04	1344	37	256	0.6	7.8	0.4	30.8	497	1.5	< 0.5
PGDW13	10.9	6.89	1155	303	196	1.9	61.0	19.9	6.2	343	0.7	1.0
PGDW14	10.8	7.85	2990	159	690	4.5	154	18.1	26.1	1820	0.4	0.7
PGDW15	11.4	7.48	1728	277	269	1.2	72.2	10.2	9.9	520	0.6	1.8
PGDW16	13.2	9.30	1011	145	188	0.3	6.4	0.1	13.4	258	0.8	< 0.5
PGDW17	12.7	9.61	1490	21	278	0.4	21.2	0.5	49.5	583	2.0	< 0.5
PGDW18	10.3	8.87	2002	21	509	0.8	84.5	0.3	27	1380	1.8	0.5
PGDW19	11.8	7.75	707	291	194	1.4	29.0	3.2	6.9	196	0.9	2.6
PGDW20	9.3	8.76	2005	70	520	1.0	79.3	9.3	34.5	1370	0.8	< 0.5
PGDW22	8.3	6.93	6180	332	837	9.0	416	126	79.9	2720	< 0.2	43.6
PGDW23	11.5	9.43	816	61	208	0.3	6.5	0.1	19.8	365	1.2	< 0.5
PGDW24	9.7	7.65	4700	165	938	7.0	327	131	55.7	3200	0.6	< 0.5
PGDW25	13.3	8.68	972	205	249	1.1	1.1	1.1	8.4	355	4.1	< 0.5
PGDW26	9.2	7.13	2390	337	220	6.8	364	57.7	14.6	1240	0.7	1.5
PGDW28	10.7	8.30	1170	258	239	2.2	40.6	12.9	16.7	298	0.5	3.7
PGDW29	11.5	9.72	1442	52	298	0.4	19.7	0.5	52.3	596	0.9	< 0.5
PGDW30	10.4	9.60	902	96	210	0.3	0.9	0.1	16.3	331	0.9	< 0.5
PGDW31	9.0	8.60	2006	83	435	0.9	31.2	0.8	13.3	1030	0.4	0.5
PGDW32	9.5	10.47	908	34	199	0.3	7.2	< 0.1	34.1	373	2.3	< 0.5
PGDW33	3.7	7.77	1662	276	178	5.0	228	40.9	28	670	0.2	2.1
PGDW34	8.3	7.87	4480	373	786	7.4	325	113	23	2690	0.5	3.5
PGDW35	10.6	8.63	2810	84	587	1.1	118	1.1	24.1	1610	0.3	0.5
PGDW36	9.8	7.62	649	232	42	2.6	89.5	28.9	3.2	195	1.0	1.2
PGDW37	10.5	8.14	819	342	187	0.9	12.1	1.3	8.7	89.9	0.9	1.2
PGDW38	9.5	8.68	2030	47	373	2.3	70.0	2.3	46.9	908	1.3	5.9
PGDW39	6.7	7.79	6410	127	1110	5.3	389	147	52.9	3640	0.4	0.6
PGDW40	11.5	9.06	1229	86	244	5.0	6.6	5.0	13.1	426	nm	< 0.3
PGDW41	7.2	7.63	4470	108	1030	2.7	270	57.5	31.4	2670	0.5	< 0.3
PGDW42	12.1	9.18	888	89	181	5.0	5.1	5.0	13.2	311	1.0	< 0.3
PGDW43	0.2	8.19	4410	113	911	5.0	208	13.7	38.4	2470	0.4	< 0.3
PGDW44	9.4	8.13	4080	100	994	5.0	259	28.3	39.5	2880	0.3	< 0.3
PGDW45	9.3	7.63	1103	379	59	2.6	138	31.2	14.5	213	1.9	0.3
PGDW46	7.9	7.79	855	329	91	1.8	90.3	9.9	8.4	126	0.5	2.3
PGDW47	8.2	9.52	970	44	183	5.0	6.9	5.0	21.6	330	1.5	< 0.3
PGDW48	8.7	8.21	3550	90	725	5.0	147	4.4	24.1	1840	0.3	< 0.3
PGDW49	7.8	7.66	5470	243	1210	11.4	486	153	64.3	3160	0.4	7.7
PGDW03-0110	8.3	8.71	1390	28	251	5.0	16.3	5.0	20.7	570	0.8	< 0.3
PGDW04-0110	8.3	9.07	1388	38	265	5.0	15.5	5.0	23.3	532	0.9	nm
PGDW05-0110	9.4	8.22	900	88	188	5.0	3.3	5.0	16.5	287	0.9	< 0.3
PGDW10-0110	10.4	8.62	985	147	195	5.0	5.8	5.0	7.5	293	0.9	< 0.3
PGDW20-0110	9.3	8.89	2690	68	550	5.0	71.7	8.1	32.6	1270	0.8	< 0.3
PGDW22-0110	8.2	7.06	4230	337	908	5.8	397	130	74.6	2780	nm	40.7
PGDW23-0110	8.2	9.72	780	54	194	5.0	5.8	5.0	19.7	368	1.5	< 0.3
PGDW25-0110	7.2	7.94	1511	295	269	5.0	70.1	9.6	9.5	441	nm	1.7
PGDW30-0110	9.2	9.39	967	94	195	5.0	4.1	5.0	15.5	333	0.9	<0.3
PGDW32-0110	8.3	9.87	1018	32	193	5.0	6.9	5.0	21.4	368	2.4	< 0.3
EPAMW01	11.8	11.91	3265	430	334	54.9	15.6	0.05	23.3	398	1.6	0.15
EPAMW02	12.3	12.01	3812	456	420	39.5	73.3	0.03	466	12.1	1.0	0.38
RD01	11.5	9.24	1068	78	208	0.2	4.3	0.10	15.2	357	1.0	0.23
LD01	10.9	8.85	2940	54	562	1.1	71.9	8.1	33.0	1320	0.9	0.35
		0.00	->.0	- · ·	0.02		,	v	55.0	1020	v.,	0.00

SI Table 2. Geochemical results for Pavillion ground water.

