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Impact to Underground Sources of Drinking Water and Domestic Wells from Production Well Stimulation and Completion Practices in the Pavillion, Wyoming, Field

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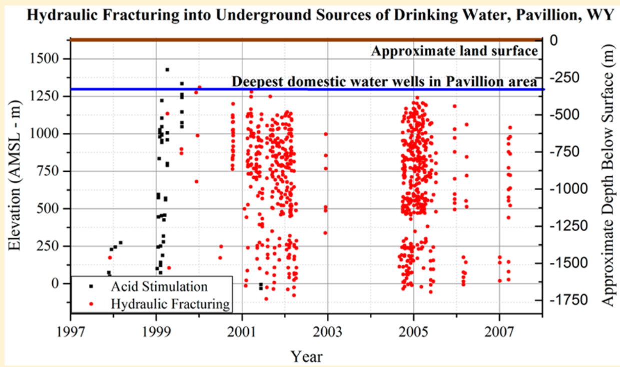
S *Supporting Information*

ABSTRACT: A comprehensive analysis of all publicly available data and reports was conducted to evaluate impact to Underground Sources of Drinking Water (USDWs) as a result of acid stimulation and hydraulic fracturing in the Pavillion, WY, Field. Although injection of stimulation fluids into USDWs in the Pavillion Field was documented by EPA, potential impact to USDWs at the depths of stimulation as a result of this activity was not previously evaluated. Concentrations of major ions in produced water samples outside expected levels in the Wind River Formation, leakoff of stimulation fluids into formation media, and likely loss of zonal isolation during stimulation at several production wells, indicates that impact to USDWs has occurred. Detection of organic compounds used for well stimulation in samples from two monitoring wells installed by EPA, plus anomalies in major ion concentrations in water from one of these monitoring wells, provide additional evidence of impact to USDWs and indicate upward solute migration to depths of current groundwater use. Detection of diesel range organics and other organic compounds in domestic wells <600 m from unlined pits used prior to the mid-1990s to dispose diesel-fuel based drilling mud and production fluids suggest impact to domestic wells as a result of legacy pit disposal practices.



INTRODUCTION

Between 2005 and 2013, natural gas production in the U.S. increased by 35% largely due to unconventional gas production in shale and tight gas formations.[1] Between 2013 and 2040, natural gas production is expected to increase another 45% with production from tight gas formations in particular increasing from 4.4 to 7.0 trillion cubic feet (59%) primarily in the Gulf Coast and Dakotas/Rocky Mountain regions.[1] Tight gas formations already account for 26% of total natural gas production in the United States today.[2]

In the U.S. Code of Federal Regulations (CFR), there are two federal regulations for protecting groundwater resources for present and future use relevant to oil and gas extraction − "Underground Source of Drinking Water" (USDW) and "usable water." A USDW is defined in 40 CFR 144.3 in requirements for the Underground Injection Control program promulgated under Part C of the Safe Drinking Water Act (SDWA) as "an aquifer or its portion: (a)(1) Which supplies any public water system; or (2) Which contains a sufficient quantity of ground water to supply a public water system; and (i) Currently supplies drinking water for human consumption; or (ii) Contains fewer than 10 000 mg/L total dissolved solids; and (b) Which is not an exempted aquifer." With the exception of use of diesel fuels, the Energy Policy Act of 2005 ("EPAct") exempted hydraulic fracturing from the SDWA, thereby allowing injection of stimulation fluids into USDWs. However, under Section 1431 of the SDWA, the Administrator of EPA may take action if impact to a USDW "may present an imminent and substantial endangerment to the health of persons."

The term "usable water" applies to lands containing federal or tribal mineral rights regulated by the Bureau of Land Management (BLM). This term is applicable to the Pavillion Field because tribal mineral rights are associated with more than half of production wells there. In the BLM Onshore Oil and Gas Order No. 2, usable water is defined as water containing ≤10 000 mg/L total dissolved solids (TDS) − a definition maintained in the March 2015 BLM rule on hydraulic fracturing (43 CFR 3160). In 43 CFR 3160, BLM retained a threshold for groundwater protection at 10 000 mg/L stating, "Given the increasing scarcity and technological improvements in water treatment, it is not unreasonable to assume aquifers with TDS levels above 5000 ppm are usable now or will be usable in the future." However, on September 30, 2015, the U.S. District Court for Wyoming granted a

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preliminary injunction filed by the States of Wyoming and Colorado to stop implementation of the BLM rule based on the assertion that the EPAct precludes BLM rulemaking.[3]

In 2004, EPA[4] documented the widespread use of hydraulic fracturing in USDWs colocated in formations used for coal bed methane (CBM) recovery. EPA[4] acknowledged likely groundwater contamination as a result of this activity but stated that the attenuation factors of dilution, adsorption, and biodegradation would reduce contaminant concentrations to safe levels prior to reaching domestic wells that are generally shallower than production wells. Thus, EPA[4] distinguished impact to USDWs from impact to domestic wells. In 2014, while defining the chemical abstract numbers of fluids designated as diesel fuels, EPA revised its position and stated that injecting stimulation fluids directly into USDWs "presents an immediate risk to public health because it can directly degrade groundwater, especially if the injected fluids do not benefit from any natural attenuation from contact with soil, as they might during movement through an aquifer or separating stratum."[5]

The Pavillion Field (Figure 1) is located east of the Town of Pavillion in Fremont County, WY, in the west-central portion

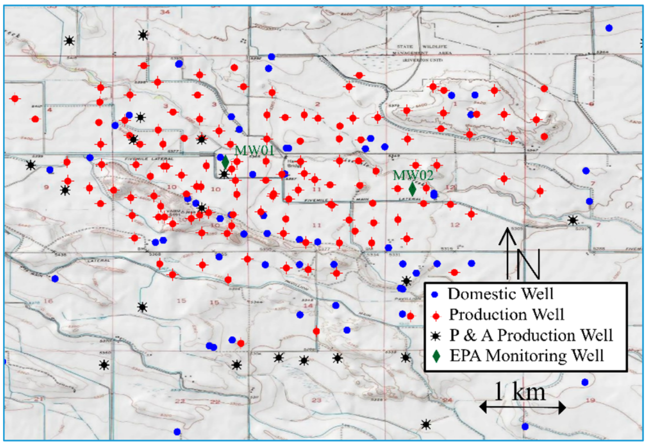

Figure 1. Central portion of the Pavillion Field illustrating locations of domestic water wells, production wells, plugged and abandoned (P&A) wells, and EPA monitoring wells (labeled). The entire Field, with labels for production and domestic wells and approximate locations of unlined pits, is illustrated in Figure SI A5. The geographic area in which the Field is located is illustrated in Figure SI A1.

of the Wind River Basin (WRB) (Figure SI A1). The field consists of 181 production wells including plugged and abandoned wells. Conventional and unconventional (tight gas) hydrocarbon production in the Pavillion Field is primarily natural gas from sandstone units in the Paleocene Fort Union and overlying Early Eocene Wind River Formations. However, oil has also been produced from production wells in these formations, primarily in the western portion of the field close to the suspected location of a fault (SI Sections A.1 and A.2).

