Baseline groundwater quality in unconventional oil and gas fields

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ABSTRACT

In recent years, expansion of unconventional oil and gas production has prompted significant interest in potential impacts on drinking water resources. In many cases, water quality investigations rely on access to landowner water wells to develop baseline data prior to drilling; respond to spills, complaints, or incidents; or evaluate potential impacts due to drilling, completion, hydraulic fracturing, water management, or well operation. However, differences in water well construction, operation, maintenance, and wellhead protection practices can complicate sampling efforts and introduce artifacts that might confound interpretation of results and definition of baseline conditions.

The frequency of sampling and the types of analyses also vary from site to site, ranging from basic field parameters such as conductivity, pH, and water level to comprehensive analyses of organics, inorganics, radionuclides, gases, stable isotopes, and microorganisms. Regulatory agencies may also specify required analytical parameters and monitoring frequency. This paper highlights some of the challenges associated with deriving baseline data from different types of wells and provides preliminary data on the use of chemical fingerprinting to differentiate sources of waterborne contaminants.

Key words | chemical fingerprinting, coalbed methane, hydraulic fracturing, methane, unconventional oil and gas, water well construction

INTRODUCTION

The central Raton Basin in southeastern Colorado has been at the forefront of coalbed methane (CBM) development where over 2300 CBM wells have been drilled, completed, hydraulically fractured (HF), and operated since the early 1990s. Water plays an integral role in CBM production and is of particular importance in the central Raton Basin’s arid environment where there are over 1500 water wells that provide freshwater for private residences, ranching, hunting, fisheries, agriculture, and some light industry. About 1.5 million m$^3$ (4,000 acre-ft) of produced water is discharged annually into surface water streams through 90 permitted outfalls and functions to augment in-stream flows and provide a water source for irrigation, livestock watering, and wildlife habitat. The intensity of CBM development in the Raton Basin has generated concerns about potential impacts on drinking water resources and prompted attention from government agencies, industry, academia, and the private sector. While some information about the chemicals used for HF is reported in various databases (e.g. http://fracfocus.org/), there are concerns about potential migration into water systems, biogeochemical reactions that could lead to increased migration of metals and minerals from subsurface formations, or other unintended consequences (National Research Council (NRC) 2010; Dahm et al. 2011; US Environmental Protection Agency (EPA) 2012; Jackson et al. 2013; Colorado Oil and Gas Conservation Commission (COGCC) 2014).

Water quality in the central Raton Basin is influenced by a variety of hydrogeological and land-use factors. Biogeochemical reactions between water and coal seams can influence...
water quality depending on the type of coal, degree of weathering, and local hydrogeology (Fendinger et al. 1989; Geldon 1989; Van Voast 2003; Van Stempvoort et al. 2005; Struchtemeyer & Elshahed 2012). For example, aliphatic or aromatic hydrocarbons, sulfur (0.2 to 7%), minerals, and trace levels of metals (Benhabib et al. 2006) can enter groundwater due to biogeochemical interactions with the highly prevalent bituminous coal in the central Raton Basin (Wood et al. 1957; Landis 1959). In contrast to groundwater systems, surface water quality is susceptible to ambient conditions and inflows from surface discharges (Benko & Drewes 2008; National Research Council (NRC) 2010; Dahm et al. 2011), runoff, and spills. In addition, surface water quality can fluctuate diurnally, seasonally, and intermittently due to precipitation, and temperature changes that affect biological activity, gas solubility, and the rate of evaporation.

The CBM and water wells in the central Raton Basin vary in depth and relative proximity to one another, depending on the local hydrogeology. Water wells tend to be shallower (25 to 250 meters below ground surface), whereas CBM well depths range from about 450 to 970 meters below ground surface (Watts 2006). Some of the freshwater sources for the water wells are in coal-bearing formations and many of the wells are vulnerable to contamination from nearby activities such as agricultural operations, cattle grazing, construction yards, repair shops, and other light industry. There are also an unknown number of abandoned water wells, mining core holes, and mine shafts in different parts of the basin that could serve as conduits for vertical flow or cross-contamination. Well driller licensing has been mandated since the 1950s (Graham 2011), however, the state has not instituted a program for inspection, water quality monitoring, or wellhead protection. In 2005, the Colorado Department of Water Resources (CDWR) issued revised water well construction regulations that require casing (State of Colorado 2005; Graham 2011), there are no mechanisms to prevent a landowner from drilling a water well into shallow coal or a methane or hydrocarbon bearing zone. In addition, most wells in the central Raton Basin were completed prior to these new requirements.