Sample ID	T (°C)	рН	SC (µS/cm)	Alkalinity mg/kg	Na (ppm)	K (ppm)	Ca (ppm)	Mg (ppm)	Cl (ppm)	SO ₄ (ppm)	F (ppm)	NO ₃ (N)
DCDW05 0411	10.5	0.00	020	00	100	0.24	2.25	0.00	16.0	276	1.0	(ppm)
PGDW05-0411	10.5	9.06	820	80	190	0.24	3.35	0.08	16.8	276	1.2	ND
PGDW14-0411	8.5	7.73	3473	156	753	3.52	154	18.6	23.7	1760	< 0.05	0.36
PGDW20-0411	8.3	8.59	2430	102	520	0.78	63	6.86	22.9	1150	1.3	< 0.03
PGDW23-0411	11.0	9.07	959	72	208	0.31	6.7	0.17	19.9	365	1.6	< 0.03
PGDW26-0411	8.3	6.95	2390	196	232	5.15	334	56	13.2	1180	1.0	1.37
PGDW30-0411	10.4	8.92	938	82	210	0.29	4.5	0.09	16.1	327	1.1	< 0.03
PGDW32-0411	11.1	9.30	885	46	198	0.09	7.2	0.03	18.8	361	2.0	< 0.03
PGDW41-0411	8.2	7.05	4866	112	896	3.18	452	46.9	97.6	2640	< 0.05	17.5
PGDW44-0411	10.0	8.17	4730	94	1060	2.09	259	19.2	32.1	2900	< 0.05	< 0.03
PGDW45-0411	9.1	6.85	1085	364	61.6	2.81	159	34.5	18.4	251	1.7	0.64
PGDW49-0411	10.4	7.34	5333	296	982	9.66	417	127	54.3	3200	< 0.05	8.75
EPAMW01-0411	11.2	11.24	2352	388	304	24.7	13.6	0.12	23.1	339	1.9	< 0.03
EPAMW02-0411	12.0	11.98	3099	482	448	43.6	60.5	0.03	457	63	1.5	< 0.03

----- not measured

SI Table 3.	Geochemical	l anomalies ir	i deep ground	d-water monitoring wells.
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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

† All values in ppb unlesss otherwise noted.

----- not analyzed.

nd - not detected.

ind - not detected.
it Includes phenol, 2,4-dimethylphenol, 2-methylphenol, 3&4 methylphenol.
it Includes naphthalene, 1-methylnapthalene, and 2-methylnapthalene.
it Value below quantitation limit of 10 µg/L.
2-Butoxyethanol determined by HPLC-MS-MS.
** 2-Butoxyethanol determined by GC-MS.

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

SI Table 4a. Summary of aqueous analysis of light hydrocarbons

Sample (matrix)	Phase	Date	C ₁ (ug/l)	C ₂ (ug/l)	C ₃ (ug/l)	C4 (ug/l)
PGDW32(w)	II	01/20/10	36.3	nd(10.0)	nd(15.0)	
PGDW32(w)	IV	04/18/11	nd(2.2)*	nd(1.2)	nd(1.3)	nd(1.5)
PGDW32(w)-dup	IV	04/18/11	discarded	discarded	nd(1.4)	nd(1.5)
PGDW35(w)	Ι	03/05/09	21.6			
PGDW38(w)	Ι	03/05/09	nd(5.0)			
PGDW39(w)	II	01/19/10	nd(5.0)	nd(10.0)	nd(15.0)	
PGDW40(w)	II	01/22/10	98.9	nd(10.0)	nd(15.0)	
PGDW41(w)	II	01/21/10	nd(5.0)	nd(10.0)	nd(15.0)	
PGDW41(w)	IV	04/20/11	385	142	nd(1.35)	nd(1.5)
PGDW42(w)	II	01/19/10	60	nd(10.0)	nd(15.0)	
PGDW43(w)	II	01/21/10	nd(5.0)	nd(10.0)	nd(15.0)	
PGDW44(w)	II	01/18/10	nd(5.0)	nd(10.0)	nd(15.0)	
PGDW44(w)	IV	4/21/2011	nd(2.2)*	nd(1.3)	nd(1.4)	nd(1.7)
PGDW45(w)	II	01/18/10	nd(5.0)	nd(10.0)	nd(15.0)	
PGDW45(w)	IV	04/19/11	nd(2.2)*	discarded	nd(1.3)	nd(1.6)
PGDW46(w)	II	01/20/10	nd(5.0)	nd(10.0)	nd(15.0)	
PGDW47(w)	II	01/19/10	nd(5.0)	nd(10.0)	nd(15.0)	
PGDW48(w)	II	01/20/10	nd(5.0)	nd(10.0)	nd(15.0)	
PGDW49(w)	II	01/20/10	nd(5.0)	nd(10.0)	nd(15.0)	
PGDW49(w)	IV	4/20/2011	nd(2.2)*	discarded	nd(1.3)	nd(1.6)
LD02(w)	III	10/20/2010	229	21	nd(0.24)	nd(0.23)
PGPW01(w)	II	01/20/10	nd(5.0)	nd(10.0)	nd(15.0)	
PGPW02(w)	II	01/20/10	nd(5.0)	nd(10.0)	nd(15.0)	
Travel Blank(w)	III	10/6/2010	23.3	nd(2.0)	nd(0.24)	nd(0.23)
Equipment Blank(w)	III	10/6/2010	23.0	nd(2.0)	nd(0.29)	nd(0.27)
Field Blank(w)	III	10/6/2010	76.4	nd(2.0)	nd(0.28)	nd(0.26)
Travel Blank(w)	IV	4/14/2011	18.5	56.4	nd(1.63)	nd(1.6)
Field Blank(w)	IV	4/18/2011	45.0	67.9	nd(1.36)	nd(1.66)
equipment blank(w) (on-site GC analysis)	IV	4/18/2011	nd(2.2)			
equipment blank(w) (on-site GC analysis)	IV	4/19/2011	nd(2.2)			
equipment blank(w) (on-site GC analysis)	IV	4/20/2011	nd(2.2)			
equipment blank(w) (on-site GC analysis)	IV	4/20/2011	nd(2.2)			
field blank(w)	IV	4/21/2011	nd(0.32)	nd(1.18)	nd(1.27)	nd(1.54)