In response to complaints regarding foul taste and odor in water from domestic wells within the Pavillion Field, EPA initiated a groundwater investigation in September 2008 under the Comprehensive Environmental Response and Liability Act (CERCLA).[6] This investigation remains the only one in which CERCLA has been invoked to investigate potential groundwater contamination due to hydraulic fracturing.[7] Under CERCLA, impact to both groundwater resources and domestic wells is evaluated, in contrast to limiting evaluation to impact to domestic wells as is common in oil- and gas-field-based investigations.

EPA conducted two domestic well sampling events in March 2009 (Phase I)[6] and January 2010 (Phase II).[8] Between June and September 2010, EPA installed two monitoring wells, MW01 and MW02, using mud rotary drilling with screened intervals at 233−239 m and 296−302 m below ground surface (bgs), respectively. These monitoring wells were installed to evaluate potential upward solute transport of compounds associated with well stimulation to maximum depths of current groundwater use (∼322 m).[9] EPA sampled MW01 and MW02 during the Phase III (October 2010) and Phase IV (April 2011) sampling events.

In December 2011, EPA[9] released a draft report summarizing results of the Phase I−IV sampling events. EPA documented groundwater contamination in surficial Quaternary unconsolidated alluvium attributable to numerous unlined pits used for disposal of diesel-oil-based (invert) drilling mud and production fluids including flowback, condensate, and produced water prior to the mid-1990s. EPA[9] also documented injection of stimulation fluids into USDWs and concluded that inorganic and organic geochemical anomalies at MW01 and MW02 appeared to be attributable to production well stimulation. EPA received numerous comments both challenging and supporting its findings in the draft EPA report.[10−37] We reviewed and considered these comments when preparing this manuscript.

A substantial amount of data has been collected since publication of the 2011 draft EPA report, adding to an already extensive data set. In April 2012 (Phase V) the EPA[38,39] split samples with the U.S. Geological Survey at MW01[40,41] and MW02.[42] In 2014, the Wyoming Oil and Gas Conservation Commission (WOGCC) released a report on production well integrity[43] and in 2015 released a report on surface pits.[44] In December 2015, the Wyoming Department of Environmental Quality (WDEQ) released a report on sample results of a subset of domestic wells previously sampled by EPA.[45]

We conducted a comprehensive analysis of all publicly available online data and reports, to evaluate impact to USDWs and usable water as a result of acid stimulation and hydraulic fracturing. Although injection of stimulation fluids into USDWs in the Pavillion Field was previously documented by EPA,[9] the potential impact to USDWs at depths of stimulation was not assessed. We evaluate potential upward migration of contaminants to depths of current groundwater use using data from MW01 and MW02. We also evaluate potential impact to domestic wells as a result of legacy disposal of production and drilling fluids in unlined pits.

■ MATERIALS AND METHODS

Sources of EPA reports, versions of the Quality Assurance Project Plan (QAPP), and Audits of Data Quality (ADQs) are provided in Table SI H1. Sources of analytical data and associated information on quality assurance and control are summarized in Table SI H2. ADQs were conducted by EPA for Phase I−IV investigations to verify the quality of analytical data and consistency with requirements specified in the QAPP.

In response to a comprehensive information request by EPA regarding oil and gas production and disposal activities in the Pavillion Field, the field operator, Encana Oil & Gas (U.S.) Inc., provided Material Safety and Data Sheets (MSDSs) of products used for well stimulation to EPA[46] (Table SI C3). During the Phase V sampling event, EPA developed a gas chromatography-

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Table 1. Summary of Major Ion Concentrations of Domestic Wells in the Wind River Indian Reservation (WRIR), Fremont County, WY, and within and around the Pavillion Field

	WRIR[a]			Fremont County[b]			within and around Pavillion Field[c]		
parameter (mg/L)	*n*	median	range	*n*	median	range	*n*	median	range
TDS	154	490	211−5110	77	1030	248−5100	65	925[†]	229[†]-4901[†]
Ca	149	10	1−486	77	45	1.7−380	48	50.8	3.32−452
Mg	128	2.2	0.1−195	77	8.2	0.095−99	45	5.32	0.024−147
Na	153	150	5−1500	77	285	4.5−1500	72	260	38.0−1290
K	149	2.0	0.2−30	77	2.45	0.1−30	43	1.36	0.179−10.5
SO_4	154	201	2−3250	77	510	12−3300	88	590	29.0−3640
Cl	154	14	2−466	77	20	3−420	48	21.1	2.60−77.6
F	154	0.7	0.1−8.8	76	0.9	0.2−4.9	46	0.88	0.20−4.1

[a]With the exception of potassium, from Daddow.[48] Information on potassium extracted from Daddow.[53] [b]From Plafcan et al.[51] There is overlap of 19 sample results with Daddow.[48,53] [c]Major ion concentrations in domestic wells[6,8,9,39,45,52]Summarized in Table SI B2. Mean values used for domestic wells sampled more than once. [n]Number of sample results. [†]TDS for EPA data estimated using linear regression equation from Daddow[48] TDS (mg/L) = 0.785 × specific conductance (μs/cm) − 130 (n = 151, r^2 = 0.979)

flame ionization-based approach to obtain a lower reporting limit (50 μg/L) for methanol compared to commercial laboratory analysis (5000 μg/L). We obtained this data set as the result of a Freedom of Information Act request to EPA.[47]

We reviewed over 1000 publicly available well completion reports, sundry notices, drilling reports, and cement bond and variable density logs accessed from the WOGCC Internet site using API search numbers to determine dates of well completion, depths of surface casing, top of original or primary cement, and numbers and depths of cement squeeze jobs (injection of cement through perforated production casing to remediate or extend existing primary cement). Similarly, we reviewed online information to document well stimulation practices summarized in Tables SI C1 and SI C2.

The field operator analyzed major ions in produced water samples at 42 production wells in 2007 (Table SI D1). EPA collected produced water samples at four production wells in 2010 and analyzed them for organic compounds (Table SI D3).[8] The field operator also conducted mechanical integrity and bradenhead (annular space between production and surface casing) testing between November 2011 and December 2012. In addition to sustained casing pressure at many production wells during that period (Table SI D2), water flowed through the bradenhead valve to the surface at four production wells (SI Section D.3). Aqueous analysis of bradenhead water samples by the field operator was limited to major ions (Table SI D1). Production well string and brandenhead gas samples were collected for benzene, toluene, ethylbenzene, xylenes (BTEX) and light hydrocarbons (Table SI D2).