Given the history of CBM development in the central Raton Basin, there is a rich inventory of water quality information from sampling and monitoring that includes data on geochemical parameters, dissolved methane, dissolved gases, stable isotopes, hydrocarbons, and trace organic and inorganic constituents. The objective of this paper is to present findings from a meta-analysis of produced water, well water, and surface water quality data from the central Raton Basin to determine if geochemical differences among the different water sources can be used to develop baseline data and identify potential impacts from HF or CBM development. The use of chemical fingerprinting to identify data anomalies and differentiate water from different formations is also explored.

METHODS

Water quality data from monitoring wells, landowner wells, CBM wells, surface water outfalls, and surface water systems were evaluated to identify potential links between water quality and CBM development. A systematic meta-analysis was conducted to review regulatory analytical data from well files, regulatory investigations, and records of complaints, spills, and notices of alleged violations (NOAVs). An overview of the sources of data used in this analysis is provided in Table 1 and the monitoring parameters are summarized in Table 2.

Data sources

Data were derived from publicly available databases and supplemental field investigations. The primary data source was compliance data from the Colorado Oil and Gas Conservation Commission (COGCC) Rule 608, which requires that CBM operators conduct baseline testing of water wells within a defined radius of proposed CBM wells (COGCC 2014). The specific testing requirements depend on the proximity of water wells to the CBM well. The first priority is to sample the two closest water wells within 1320 ft (400 m) of the CBM well. In cases where two water wells do not exist within that radius, then the nearest single water well should be tested, ideally within an 800 m radius from the proposed well site. The testing is conducted prior to drilling, within 1 year after well completion, and at 3 and 6 year intervals after well completion (Colorado Oil and Gas Conservation Commission (COGCC) 2015). In cases where the dissolved methane is over 2 mg/L, supplemental analyses of gas composition and stable-isotope ratios are required (COGCC 2015). Comprehensive analyses of
hydrocarbons and trace organic and inorganic constituents are required in response to landowner complaints and in the aftermath of spills, accidents, or NOAVs. Between 1998 and 2012, a subset of 93 to 134 CBM wells were tested for other organic constituents including chlorinated solvents, pesticides, aromatics, phthalates, cresols, anilines, phenols, ethers, and other anthropogenic compounds. All of the analyses were conducted by certified laboratories using standardized methods. All data used for this project underwent a quality assurance review prior to conducting the meta-analysis.

Data processing

A hierarchical approach (Figure 1) was used to downselect specific parts of the basin and individual CBM wells, groundwater wells, and surface water sites for more detailed evaluation. Data were organized by drainage, sample type,
and formation to tally the type of data available for each category and determine the feasibility of running statistical analyses. This approach indirectly selects areas where there have been historic concerns (complaints, spills, NOAVs), since water quality sampling is almost always one of the follow-up actions. It also selects for drainage areas with a relatively high number of CBM wells. The fact that monitoring data stem from concerns related to significant CBM activity provides a higher probability of identifying potential linkages between CBM activities and water resources as compared to other areas with less data availability.

### Exploratory chemical fingerprinting

During 2011 and 2012, supplemental analyses on selected wells and surface water samples were conducted in parallel with other ongoing investigations in the central Raton Basin (US Environmental Protection Agency (EPA) 2012). Water samples were analyzed for a wide suite of hydrocarbons to determine the source of material detected in water samples. This “chemical fingerprinting” approach is often for source attribution of fugitive hydrocarbons. The analytical methods used for chemical fingerprinting are provided in the