* Determined by on-site GC analysis in Phase IV. Fixed laboratory analysis rejected if detection of methane and ethane < 100 ug/l. Maximum level of methane in blank 76.4 ug/L. All values of methane in Phase III > 100 ug/L accepted. Ultrapure nitrogen was used for equipment and travel blanks for on-site GC analysis. nd() - not detected(detection limit) ------ not analyzed

SI Table 4b. Summary of gas and headspace analysis of light hydrocarbons

Sample (matrix)	Phase	Date	C ₁ (%)	C2 (%)	C ₂ H ₄ (%)	C ₃ (%)	iC4 (%)	nC4 (%)	iC5 (%)	nC ₅ (%)	C ₆ + (%)
Tribal Pavillion 14-6(g) (WR)		Johnson and Rice (1993)	95.28	2.83		0.3	0.11	0.18	0.05	0.02	
Govt 21-5(g) (WR)		Johnson and Rice (1993)	93.24	3.75		0.73	0.33	0.22	0.16	0.09	
Tribal Pavillion 41-09(g) (FU)		Johnson and Rice (1993)	88.17	3.35		0.36	0.14	0.09	nd	nd	
Tribal Pavillion 14-11(g) (FU)		Johnson and Rice (1993)	66.00	1.96		0.06	0.054	0.006	0.006	0.002	
Blankenship 4-8(g) (FU)		Johnson and Rice (1993)	93.38	4.00		0.41	0.05	0.06	0.07	0.01	
Tribal Pavillion 14-10(g) (WR)(PGPP01)	II	01/21/10	92.47	4.04	0.001	1.21	0.415	0.372	0.183	0.114	0.486
Tribal Pavillion 43-10(g) (FU)(PGPP02)	II	01/21/10	94.86	3.48	0.0001	0.356	0.143	0.0618	0.0501	0.0194	0.18
Tribal Pavillion 24-2(g) (WR)(PGPP04)	II	01/21/10	90.16	4.64	0.0017	1.46	0.581	0.512	0.335	0.211	1.39
Tribal Pavillion 33-10(g) (FU)(PGPP05)	II	01/21/10	94.68	3.64	nd	0.373	0.131	0.055	0.0427	0.014	0.107
Tribal Pavillion 14-2(g) (FU)(PGPP06)	Π	01/21/10	93.23	3.93	0.0012	0.903	0.321	0.25	0.151	0.0905	0.506
MW01(g)	III	9/23/2010	84.22	3.43	0.0007	0.791	0.327	0.191	0.143	0.0632	0.111
MW01(w)	III	10/6/2010	35.11	2.02	0.0008	0.414	0.114	0.0871	0.0499	0.0241	0.0539
MW01(g)	IV	4/18/2011	89.43	3.92	0.0013	0.907	0.298	0.211	0.109	0.0574	0.0972
MW01(g)-dup	IV	4/18/2011	89.49	3.91	0.0013	0.902	0.295	0.206	0.103	0.0533	0.0804
MW01(w)	IV	4/20/2011	38.33	2.46	0.0016	0.504	0.113	0.101	0.0422	0.0229	0.0566
MW02(g)	III	9/24/2010	1.05	0.048	nd	0.022	0.0089	0.0053	0.0020	0.0008	0.0012
MW02(g)-dup	III	9/24/2010	1.04	0.048	nd	0.022	0.0089	0.0053	0.0020	0.0008	0.0009
MW02(w)	III	10/6/2010	28.03	2.16	nd	0.693	0.128	0.101	0.0185	0.0067	0.0174
MW02(g)	IV	4/18/2011	6.74	0.383	nd	0.142	0.0401	0.026	0.0070	0.0025	0.0034
MW02(g)-dup	IV	4/18/2011	7.41	0.422	nd	0.156	0.0439	0.0284	0.0077	0.0027	0.0035
MW02(w)	IV	4/19/2011	26.17	1.80	nd	0.765	0.259	0.147	0.0416	0.0141	0.0237
MW02(w)-dup	IV	4/19/2011	21.32	1.49	nd	0.623	0.204	0.118	0.0324	0.011	0.018
PGMW01(w)	II	01/21/10	2.47	nd	nd	nd	0.0054	0.005	0.0287	0.0092	0.537
PGMW02(w)	II	01/21/10	3.57	1.13	nd	0.103	0.402	0.0134	0.13	0.0003	0.398
PGDW03(w)	II	01/20/10	0.0122	nd	nd	nd	nd	nd	nd	nd	nd
PGDW04(w)	II	01/21/10	0.0036	nd	nd	nd	nd	nd	nd	nd	nd
PGDW05(w)	IV	04/19/11	0.0966	nd	nd	nd	nd	nd	nd	nd	nd
PGDW10(w)	II	01/18/10	0.0266	nd	nd	nd	nd	nd	nd	nd	nd
PGDW14(w)	IV	04/20/11	0.0005	nd	nd	nd	nd	nd	nd	nd	nd
PGDW20 (w)	III	10/06/10	0.191	0.007	nd	0.0006	nd	nd	nd	nd	nd