To evaluate the effect of purging volume on water quality, EPA collected ten samples through time (Table SI 3a) during the Phase V sampling event at MW01. Based on EPA's purging procedure, we developed a model incorporating plug flow in casing and mixing in the screened interval (SI Section E.3, Figure SI E4). Our simulations indicated that virtually all (99.997%) of water entering the sampling train at the surface at the time of the first sample collection at MW01 originated directly from the surrounding formation (i.e., no stagnant casing water). MW02 was a low flow monitoring well (Figure SI E6). The cause of low flow is unknown but could be due to several factors, including low relative aqueous permeability due to gas flow or insufficient removal of drilling mud during well development. During the Phase V sampling event, MW02 was repeatedly purged over a 6-day period to ensure that sampled water originated from the surrounding formation (SI Section E.2, Figure SI E5). A discussion of monitoring well construction, including schematics for MW01 (Figure SI E1) and MW02 (Figure SI E2), is provided in SI Section E.1.

■ RESULTS AND DISCUSSION

Groundwater Resources in the Pavillion Area. The Wind River and Fort Union Formations are variably saturated fluvial depositional systems characterized by shale and fine-, medium-, and coarse-grained sandstone sequences. Lithology is highly variable and difficult to correlate from borehole data. No laterally continuous confining layers of shale exist below the maximum depth of groundwater use to retard upward solute migration. A comprehensive review of regional and local geology, including a lithologic cross-section in the vicinity of MW01 and MW02 (Figure SI A4), is provided in SI Sections A.1−A.6.

Domestic wells in the Pavillion area draw water from the Wind River Formation—a major aquifer system in the WRB.[48,49] From the surface to approximately 30 m bgs, groundwater exists under unconfined conditions.[50] Below this depth, groundwater is present in lenticular, discontinuous, confined sandstone units with water levels above hydrostatic pressure, and in some instances flowing to the surface,[48,50,51] indicating the presence of strong localized upward gradients. The majority of documented domestic well completions in Fremont County[51] and five municipal wells in the Town of Pavillion[52] west of the Field are completed in the Wind River Formation.

Flow to the surface was observed in a domestic well during the Phase II sampling event,[6] and as mentioned, at four production wells during bradenhead testing in 2012. While the overall vertical groundwater gradient in the Pavillion Field is downward, these observations indicate that localized upward hydraulic gradients exist in the field, which is relevant to potential upward solute migration from depths of production well stimulation. The deepest domestic wells in the Pavillion Field and immediate surrounding area are 229 and 322 m bgs, respectively (Table SI B1). Two municipal wells were proposed, but not drilled, in the Pavillion Field as replacement water for domestic wells at depths of 305 m bgs,[52] similar to the depth of MW02 installed by EPA.

Major ion concentrations of domestic wells in the Pavillion field (summarized in Table SI B2) are typical of the Wind River Indian Reservation (WRIR),[48] west of the Pavillion Field, and

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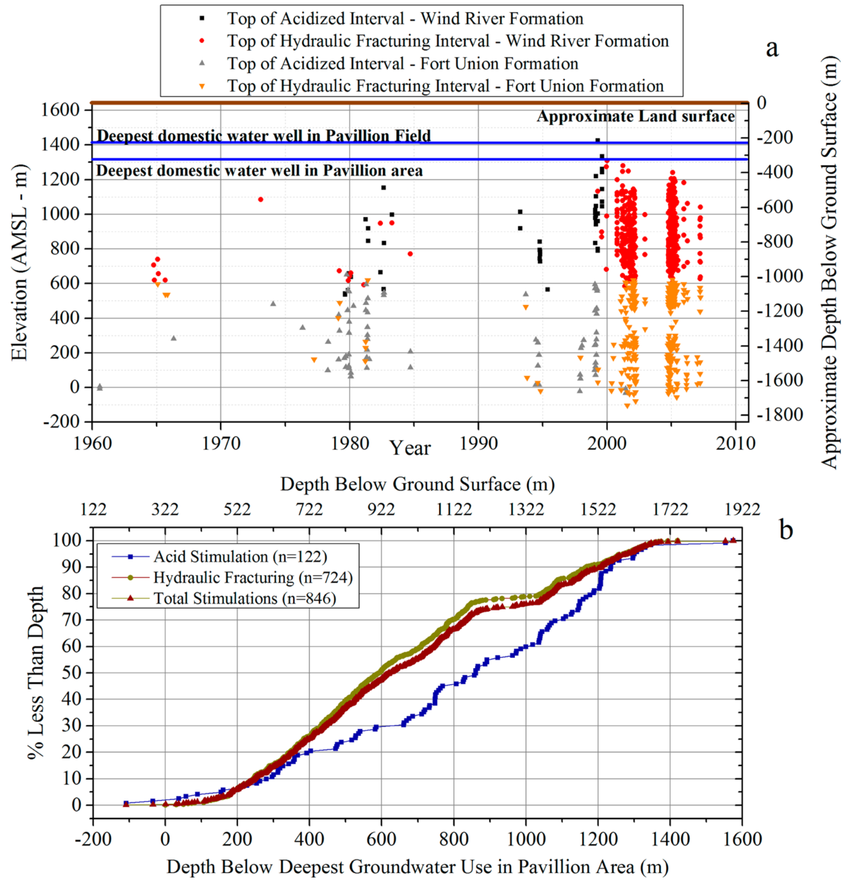

Figure 2. (a) Elevation in absolute mean seal level (AMSL) and approximate depth below ground surface of documented acid and hydraulic fracturing stimulation stages. (b) Cumulative distribution of stimulation stages as a function of depth below deepest groundwater use in the Pavillion Field. Documentation of stimulation stages is absent at a number of production wells so that numbers presented here are a lower bound.

in Fremont County,[51] where the Pavillion Field lies, (Table 1) with TDS levels <5000 mg/L. TDS concentrations in the Wind River Formation appear to vary with lithology rather than depth (white coarse sandstone associated with lower TDS values).[52] There are no apparent trends in TDS levels with depth from data sets from the WRIR,[53] Fremont County,[51] and domestic wells in and around the Pavillion Field.

The Fort Union Formation is not used for water supply in the Pavillion area. However, the formation is highly productive and permeable where fractured[49] with TDS values from 1000 to 5000 mg/L.[54] An aquifer exemption was obtained to enable disposal of produced water in a disposal well perforated in the Fort Union Formation[55] at a location 5.6 km northwest of the Pavillion Field. Use of this well was suspended due to failure of well casing. Thus, the Wind River and Fort Union Formations in the Pavillion Field meet the regulatory definition of USDWs, as explicitly stated by EPA,[9,55] and of usable water as defined by the BLM.