#### Table 2: Overview of monitoring parameters associated with different monitoring programs

<table>
<thead>
<tr>
<th>Purpose of monitoring</th>
<th>Sample type</th>
<th>Parameters</th>
<th>Date range</th>
<th>Frequency</th>
<th>Role in meta-analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rule 608b (Colorado Oil and Gas</td>
<td>Groundwater</td>
<td>pH, alkalinity, anions, cations, metals, dissolved gases, total petroleum</td>
<td>2008 to</td>
<td>One pre-drilling sample; follow-up samples 1, 3 and 6 years after drilling</td>
<td>Data that can be compared with historic data and monitoring from other activities</td>
</tr>
<tr>
<td>Conservation Commission (COGCC) 2015)</td>
<td></td>
<td>hydrocarbons (TPH), benzene, toluene, ethylbenzene and xylenes (BTEX),</td>
<td>present</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>and field parameters</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Surface Use Agreement</td>
<td>Voluntary testing of</td>
<td>Similar to 608b</td>
<td>1998-</td>
<td>Pre- and post-drilling</td>
<td>Data that can be compared across the basin</td>
</tr>
<tr>
<td></td>
<td>landowner water wells</td>
<td></td>
<td>present</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Complaints, NOAVs</td>
<td>Groundwater</td>
<td>Similar to 608b</td>
<td>2004-</td>
<td>Typically 1–2 samples per complaint or NOAV</td>
<td>Detailed analysis of specific wells</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>present</td>
<td></td>
<td></td>
</tr>
<tr>
<td>County Health Department</td>
<td>Groundwater</td>
<td>Dissolved gas, ions, metals</td>
<td>2011–2012</td>
<td>Typically one sample per location collected by well owner</td>
<td>Supplemental information on well water in the basin</td>
</tr>
<tr>
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<td></td>
<td></td>
</tr>
<tr>
<td>CBM</td>
<td>Produced water</td>
<td>Bacteria, dissolved gas, pH, temperature, solids, water production,</td>
<td>1993-</td>
<td>Typically single sample per well collected 30 to 60 days after the</td>
<td>Compare across wells and with data from groundwater and surface water samples</td>
</tr>
<tr>
<td></td>
<td></td>
<td>organics, anions, cations, stable isotopes, metals, radionuclides, whole</td>
<td>present</td>
<td>initial production date. Occasionally multiple samples per well</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>effluent toxicity (WET)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NPDES requirements</td>
<td>Produced water</td>
<td>Field parameters, solids, anions, cations, metals, organics, WET</td>
<td>1995-</td>
<td>Specified in permit requirements, typically quarterly</td>
<td>Comparison to surface water trends. Evaluate changes in produced water quality over time</td>
</tr>
<tr>
<td></td>
<td>discharge</td>
<td></td>
<td>present</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Watershed monitoring</td>
<td>Surface water</td>
<td>On-line monitoring of field parameters, periodic monitoring of other</td>
<td>2007-</td>
<td>Continuous monitoring (2010-present); periodic grab samples for other</td>
<td>Time series analysis; comparison with other data</td>
</tr>
<tr>
<td></td>
<td></td>
<td>parameters, metals</td>
<td>present</td>
<td>parameters</td>
<td></td>
</tr>
<tr>
<td>Special studies</td>
<td>Surface, groundwater,</td>
<td>Detailed analysis of trace organics, minerals, metals, radionuclides</td>
<td>2004-</td>
<td>1–3 samples per site</td>
<td>Patterns of detect/non-detect; chemical fingerprinting</td>
</tr>
<tr>
<td></td>
<td>and produced water</td>
<td></td>
<td>present</td>
<td></td>
<td></td>
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</tbody>
</table>
Supplemental Materials (available in the online version of this paper). One hundred and twenty three (123) individual volatile organic compounds were measured by purge-and-trap gas chromatography/mass spectrometry (GC/MS) to detect paraffin, isoparaffin, aromatic, naphthenic, and olefin (PIANO) compound classes. A subset of the sample was filtered, and both whole-water and filtered samples were also liquid-liquid extracted and analyzed by GC/MS or GC with flame ionization detection (GC/FID) for: 34 alkyl-phenols, 74 polycyclic aromatic hydrocarbons (PAHs) and PAH alkyl-homologues, and 37 saturated hydrocarbons (SHCs), including n-alkanes and selected isoprenoids. In addition to quantitative determination of selected hydrocarbons, the GC/FID chromatograms provide a qualitative indication of the boiling point range of extracted hydrocarbons and, in some cases, can provide insight into the type of material contributing to the hydrocarbon signature (e.g. crude or refined oil, diesel, or coal-derived hydrocarbons, etc.).

Detailed analyses of individual polycyclic aromatic hydrocarbons (PAH) compounds were conducted on a subset of samples from CBM wells, monitoring wells, and surface water discharges. The PAHs, including the parent compound and selected alkyl-homologues, were extracted by liquid-liquid extraction and analyzed by GC/MS yielding detection limits around 1 ng/L.