10/06/ 04/18/ 01/18/ 01/18/ 04/21/ 01/19/ 04/21/ 01/19/ 04/21/ 01/19/ 04/21/ 01/19/ 04/21/ 04/21/ 04/21/ 09/23/ 10/05/ 04/18/ 01/20/ 04/18/ 01/19/ 01/21/ 01/21/ 01/21/ 01/19/ 01/19/ 01/21/	II 0.221 10 nd 11 0.248 10 nd 11 nd 10 5.99 10 0.0123 10 1.19 11 1.46 10 0.197 11 0.0522 10 nd 10 0.418 10 0.0091 11 0.0005 10 0.291	0.005 0.007 nd nd nd nd nd nd nd nd nd nd nd nd nd	nd nd nd nd nd nd nd nd nd nd nd nd nd n	nd 0.0007 nd nd nd nd nd nd nd nd nd nd nd nd nd	nd nd nd nd nd nd nd nd nd nd nd nd nd n	nd nd 0.0015 nd nd nd nd nd nd nd nd nd nd nd nd nd	nd nd nd nd nd nd nd nd nd nd nd nd nd n	nd nd nd nd nd nd nd nd nd nd nd nd nd n	nd nd 0.0008 nd nd nd nd nd 0.0085 0.0019 0.0013 nd nd nd nd 0.0013
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04/18/ 01/20/ 04/18/ 04/18/ 01/19/ 01/22/ 01/21/ 01/21/ 04/20/ 01/19/	11 1.46 10 0.197 11 0.0752 11 0.0522 10 nd 10 0.418 10 0.0091 11 0.0005 10 0.291	nd nd nd nd nd nd nd nd nd nd nd	nd nd nd nd nd nd nd nd nd	nd nd nd nd nd nd nd nd nd	nd nd nd nd nd nd nd nd	nd nd nd nd nd nd nd	nd nd nd nd nd nd nd	nd nd nd nd nd nd nd nd	nd 0.0085 0.0019 0.0013 nd nd nd
01/20/ 04/18/ 04/18/ 01/19/ 01/22/ 01/21/ 04/20/ 01/19/	10 0.197 11 0.0752 11 0.0522 10 nd 10 0.418 10 0.0091 11 0.0005 10 0.291	nd nd nd nd nd nd nd nd nd	nd nd nd nd nd nd nd	nd nd nd nd nd nd nd nd	nd nd nd nd nd nd nd	nd nd nd nd nd nd	nd nd nd nd nd nd	nd nd nd nd nd nd	0.0085 0.0019 0.0013 nd nd nd
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01/21/	10 0.0016	nd			nd	nd	nd	nd	nd
		nu	nd	nd	nd	nd	nd	nd	nd
4/21/1	1 0.0022	nd	nd	nd	nd	nd	nd	nd	nd
01/18/	10 nd	nd	nd	nd	nd	nd	nd	nd	nd
04/19/	11 nd	nd	nd	nd	nd	nd	nd	nd	nd
01/20/	10 0.0016	nd	nd	nd	nd	nd	nd	nd	nd
01/19/	10 0.0428	nd	nd	nd	nd	nd	nd	nd	nd
01/19/	10 0.0365	nd	nd	nd	nd	nd	nd	nd	nd
4/20/1	1 nd	nd	nd	nd	nd	nd	nd	nd	nd
10/20/	10 0.12	0.007	nd	0.001	0.0008	0.0007	nd	0.0005	nd
01/20/	10 0.0253	nd	nd	nd	nd	nd	nd	nd	nd
01/20/	10 0.0389	nd	nd	nd	nd	nd	nd	nd	nd
01/21/	10 0.0068	nd	nd	nd	nd	nd	nd	nd	0.0021
01/22/	10 nd	nd	nd	nd	nd	nd	nd	nd	nd
9/23/1	0 nd	nd	nd	nd	nd	nd	nd	nd	nd
9/23/1	0 0.0029	nd	nd	nd	nd	nd	nd	nd	nd
9/24/1	0 nd	nd	nd	nd	nd	nd	nd	nd	nd
9/24/1	0 nd	nd	nd	nd	nd	nd	nd	nd	nd
4/18/1	1 nd	nd	nd	nd	nd	nd	nd	nd	nd
	1 nd	nd	nd	nd	nd	nd	nd	nd	nd
		nd	nd	nd	nd	nd	nd	nd	nd
	9/23/1 9/24/1 9/24/1 4/18/1 4/18/1	9/23/10 0.0029 9/24/10 nd 9/24/10 nd 9/24/10 nd 4/18/11 nd	9/23/10 0.0029 nd 9/24/10 nd nd 9/24/10 nd nd 9/24/10 nd nd 4/18/11 nd nd 4/18/11 nd nd 4/18/11 nd nd	9/23/10 0.0029 nd nd 9/24/10 nd nd nd 9/24/10 nd nd nd 9/24/10 nd nd nd 4/18/11 nd nd nd 4/18/11 nd nd nd 4/18/11 nd nd nd	9/23/10 0.0029 nd nd nd 9/24/10 nd nd nd nd nd 9/24/10 nd nd nd nd nd 9/24/10 nd nd nd nd nd 4/18/11 nd nd nd nd nd 4/18/11 nd nd nd nd nd 4/18/11 nd nd nd nd nd	9/23/10 0.0029 nd nd nd nd 9/24/10 nd nd nd nd nd nd 9/24/10 nd nd nd nd nd nd 9/24/10 nd nd nd nd nd nd 4/18/11 nd nd nd nd nd nd 4/18/11 nd nd nd nd nd nd 4/18/11 nd nd nd nd nd nd	9/23/10 0.0029 nd nd nd nd nd nd 9/24/10 nd nd nd nd nd nd nd nd 9/24/10 nd nd nd nd nd nd nd nd 9/24/10 nd nd nd nd nd nd nd 4/18/11 nd nd nd nd nd nd nd 4/18/11 nd nd nd nd nd nd nd 4/18/11 nd nd nd nd nd nd nd	9/23/10 0.0029 nd nd	9/23/10 0.0029 nd nd