Well Stimulation Depths, Treatments, and Chemical Additives. Exploration of oil and gas in the Pavillion Field commenced in August 1953 with increasingly shallow stimulations through time (Figure 2). The first acid stimulation and hydraulic fracturing stages (injection over one or more discrete intervals) occurred in June 1960 and October 1964, respectively. Acid stimulation ceased in 2001. To date, the last stimulation stage (hydraulic fracturing) occurred in April 2007. Most production wells were completed and stimulated during several periods of increased activity, especially after 1997 (Figure 2a). Acid stimulation and hydraulic fracturing occurred as shallowly as 213 and 322 m bgs, respectively, at depths comparable to deepest domestic groundwater use in the area (Figure 2a). Approximately 10% of stimulation stages were <250 m of deepest domestic groundwater use whereas approximately 50% of stimulation stages were <600 m and 80% were <1 km of deepest domestic groundwater use (Figure 2b).

Surface casing of production wells—the primary line of defense to protect groundwater during conventional and unconventional oil and gas extraction—is relatively shallow in the Pavillion field with a median depth of 185 m bgs (i.e., shallower than the deepest groundwater use) and range of 100−706 m bgs (Figure SI C1). There is no primary cement below surface casing, often for hundreds of meters, for 55 of 106 (~52%) production wells for which cement bond logs are available (Table SI C1, Figure SI C1). There is currently no requirement in Wyoming for placement of primary cement to surface casing or to ground surface.[45]

Instantaneous shut in pressures (ISIP) (wellhead gauge pressure immediately following fracture treatment) were similar for acid stimulation and hydraulic fracturing (Figure SI C2) suggesting that both matrix acidizing and acid fracturing (no proppants used[56]) occurred in the Pavillion Field. Acidizing solutions used in the Pavillion Field typically consisted of a 71/2% or 15% hydrochloric acid solution plus additives described in well completion reports as inhibitors, surfactants, diverters, iron sequestration agents, mutual solvents, and clay

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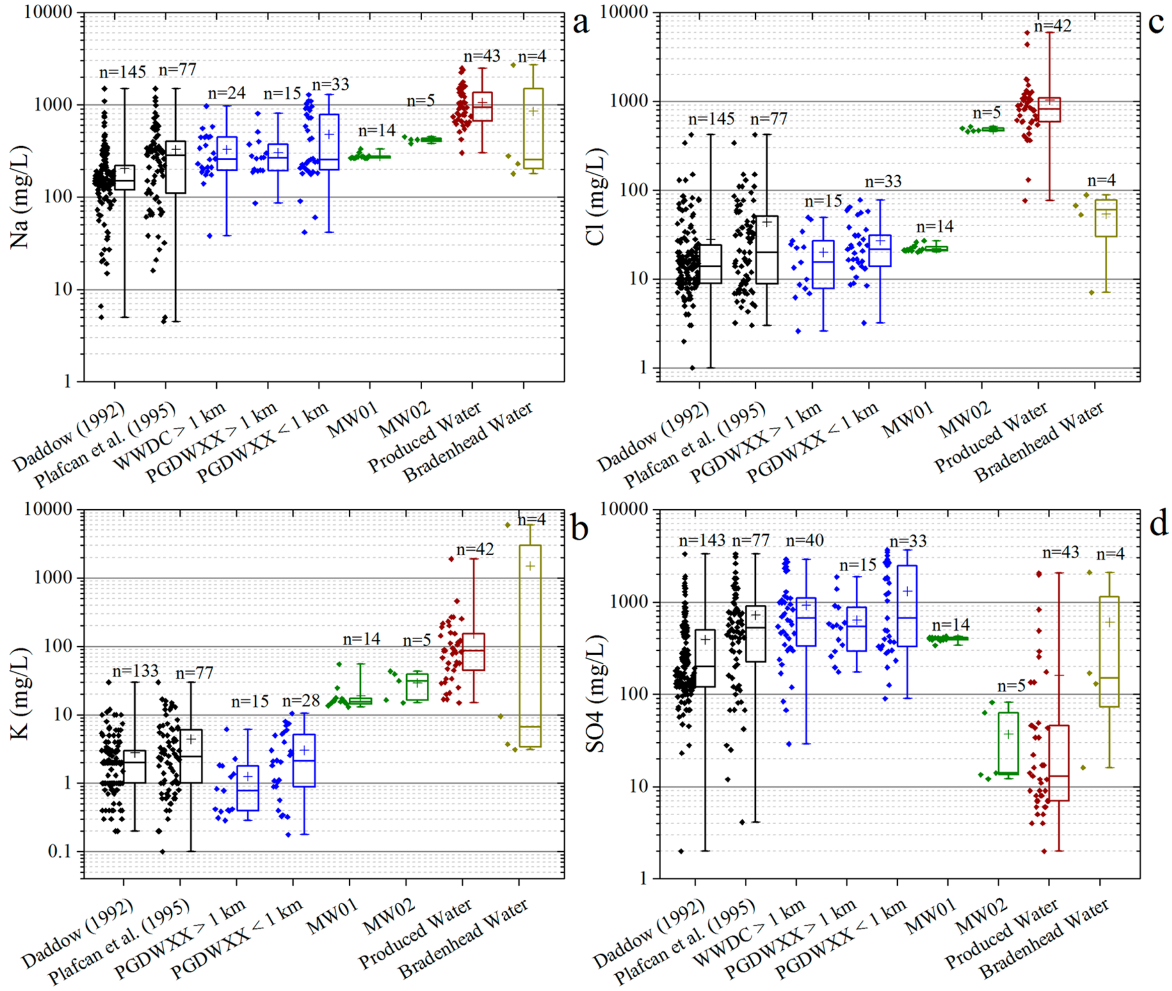

Figure 3. Box and whisker plots of minimum and maximum, quartiles, median (line in boxes), mean (crosses in boxes) of (a) Na, (b) K, (c) Cl, (d) SO_4 for domestic wells inventoried by Daddow[48,53] and Plafcan[51] in the Wind River Indian Reservation and Fremont County, respectively, sampled by EPA[6,8,9,39] and WDEQ[45] (PGDWXX series) greater than and less than 1 km from a production well, Wyoming Water Development Commission[52] (WWDC series) greater than 1 km from a production well, EPA monitoring wells[9,39] (Tables SI E2b, SI E3b), and produced water and bradenhead water samples (Table SI D1). Domestic wells sampled more than once, including data from Daddow,[53] are represented with a mean value. Fourteen measurements in Daddow[53] < 1 mg/L for potassium are not illustrated. Data points at MW01 and MW02 are samples collected during Phase III, IV, and V sample events.

stabilizers. Acidizing solutions were often flushed with a 2, 4, or 6% potassium chloride (KCl) solution. Pad acid, to initiate fractures, contained 10−50% heavy aromatic petroleum naptha. Corrosion inhibitors contained isopropanol and propargyl alcohol. Clay stabilizers contained methanol. Musol solvents used for acid stimulation consisted of 60−100% 2-butoxyethanol and 10−30% oxylated alcohol (Table SI C3).

Prior to 1999, "salt solutions" were commonly used for hydraulic fracturing. After 1999, a 6% KCl solution was used extensively for hydraulic fracturing often combined with CO_2 foam, with subsequent flushing using a 6% KCl solution. There were reported losses of KCl solutions during stimulation (e.g., at Tribal Pavillion 12−13 "lost thousands of bbls KCl"). Undiluted diesel fuel was used for hydraulic fracturing at three production wells before 1985. From the mid-1970s through 2007, there was widespread use of gelled fracture fluids (gelled water, linear gel, and cross-linked gel). Diesel fuel #2 was used for liquid gel concentrates (Table SI C3). Ammonium chloride, potassium hydroxide, potassium metaborate, and a zirconium complex were used as cross-linkers.

Gelled fracture fluids were used extensively with CO_2 foam (Table SI C4). Between 2001 and 2005, "WF-125" was used with CO_2 foam (often with a 6% KCl solution) for hydraulic fracturing (Table SI C5). A stimulation report (one of only three publicly available throughout the operating history of the Field) and MSDSs indicate that WF-125 contained diesel fuel #2, 2-butoxyethanol, isopropanol, ethoxylated linear alcohols, ethanol, and methanol. During 2001, WF-125 and unidentified product mixtures were used with a 6% KCl and a 10% methanol solution and CO_2 foam for hydraulic fracturing followed with a 6% KCl and 10% methanol solution flush. Other WF-series compound mixtures of unknown composition were also used with CO_2 foam and in some cases with N_2 gas. Methanol, isopropanol, glycols, and 2-butoxyethanol were used in foaming agents (Table SI C3). Ethoxylated linear alcohols, isopropanol, methanol, 2-butoxyethanol, heavy aromatic petroleum naptha, naphthalene, and 1,2,4-trimethylbenzene were used in surfactants (Table SI C3). Slickwater (commonly with a 6% KCl solution) was used for hydraulic fracturing with and without CO_2 foam in 2004 and 2005, respectively (Table SI C6).

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At least 41.5 million liters (or ∼11 million gallons) of fluid was used for well stimulation in the Pavillion Field (calculated from Table SI C2). Given lack of information at numerous production wells, this is an underestimate of actual cumulative stimulation volume. The cumulative volume of well stimulation in closely spaced vertical wells in the Pavillion Field is characteristic of high volume hydraulic fracturing in shale units.[57] In evaluating solute attenuation in USDWs, EPA[4] did not consider cumulative volumes of injection of well stimulation fluids in closely spaced vertical production wells common to CBM and tight gas production.

Evaluation of Impact to USDWs and Usable Water. In the Pavillion Field, impact to USDWs and usable waters depends upon the advective-dispersive solute transport of compounds (or their degradation products) used for well stimulation to water-bearing units (sandstone units at or near water saturation). Water-bearing units exist throughout the Wind River and Fort Union Formations in the Pavillion Field. For instance, production well Unit 41X-10 was recommended for plugging and abandonment in 1980 because of "problems with water production and casing failure." In 1980, drilling logs at Tribal Pavillion 14−2 stated "Hit water flow while drilling at 4105−4109 ft" bgs. The magnitude of produced water production in the Pavillion Field is variable with some wells having high produced water production (e.g., 17.9 million liters ∼4.7 million gallons at Tribal Pavillion 23−10 from July 2000 to present) (Table SI C2). In some cases, stimulation fluids were injected directly into water bearing units. For instance, at Tribal Pavillion 14−1, a cast iron bridge plug was used to stop water production in 1993 from an interval where hydraulic fracturing occurred using undiluted diesel fuel in 1964 (Table SI C2).

The migration of stimulation fluid to water-bearing sandstone units in the Pavillion Field also likely occurred during fracture propagation and subsequent leakoff (loss of fluid into a formation in or near the target stratum). Leakoff increases in complex fracture networks as a result of lithologic variation over short distances and contact of stimulation fluid with permeable strata[58−61] expected during hydraulic fracturing in fluvial depositional environments of the Wind River and Fort Union Formations. Leakoff can remove much or most of the fracturing fluid even for moderate sized induced fractures.[58,59] Maximum ISIP values for acid stimulation and hydraulic fracturing were 19.5 and 40.1 MPa (Figure SI C2), respectively, equivalent to ∼2000 and ∼4100 m of hydraulic head. Pressure buildup during hydraulic fracturing far in excess of drawdown expected during produced water extraction makes full recovery of stimulation fluids unlikely.[4,62]

The migration of stimulation fluids to water-bearing units also likely occurred as a result of loss of zonal isolation during well stimulation (SI Section D.1). Casing failure occurred at five production wells following well stimulation. Cement squeezes were performed above primary cement often days after hydraulic fracturing without explanation[63] at six production wells, potentially because of migration of stimulation fluid above primary cement. At one production well, stimulation fluid was injected just 4 m below an interval lacking cement outside of the production casing with a stimulation pressure of only 1.3 MPa indicating potential entry into the annular space.

Major ion concentrations in produced water sampled after stimulation (Table SI D1) were distinct from values expected in the Wind River Formation as evidenced by sample data from the WRIR,[48,53] Fremont County,[51] and domestic wells in and around the Pavillion Field which were representative of the Wind River Formation regardless of distance from production wells (Table 1, Figure 3). Using combined data sets in and around the Pavillion Field, and the nonparametric Mann−Whitney test (null hypothesis that two sample sets come from the same population), sodium, potassium, and chloride concentrations were higher and sulfate concentrations lower in produced water compared to concentrations expected in the Wind River Formation ($p = 6.6 \times 10^{-19}$, 2.1×10^{-15}, 2.6×10^{-16}, and 4.4×10^{-19}, respectively), providing direct evidence of impact to USDWs at depths of stimulation. Also, potassium increased with calcium concentrations and sulfate increased with TDS concentrations, respectively, in domestic wells but not in production wells (Figures SI D1). Chloride is a major component of TDS concentrations in production wells. Potassium/calcium and chloride/sulfate concentration ratios were higher in production wells than in domestic wells (Figures SI D2), further indicating anomalous potassium, chloride, and sulfate concentrations in production wells.