Sample (matrix)	Phase	Date	δ^{13} C- C ₁ (‰)	δD- C ₁ (‰)	$\delta^{13}C-C_2$ (‰)	δD- C ₂ (‰)	δ ¹³ C- C ₃ (‰)	δD-C ₃ (‰)	δ ¹³ C- iC ₄ (‰)	δD-iC4 (‰)	δ ¹³ C- nC ₄ (‰)	δD-nC ₄ (‰)	δ ¹³ C- iC ₅ (‰)	δ ¹³ C- nC ₅ (‰)	¹⁴ C ₁ (pMC)	δ ¹³ C DIC (‰)	δ ¹⁸ Ο H ₂ Ο (‰)	δD H ₂ O (‰)
Tribal Pavillion 14-6(g) (WR)		Johnson and Rice (1993)	-39.24															
Govt 21-5(g) (WR)		Johnson and Rice (1993)	-40.2															
Tribal Pavillion 41-09(g) (FU)		Johnson and Rice (1993)	-38.04															
Tribal Pavillion 14-11(g) (FU)		Johnson and Rice (1993)	-38.4															
Blankenship 4-8(g) (FU)		Johnson and Rice (1993)	-38.08															
Tribal Pavillion 14-10(g) (WR)(PGPP01)	П	01/21/10	-38.75	-203.4	-26.93	-162.5	-24.93	-147.2	-25.83	-152.4	-25.26	-151.3						
Tribal Pavillion 43-10(g) (FU)(PGPP02)	II	01/21/10	-39.07	-212.9	-25.99	-157.5	-19.4				-23.87							
Tribal Pavillion 24-2(g) (WR)(PGPP04)	Π	01/21/10	-39.26	-204.9	-26.79	-166.2	-25.33	-148.0	-25.66	-155.5	-25.05	-154						
Tribal Pavillion 33-10(g) (FU)(PGPP05)	Π	01/21/10	-39.05	-207.3	-26.21	-161.1	-18.46	-101.7	-23.96		-23.64							
Tribal Pavillion 14-2(g) (FU)(PGPP06)	Π	01/21/10	-39.28	-215.3	-26.42	-162.3	-24.01	-145.2	-25.33	-150.1	-24.87	-152						
MW01(g)	III	9/23/2010	-39.44	-209.1	-26.63	-165.0	-23.76	-143.7							<0.2			
MW01(w)	III	10/6/2010	-38.89	-191.3	-26.55		-23.85									-12.18	-13.77	-113.77
MW01(g)	IV	4/18/2011	-39.25	-211.2	-26.67	-166.8	-23.74	-146.1										
MW01(g)-dup	IV	4/18/2011	-39.28	-210.1	-26.67	-167.4	-23.91	-146.6										
MW01(w)	IV	4/20/2011	-38.88	-211.6	-26.70		-24.40		-25.3		-24.4		-25.0	-24.7		-12.01	-13.26	-109.53
MW02(g)	III	9/24/2010	-41.85	-209.4											< 0.2			
MW02(g)-dup	III	9/24/2010	-41.72	-209.2											< 0.2			
MW02(w)	III	10/6/2010	-41.83	-203.8	-26.4		-24.28									Low DIC	-15.55	-117.41

SI Table 4c. Summary of isotopic data for dissolved, gas phase, and headspace analysis