Produced water samples were collected from gas−water separators at four production wells and analyzed for organic compounds (Table SI D3, Figure SI D3) during the Phase II sampling event.[6] Samples from one production well appeared to be from both an aqueous and an apparent nonaqueous phase liquid with the latter exhibiting thousands of mg/L of benzene, toluene, ethylbenzene, xylenes (BTEX). Synthetic organic compounds methylene chloride and triethylene glycol (TEG) were detected in produced water samples at 0.51 and 17.8 mg/L, respectively indicating anthropogenic origin. Methylene chloride has been detected in flowback water in other systems,[64] including 122 domestic wells above the Barnett Shale TX,[65] and in air sampled near well sites.[66]

Sample Results at MW01 and MW02. Concentrations of potassium in MW01 and MW02 were higher than expected values in the Wind River Formation (Figure 3) at *p*-values of 2.6×10^{-13} and 1.2×10^{-06}, respectively. High pH values (>11 standard units) were observed during purging at both monitoring wells (Tables SI E3b, SI E4b, Figures SI E5, SI E6, SI E7), indicating that elevated potassium concentrations may have been attributable to release of potassium from potassium oxides and sulfates during curing of cement[67−71] used for monitoring well construction. However, a number of observations were inconsistent with cement interaction as a causative factor for elevated pH, and there was extensive use of compounds containing potassium including potassium hydroxide during stimulation (Table SI C3). Water in contact with hydrating cement is saturated or oversaturated to portlandite ($Ca(OH_2)$)[72−74] and remains oversaturated prior to degradation or carbonation.[75−78] In contrast, water from monitoring wells was highly undersaturated to portlandite. Elevated pH in monitoring wells was not observed during monitoring well development until natural gas intrusion occurred in the wells, suggesting degassing as a possible cause of elevated pH (SI Section E.5). Also, potassium was detected at a concentration of 6000 mg/L in a bradenhead water sample having a pH of 10.86 standard units from Tribal Pavillion 13−1 (Table SI D1). This may indicate either high potassium concentration at depths below EPA monitoring wells due to well stimulation (water from bradenhead samples originated at some unknown distance above cement outside production casing at each production well) or interaction of bradenhead water with wellbore cement.

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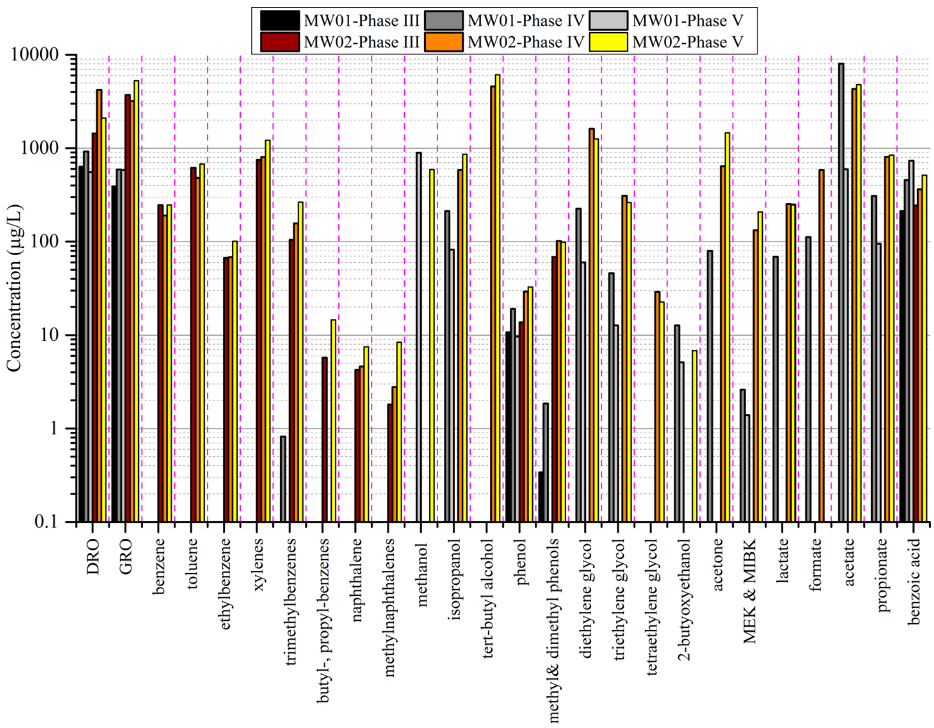

Figure 4. Summary of organic compounds detected by EPA in MW01 and MW02 during Phase III, IV, and V sampling events. Glycols, alcohols, and low molecular weight organic acids were not analyzed in Phase III. Alkylphenols and methanol (GC-FID method) were only analyzed in Phase V. Organic compounds detections for MW01 and MW02 are summarized in Table SI E3a and Table SI E4a, respectively.

The median chloride concentration at MW02 was 469 mg/L (Figure 3), well above expected values in the Wind River Formation ($p = 7.0 \times 10^{-07}$). Compounds containing chlorides (e.g., KCl solutions) were used extensively for stimulation in the Pavillion Field. Sulfate concentrations in MW02 were below expected values in the Wind River Formation ($p = 2.7 \times 10^{-07}$) and not dissimilar ($p = 0.40$) to produced water concentrations. The Cl/SO_4 concentration ratio was similar to produced water (Figure SI D2) at MW02. Chloride and sulfate concentrations in MW01 were more typical of the Wind River Formation which may be due variation in well stimulation practices both spatially and over time.

Concentrations of organic compounds detected in MW01 and MW02 are summarized in Tables SI E3a, SI E4a and Figure 4. Diesel range organics (DRO) and gasoline range organics (GRO) were detected in MW01 and MW02 with maximum DRO concentrations of 924 and 4200 μg/L, respectively and GRO concentrations of 760 and 5290 μg/L, respectively. Benzene, toluene, ethylbenzene, *m*,*p*-xylenes, and *o*-xylene were detected in MW02 at maximum concentrations of 247, 677, 101, 973, and 253 μg/L, respectively, but were not detected at MW01. The maximum contaminant level (MCL) of benzene is 5 μg/L, so the observed maximum value was 50 times higher than the MCL. Nondetection of BTEX at MW01 is surprising given that the well was gas-charged (foaming during sampling, Figure SI E9) with similar light hydrocarbon composition to MW02 (Table SI E5). Nondetection of BTEX may be due to increased dispersion and biodegradation of these compounds at the shallower depth of this well. We could find no published information on BTEX compounds in groundwater at concentrations detected in MW02 occurring above a gas field in the absence of well stimulation. However, further testing, such as compound specific isotope analysis of BTEX components present in natural gas from the Pavillion Field (Table SI D2) and water from MW02, is necessary to attribute detection of BTEX to well stimulation.

1,3,5-, 1,2,4-, and 1,2,3-Trimethylbenzene were detected at maximum concentrations of 71.4, 148, and 45.8 μg/L, respectively in MW02 and at an order of magnitude lower concentrations in MW01. Naphthalene, methylnaphthalenes, and alkylbenzenes were also detected in MW02 at concentrations up to 7.9, 10.2, and 21.2 μg/L, respectively. Similar to BTEX compounds, detection of trimethylbenzenes, alkylbenzenes, and naphthalenes could in principle reflect non-anthropogenic origin but natural gas from the Pavillion Field and in EPA monitoring wells is "dry" (ratio of methane to methane through pentane concentration >0.95) (SI Section A.2, Table SI E5). Also, oil production in the vicinity of monitoring wells is very low or zero especially in the vicinity of MW02 (Table SI C2, Figure SI A5). Thus, the detection of higher molecular weight hydrocarbons in groundwater is unexpected. Trimethylbenzenes and naphthalenes were present in mixtures used for well stimulation (Table SI C3).

Other organic compounds used extensively for well stimulation were detected in MW01 and MW02 (Figure 4). Methanol, ethanol, and isopropanol were detected in monitoring wells at up to 863, 28.4, and 862 μg/L, respectively (Figure 4). *Tert*-butyl alcohol (TBA) was detected at 6120 μg/L in MW02. Detection of TBA in groundwater has been associated with degradation of *tert*-butyl hydroperoxide used for hydraulic fracturing.[79] Another potential source of TBA is degradation of methyl *tert*-butyl ether (MTBE) associated with diesel fuel.[80−84]

Diethylene glycol (DEG) and TEG were detected in both monitoring wells at maximum concentrations of 226 and 12.7 μg/L, respectively, in MW01, and at 1570 and 310 μg/L respectively, in MW02 (Figure 4). Tetraethylene glycol was detected only in MW02 at 27.2 μg/L. MSDSs indicate that

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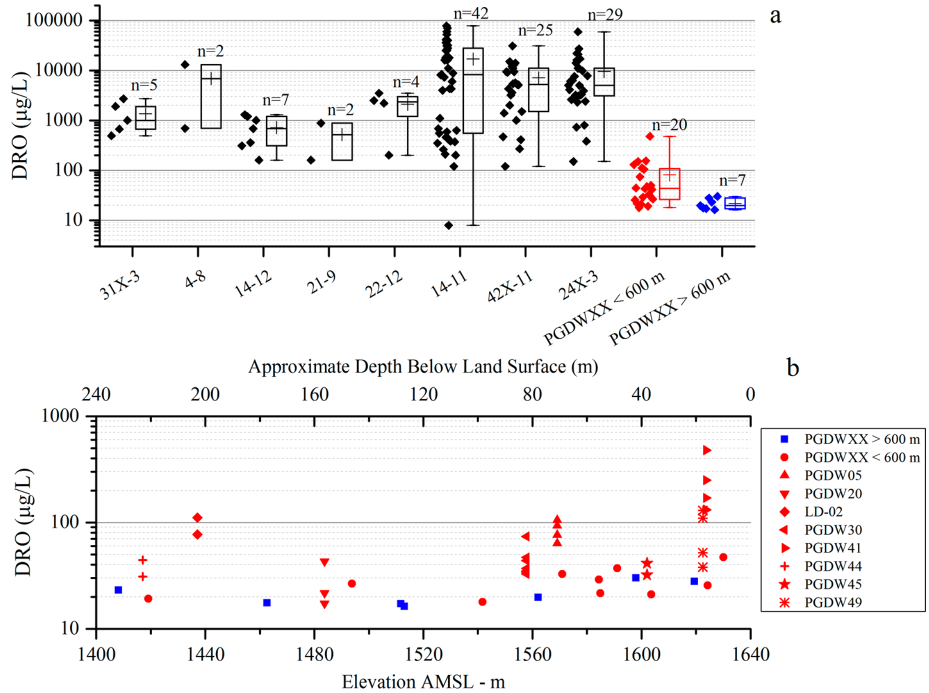

Figure 5. (a) Box and whisker plots of minimum and maximum, quartiles, median (line in boxes), mean (crosses in boxes) of diesel range organics (DRO) in shallow monitoring wells near unlined pits potentially receiving production fluids (abbreviations of production wells in Table SI C1) and domestic wells[6,8,9,39,45] (LD-20 and PGDWXX series) less than and greater than 600 m from pits. Mean values are used for domestic well sampled more than once. (b) DRO as a function of elevation and approximate depth below surface for domestic wells with results of multiple sample events illustrated.

DEG was used for well stimulation. Use of TEG was not specified. Polar organic compounds, including DEG, are commonly used as cement grinding agents.[85−88] DEG and TEG have been detected in leachate from cured cement samples under static (no flow) conditions.[89] Similar to elevated potassium detection, it is possible that detection of glycols could be attributable to cement used for monitoring well construction. However, mass flux scenario modeling, commonly used to evaluate potential concentrations of exposure of compounds released from materials in contact with drinking water under dynamic (flowing) conditions,[90] was conducted on MW01 (SI Section E.7) indicating unlikely impact. The relevance of dynamic testing is corroborated by the observation that detection of DEG and TEG was limited to a water sample from a gas production well[91] with nondetection in water samples from 83 domestic wells at five retrospective study sites[79,91−94] using high performance liquid chromatography with dual mass spectrometry at a reporting limit 5 μg/L in EPA's national study on hydraulic fracturing. 2-Butoxyethanol, a glycol ether used extensively for well stimulation in the Pavillion Field (Table SI C3), was detected in both monitoring wells at a maximum concentration of 12.7 μg/L. 2-Butoxyethanol was not detected in leachate from cured cement.[89].

The low molecular weight organic acids (LMWOAs) lactate, formate, acetate, and propionate were detected in both monitoring wells at maximum concentrations of 253, 584, 8050, and 844 μg/L, respectively (Figure 4). LMWOAs are anaerobic degradation products associated with hydrocarbon contamination in groundwater.[95,96] Acetate has been detected in produced water,[97−99] in impoundments used to hold flowback water from the Marcellus Shale,[100] and in produced water from the Denver-Julesburg Basin, CO.[101] Acetate and formate were detected in flowback water from two different fracturing sites in Germany with investigators concluding that these compounds were likely of anthropogenic origin resulting from degradation of polymers used in the fracturing fluid.[102] Formate and acetate are also degradation products of methylene chloride.[103] Benzoic acid, a degradation product of aromatics, was also detected in both monitoring wells at a maximum concentration of 513 μg/L.