Sample (matrix)	Phase	Date	$\begin{array}{c} \delta^{13}C \\ C_1 \\ (\%) \end{array}$	δD- C ₁ (‰)	$\delta^{13}C-C_2$ (‰)	δD- C ₂ (‰)	$\begin{array}{c} \delta^{13}C \\ C_3 \\ (\%) \end{array}$	δD-C ₃ (‰)	δ ¹³ C- iC ₄ (‰)	δD-iC4 (‰)	δ ¹³ C- nC ₄ (‰)	δD-nC ₄ (‰)	$\delta^{13}C-iC_5$ (‰)	δ ¹³ C- nC ₅ (‰)	¹⁴ C ₁ (pMC)	δ ¹³ C DIC (‰)	$\delta^{18}O$ H ₂ O (‰)	δD H ₂ O (‰)
MW02(g)	IV	4/18/2011	-41.05	-208.9	-26.10	-170.5	-24.05											
MW02(g)-dup	IV	4/18/2011	-41.01	-210.8	-26.09	-171.4	-24.06											
MW02(w)	IV	4/19/2011	-41.30	-210.7	-26.25		-24.29		-25.3		-24.3					Low DIC	-14.24	-113.42
MW02(w)-dup	IV	4/19/2011	-41.37	-208.2	-26.28		-24.28		-25.3		-24.5					Low DIC	-14.27	-113.46
PGDW05(w)	IV	04/19/11														-15.12	-13.11	-109.64
PGDW14(w)	IV	04/20/11														-11.94	-15.79	-126.04
PGDW20 (w)	III	10/06/10														-16.04	-13.22	-107.70
PGDW20(w)- dup	III	10/06/10														-15.91	-13.18	-107.38
PGDW20(w)	IV	04/18/11	-33.1	-175												-16.24	-13.31	-108.35
PGDW23(w)	IV	04/21/11														-13.29	-12.40	-97.35
PGDW30(w)	II	01/19/10	-28.77	-143.6														
PGDW30(w)	III	10/05/10	-28.76	-145.8												-12.18	-13.02	-109.78
PGDW30(w)	IV	04/18/11	-27.8	-133												-11.66	-13.23	-108.11
PGDW32(w)	IV	04/18/11	-34.2													-11.32	-13.33	-108.10
PGDW32(w)- dup	IV	04/18/11	-34.0													-10.84	-13.28	-108.24
PGDW41(w)	IV	04/20/11														-12.31	-15.91	-121.93
PGDW44(w)	IV	4/21/2011														-10.35	-13.29	-100.29
PGDW45(w)	IV	04/19/11														-14.18	-16.59	-128.18
PGDW49(w)	IV	4/20/2011														-11.05	-15.57	-122.19
LD02(w)	III	10/20/201 0														-18.58	-13.22	-109.20

WR - Wind River Formation

FU - Fort Union Formation

on ----- not analyzed

nd () - not detected

Sample Type	Analysis Method (EPA Method)	Sample Bottles/# of bottles*	Preservation/ Storage	Holding Time(s)
Dissolved gases	RSKSOP-194v4 &-175v5 (No EPA Method)	60 mL serum bottles/2	No Headspace TSP [†] , pH>10; refrigerate 4°C ^{††}	14 days
Metals (filtered)	RSKSOP-213v4 &-257v3 (EPA Methods 200.7 and 6020)	125 mL plastic bottle/1	HNO ₃ , pH<2; room temperature	6 months (Hg 28 days)
SO ₄ , Cl, F, Br	RSKSOP-276v3 (EPA Method 6500)	30 mL plastic/1	Refrigerate ≤4°C	28 days
$NO_3 + NO_2, NH_4$	RSKSOP-214v5 (EPA Method 350.1 and 353.2)	30 mL plastic/1	H ₂ SO ₄ , pH<2; refrigerate <u><4</u> °C	28 days
DIC	RSKSOP-102v5 or 330v0 (EPA Method 9060A)	40 mL clear glass VOA vial/2	refrigerate <u><4</u> °C	14 days
DOC	RSKSOP-102v5 or 330v0 (EPA Method 9060A)	40 mL clear glass VOA vial/2	H ₃ PO ₄ , pH<2; refrigerate <u><4</u> °C	28 days
Volatile organic compounds (VOC)	RSKSOP-299v1 or 259v1 (EPA Method 5021A plus 8260C)	40 mL amber glass VOA vial/2	No Headspace TSP [†] , pH>10; refrigerate ≤4°C	14 days
Low Molecular Weight Acids	RSKSOP-112V6 (No EPA Method)	40 mL glass VOA vial/2	TSP [†] , pH>10; refrigerate ≤4°C	30 days
O, H stable isotopes of water	RSKSOP-296v0 (No EPA Method)	20 mL glass VOA vial/1	Refrigerate at ≤4°C	Stable
$\delta^{13}C$ of inorganic carbon	Isotech: gas stripping and IRMS (No EPA Method)	60 mL plastic bottle/1	Refrigerate ≤4°C	No information
$\delta^{13}C$ and $\delta^{2}H$ of methane	Isotech: gas stripping and IRMS (No EPA Method)	1 L plastic bottle/1	Caplet of benzalkonium chloride; refrigerate ≤4°C	No information
Semi-volatile organic compounds	ORGM-515 r1.1 (EPA Method 8270D)	1L Amber glass bottle/2 and for every 10 samples of ground water need 2 more bottles for one selected sample, or if <10 samples collected, collect 2 more bottles for one select sample	Refrigerate ≤4°C	7 days until extraction, 30 days after extraction
DRO	ORGM-508 r1.0 (EPA Method 8015D)	1L Amber glass bottle/2 and for every 10 samples of ground water need 2 more bottles for one selected sample, or if <10 samples collected, collect 2 more bottles for one select sample	HCl, pH<2; refrigerate ≤4°C	7 days until extraction, 40 days after extraction
GRO	ORGM-506 r1.0 (EPA Method 8015D)	40 mL amber glass VOA vial/2 and for every 10 samples of ground water need 2 more bottles for one selected sample, or if <10 samples collected, collect 2 more bottles for one select sample	No headspace; HCl, pH<2; refrigerate ≤4°C	14 days
Glycols	Region III method (Under development) **	40 mL amber glass VOA vial/2	Refrigerate ≤4°C	14 days

SI Table 5. Sample collection containers, preservation, and holding times for ground-water samples.

[†] Trisodium phosphate ^{††} Above freezing point of water

*Spare bottles made available for laboratory QC samples and for replacement of compromised samples (broken bottle, QC failures, etc.). **EPA Methods 8000C and 8321 followed for method development and QA/QC limits where applicable.

SI Table 6. Field QC samples for ground-water analysis

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

* Reporting limit or Quantitation Limit ** Blank samples were not collected for isotope measurements, including O, H, C.

SI Table 7. QA/QC requirements for analysis of metals and major ions

Measurement	Analysis Method (EPA Method)	Blanks (Frequency)	Calibration Checks (Frequency)	Second Source (Frequency)	Duplicates (Frequency)	Matrix Spikes (Frequency)
Metals	RSKSOP- 213v4 (EPA Method 200.7)	<ql 80%="" for="" of<br="">metals; (Beginning and end of each sample queue, 10- 15 samples)</ql>	90-110% of known value (Beginning and end of each sample queue, 10-15 samples)	PE sample acceptance limits or 90- 110% of known value (Immediately after first calibration check)	RPD<10 for 80% of metals; for results <5x QL, difference of ≤QL(Every 15 samples)	90-110% Rec. for 80% of metals w/ no individual exceeding 50-150% Rec. (one per sample set, 10-15 samples)
Metals	RSKSOP- 257v3 (EPA Method 6020)	 <ql 80%="" for="" of<br="">metals; none>10xMDL</ql> (Beginning and end of each sample queue, 10- 15 samples) 	90-110% of known value (Beginning and end of each sample queue, 10-15 samples)	PE sample acceptance limits or 90- 110% of known value (Immediately after first calibration check)	RPD<10 for 80% of metals; for results <5xQL, difference of <ql (every="" 15<br="">samples)</ql>	90-110% Rec. for 80% of metals w/ no individual exceeding 70-130% (one per sample set, 10-15 samples)
SO ₄ , Cl, F, Br	RSKSOP- 276v3 (EPA Method 6500)	<mdl (Beginning and end of each sample queue)</mdl 	90-110% Rec. (Beginning, end, and every 10 samples)	PE sample acceptance limits (One per sample set)	RPD<10 (every 15 samples)	80-120% Rec. (one per every 20 samples)
NO ₃ + NO ₂ , NH ₄	RSKSOP- 214v5 (EPA Method 350.1 and 353.2)	<1/2 lowest calib. std. (Beginning and end of each sample queue)	90-110% Rec. (Beginning, end, and every 10 samples)	PE sample acceptance limits (One per sample set)	RPD<10 (every 10 samples)	80-120% Rec. (one per every 20 samples)

SI Table 8. QA/QC requirements for analysis of dissolved gases, DIC/DOC, VOCs, low molecular weight acids and stable isotopes of water

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

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

**Surrogate compounds spiked at 100 ug/L: p-bromofluorobenzene and 1,2-dichlorobenzene-d4,

85-115% recovery.

***Additional checks: internal reproducibility prior to each sample set, std dev ≤ 1 % for δ^2 H and ≤ 1 % for δ^{18} O †International Atomic Energy Agency (VSMOW, GISP, and SLAP)

Corrective actions are outlined in the SOPs.

MDL = Method Detection LimitQL = Quantitation Limit

PE = Performance Evaluation

SI Table 9. QA/QC re	quirements for analysis of semi-volati	les, GRO, and DRO
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QC Type	Semivolatiles	DRO	GRO	Frequency
Method Blanks	<rl Preparation or Method Blank, one with each set of extraction groups. Calibration Blanks are also analyzed</rl 	<rl Preparation or Method Blank</rl 	<rl Preparation or Method Blank and IBL</rl 	At least one per sample set
Surrogate Spikes	Limits based upon DoD statistical study (rounded to 0 or 5) for the target compound analyses.	60-140% of expected value	70-130% of expected value	Every field and QC sample
Internal Standards Verification	Every sample, EICP area within -50% to +100% of last ICV or first CCV.	NA	NA	Every field and QC sample
Initial multilevel calibration	ICAL: minimum of 6 levels (0.25 -12.5 ug/L), one is at the MRL (0.50 ug/L), prior to sample analysis (not daily) RSD \leq 20%, r ² \geq 0.990	ICAL: 10-500 ug/L RSD<=20% or r ² >=0.990	ICAL: .25-12.5 ug/L for gasoline (different range for other compounds) RSD<=20% or r2>=0.990	As required (not daily if pass ICV)
Initial and Continuing Calibration Checks	80-120% of expected value	80-120% of expected value	80-120% of expected value	At beginning of sample set, every tenth sample, and end of sample set
Second Source Standards	ICV1 70-130% of expected value	ICV1 80-120% of expected value	ICVs 80-120% of expected value	Each time calibration performed
Laboratory Control Samples (LCS)	Statistical Limits from DoD LCS Study (rounded to 0 or 5) or if SRM is used based on those certified limits	Use an SRM: Values of all analytes in the LCS should be within the limits determined by the supplier. Otherwise 70- 130% of expected value	Use and SRM: Values of all analytes in the LCS should be within the limits determined by the supplier. Otherwise 70-130% of expected value	One per analytical batch or every 20 samples, whichever is greater
Laboratory Control Samples (LCS)	Statistical Limits from DoD LCS Study (rounded to 0 or 5) or if SRM is used based on those certified limits	Use an SRM: Values of all analytes in the LCS should be within the limits determined by the supplier. Otherwise 70- 130% of expected value	Use and SRM: Values of all analytes in the LCS should be within the limits determined by the supplier. Otherwise 70-130% of expected value	One per analytical batch or every 20 samples, whichever is greater
Matrix Spikes (MS)	Same as LCS	Same as LCS	70-130% of expected value	One per sample set or every 20 samples, whichever is more frequent
MS/MSD	% Recovery same as MS RPD ≤ 30	% Recovery same as MS RPD ≤ 25	% Recovery same as MS RPD ≤ 25	One per sample set or every 20 samples, whichever is more frequent
Reporting Limits*	0.1 μg/L (generally) ¹ for target compounds HF special compounds are higher	20 μg/L ¹	20 μg/L ²	NA