Phenols were detected in both monitoring wells with maximum concentrations of phenol, 2-methylphenol, 3&4-methylphenol, and 2,4-dimethylphenol at MW02 at 32.7, 22.2, 39.8, and 46.3 μg/L, respectively. Ketones were also detected in both monitoring wells with maximum concentrations of acetone, 2-butanone (MEK), and 4-methyl-2-pentanone (MIBK) at MW02 at 1460, 208, and 12.5 μg/L, respectively. Acetone, MEK, phenol, 2-methylphenol, 3&4 methylphenol, and 2,4-dimethylphenol were detected in produced water from the Denver-Julesburg Basin.[101] MIBK, MEK, and acetone may result from microbial degradation of biopolymers used for hydraulic fracturing.[101] Nonylphenol and octylphenol, commonly present in mixtures of ethoxlyated alcohols, were detected in both monitoring wells with maximum concentrations at MW02 at 28 and 2.9 μg/L, respectively. Ethoxlyated alcohols were used for well stimulation in the Pavillion Field.

Detection of organic compounds, especially those that cannot be attributed to cement, and degradation products of compounds known to have been used for production well stimulation in both MW01 and MW02 provide additional evidence of impact to USDWs and indicate upward solute migration to depths of current groundwater use. Installation of additional monitoring wells at depths similar to MW02, with sample analysis supplemented by state-of-the-art analytical methods better suited to detection of compounds present in

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stimulation fluids (e.g., liquid chromatography coupled with quadrupole time-of-flight mass spectrometry[104−106]), is necessary to evaluate long-term risk to domestic well users in the Pavillion Field.

Assessment of Potential Impact of Unlined Pits to Domestic Wells. EPA[7] previously reported disposal of diesel fuel-based (invert) drilling mud and production fluids (flowback, condensate, produced water) in unlined pits in the Pavillion Field and resultant groundwater contamination in surficial Quaternary deposits in shallow monitoring wells sampled by EPA in the vicinity of three unlined pits but did not document the extent of these disposal practices. At least 64 unlined pits were used for disposal of drilling fluids of which invert mud was disposed in 57 pits consisting of up to 79% diesel fuel (Tables SI F1, SI F2). As many as 44 of 64 unlined pits were used or likely used for disposal of production fluids. Unlined pits were emptied and closed in 1995.[107,108]

A summary of information available on disposal of drilling and production fluids in pits is provided in Table SI F2. This summary includes results of soil and groundwater sampling, excavation volumes and associated criteria (1000−8500 mg/kg total petroleum hydrocarbons), proximity and direction of unlined pits to domestic wells, and recommendations by WOGCC[44] for further investigation (or no investigation).

The field operator has collected groundwater samples in surficial Quaternary deposits at 12 unlined pit locations.[44] The highest reported concentrations of GRO and DRO were 91 000 and 78 000 μg/L, respectively (Figure 5, Table SI F2). Benzene, toluene, ethylbenzene, and xylenes were detected at five locations at concentrations up to 1960, 250, 240, and 1200 μg/l, respectively (Table SI F2). Thus, sample results indicate impact to surficial groundwater in Quaternary deposits.

There may be as many as 48 domestic wells within 600 m of unlined pits of which 22 domestic wells were sampled by EPA[6,8,9,39] and 11 were resampled by WDEQ[45] (Table SI F3). DRO concentrations in domestic wells <600 m from unlined pits likely receiving production fluids were elevated ($p = 0.003$) compared to domestic wells >600 m from unlined pits (Figure 5a). DRO was detected at 752 mg/kg in a reverse osmosis filter sample from a domestic well (PGDW20) during the Phase II sampling event[8] (Table SI F3). Concentrations of DRO in domestic wells generally decreased with depth (Figure 5b). Another potential source of DRO in some domestic wells (Table SI G1) is invert mud remaining in boreholes. However, differentiation from other source terms (unlined pits and stimulation) is not possible with currently available data (SI Section G.1).

At two domestic wells (PGDW05 and PGDW30), chromatograms for DRO analysis suggest a diesel fuel source (Figure SI F1a, b). Chromatograms of aqueous (Figure SI F2a) and carbon trap samples (Figure SI F2b) for DRO at another domestic well (PGDW20) indicated the presence of heavy hydrocarbons in water. All three domestic wells are located near unlined pits likely used for disposal of production fluids.

Adamantanes were detected at low aqueous concentrations (<5 μg/L) at four domestic wells (PGDW05, PGDW20, PGDW30, and PGDW32) (Table SI F3). Admantane, 2-methyl adamantane, and 1,3-dimethyladamantane were detected in a reverse osmosis filter sample at PGDW20 at concentrations of 420, 9400, and 2960 μg/kg, respectively. Adamantanes were detected in produced water up to 74 mg/L (Table SI D3) indicating disposal in unlined pits as a potential source term. The inherent molecular stability of admantanes and other diamondoid compounds imparts thermal stability resulting in enrichment in manufactured petroleum distillates.[109] Diamondoids are resistant to biodegradation[110,111] resulting in their use as a fingerprinting tool to characterize petroleum and condensate induced groundwater contamination.[112]

2-Butoxyethanol was detected at 3300 μg/L in a domestic well (PGDW33)[45] (Table SI F3). The depth of this domestic well is only 9.1 m bgs and is located within 134 m of an unlined pit used for disposal of production fluids. Other compounds, including BTEX, associated with production well stimulation (e.g., isopropanol) were detected at lower concentrations (<10 μg/L) in other domestic wells (Table SI F3). Sample results at domestic wells suggest impact from unlined pits and the immediate need for further investigation including installation of monitoring wells in the Wind River Formation. Since flood irrigation is common in the vicinity of unlined pit areas, the lateral extent of groundwater contamination is potentially greater in the Wind River Formation than in overlying surficial Quaternary deposits due to "plume diving" (i.e., uncontaminated water overlies portions of a contaminant plume).[113−115]

Our investigation highlights several important issues related to impact to groundwater from unconventional oil and gas extraction. We have, for the first time, demonstrated impact to USDWs as a result of hydraulic fracturing. Given the high frequency of injection of stimulation fluids into USDWs to support CBM extraction and unknown frequency in tight gas formations, it is unlikely that impact to USDWs is limited to the Pavillion Field requiring investigation elsewhere.

Second, well stimulation in the Pavillion Field occurred many times less than 500 m from ground surface and, in some cases, at or very close to depths of deepest domestic groundwater use in the area. Shallow hydraulic fracturing poses greater risks than deeper fracturing does,[57,116] especially in the presence of well integrity issues[117,118] as documented here in the Pavillion Field. Additional investigations elsewhere are needed.

Finally, while disposal of production fluids in unlined pits is a legacy issue in Wyoming, this practice has nevertheless caused enduring groundwater contamination in the Pavillion Field. Impact to groundwater from unlined pits is unlikely to have occurred only in the Pavillion Field, necessitating investigation elsewhere.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.5b04970.

Supplemental discussion and tables summarizing data sets are provided in the Supporting Information (SI) portion of the paper (PDF)

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Notes

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