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

SI Table 10. QA/QC requirements for LC/MS/MS analysis of glycols

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

RL = Reporting Limit

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

SI Table 11. QA/QC requirements for analysis of δ^{13} C of DIC

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

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

**If < 5 samples are submitted, run a duplicate regardless of total number.

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

SI Table 12. QA/QC requirements for analysis for δ^{13} C and δ D of light hydrocarbons for aqueous and	d gas
samples	

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

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

Working standards calibrated against VSMOW, SLAP, and GISP; referenced to VSMOW. *If < 10 samples were submitted, duplicate run regardless of total number. Corrective Actions: If re-analysis is not possible (such as lack of sample volume), the data will be qualified with a determination about the impact on the sample data.

SI Table 13. QA/QC requirements for analysis of fixed gases and	light hydrocarbons for aqueous and gas
samples	

Measurement	Analysis	Blanks	Calibration Checks	Second Source	Duplicates	Matrix Spikes
	Method	(Frequency)	(Frequency)	(Frequency)	(Frequency)	(Frequency)
$\begin{array}{c} \text{Ar, He, H_2, O_2,} \\ \text{N}_2, \text{CO}_2, \text{CH}_4, \\ \text{C}_2\text{H}_6, \text{C}_2\text{H}_4, \text{C}_3\text{H}_6, \\ \text{C}_3\text{H}_8, \text{i}\text{C}_4\text{H}_{10}, \\ \text{n}\text{C}_4\text{H}_{10}, \text{i}\text{C}_5\text{H}_{12}, \\ \text{n}\text{C}_5\text{H}_{12}, \text{C}_6\text{+} \end{array}$	Modification of ASTM D1945-03	None Detected (beginning every 10 samples, end of run)	85-115% (beginning every 10 samples, end of run)	85-115% (after each calibration)	RPD <15% (every 10 samples)	NA

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

Analyte	Instrument (Detector)	Method	Range	Calibration	Check Standard	Accuracy
O ₂	GEM-2000 Plus CES-	RSKSOP-314v1*	0 - 21%	4%, 10%, or	4% 10%, 20.9%	±1.0% (0-5%)
	LANDTEC (EC Cell)			20.9%		±1.0% (5-21%)
CH ₄	GEM-2000 Plus CES-	RSKSOP-314v1*	0 - 100%	2.5% or 50%	2.5%, 50%	±0.3% (0-5%)
	LANDTEC (IRGA)					±1% (5-15%)
						±3% (15-100%)
CO_2	GEM-2000 Plus CES-	RSKSOP-314v1*	0 - 100%	5%, 20%, or	5%, 20%, 35%	±0.3% (0-5%)
	LANDTEC (IRGA)			35%		±1.0% (5-15%)
						±3.0% (15-50%)
VOCs	Thermo Scientific TVA-	RSKSOP-320v1*	1.0 -	0.0, 10, 100,	10, 100, 1000,	±25% or ±2.5 ppmv,
	1000B (FID)		10,000	1000, 9000	9000 ppmv CH ₄	whichever is greater, from 1.0
			ppmv	ppmv CH ₄		to 10,000 ppmv.
VOCs	Thermo Scientific TVA-	RSKSOP-320v1*	0.5 - 500	0.0, 250, 475	250,	±25% or ±2.5 ppmv,
	1000B (PID)		ppmv	ppmv	475 ppmv	whichever is greater, from 0.5
					Isobutylene	to 500 ppmv.

Table 15. Summary of analytes, instruments, calibration, and check standards for portable gas analyzers

*Based on equipment manufacturer guidance

Table 16.	QA/QC Red	quirements f	for portable	gas analyzers
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Measurement	Method	Blanks** (Frequency)	Calibration Check Standards (Frequency)	Second Source Standards (Frequency)
O ₂ , CO ₂ , CH ₄ ,	RSKSOP-314v1***	beginning & end of each sample event)	+/-1% of reading (beginning & end of each sample event)	+/-1% of reading (after each calibration, optional for this project)
Hydrocarbons	RSKSOP-320v1***	beginning & end of each sample event)	90-110% of known value for FID and 80-120% for PID (after calibration, beginning & end of each sample event)	NA

Corrective actions are detailed in the SOPs.

*Duplicate sample not appropriate for measurements from a sample train. **Meter reading ***Based on equipment manufacturer guidance