RESULTS AND DISCUSSION

The results of the meta-analysis and well-file review provided insight into the approaches used for drilling, cementing, and HF. In general, the relatively low pore pressures in the formations penetrated by CBM wells in the central Raton Basin require specialized drilling and cementing procedures. The CBM wells were drilled with air and foam mist. Typically 50–100% excess cement (by volume) was used to achieve the appropriate cement fill-up and ensure casing integrity. Other cementing modifications to minimize the hydrostatic weight of the cement column include the use of lightweight cement mixtures and/or cementing the casing in multiple stages by running a multiple stage cement tool in the casing string. Accelerants used for curing the cement are calcium-based and include chloride, sulfate, or nitrate.

Part of the meta-analysis was to determine if any of the HF ingredients or accelerants could indicate potential cementing or waste containment issues. The HF fluid used in the central Raton Basin consisted of water (100 to over 550 m³ per fracturing procedure) augmented with nitrogen, guar gum, gelling agents, foaming agents, and other additives including methanol, 2-butoxy-ethanol, ethylene glycol, sucrose, and acetic acid. Dilute hydrochloric acid was used to clean perforations of cement. Sodium chloride and sucrose were used as enzyme breakers. Quartz sand was used as a proppant to keep the fractures from closing. The chemicals (pre-2010) or biological agents (post-2010) that were used to prevent proliferation of nuisance microorganisms in wellbores, pipelines, and on surfaces of equipment are summarized in Table 3.

Water quality comparisons

Monitoring data were reviewed to identify dominant characteristics of produced water, groundwater and surface water.
A comparison of the total dissolved solids (TDS) and the dominant anions (alkalinity, chloride, and sulfate) and dominant cations (sodium, calcium, and magnesium) for different water sources is shown in Figure 2. The average TDS for the produced water in the central Raton Basin is about 2500 mg/L, about five-fold higher than the TDS levels in shallower groundwater or surface water. Water quality across the basin is dominated by the carbonate system. Average alkalinity levels in produced water are about 1200 mg/L as CaCO₃ and about four-fold higher than the levels typical in shallow groundwater or surface water. The major cation is sodium, which averages about 1000 mg/L in produced water, 150 mg/L in shallow groundwater, and about 50 mg/L in surface water. Chloride levels are about ten-fold higher in produced water (average about 750 mg/L) as compared to other waters. Sulfate was only detected in 5% of the produced water samples with a median concentration of 20 mg/L. Produced water tends to have lower concentrations of sulfate, calcium, and magnesium than shallow groundwater or surface water. Bromide was detected in 87% of the CBM wells with a median concentration of 1.6 mg/L and boron was detected in 89% of the CBM wells with a median concentration of 0.24 mg/L. Another difference among the water sources was the extent of well-to-well variability as is evidenced by the over four-fold difference in CBM concentrations of TDS, chloride, sulfate, and sodium.

Specific trends were observed in the relationship between sodium and chloride as shown in Figure 3. For the produced water, there was a linear correlation of 0.53 mg sodium per mg of chloride (R² = 0.93), which is slightly lower than the stoichiometric ratio of 0.65 mg sodium per mg chloride. The correlation for the groundwater wells was not as strong (R² = 0.63) and the relationship between sodium and chloride was about 1.3 mg sodium per mg of chloride.

The nitrogen content of the produced water was fairly low (below 2 ppm) and consisted primarily of ammonia-nitrogen in the 174 CBM wells that were monitored for nitrogen. Oxidized forms of nitrogen (e.g. nitrite and nitrate) were detected in less than 10% of the monitored wells. Orthophosphate concentrations were also fairly low with a median concentration of 0.03 mg/L (as PO₄). Comparison of nitrogen and phosphorus concentrations and speciation might be helpful in differentiating shallower groundwater sources from produced water.

The sodium adsorption ratio (SAR) is frequently used to evaluate the potential for using water for irrigation purposes.

### Table 3
Summary of microbial control products used for CBM operations in the central Raton Basin, Colorado

<table>
<thead>
<tr>
<th>Time frame</th>
<th>Trade name</th>
<th>Ingredients</th>
<th>Chemical Abstracts Service Number (CAS #)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-2010</td>
<td>Bioclear</td>
<td>2,2-Dibromo-2-cyanoacetamide and dibromo-3-nitrilopropionamide (10–30% by weight)</td>
<td>10222-01-2</td>
</tr>
<tr>
<td></td>
<td>Bioclear</td>
<td>1,2-Dibromo,2,4-dicyanobutane (60–100% by weight)</td>
<td>35691-65-7</td>
</tr>
<tr>
<td></td>
<td>Bioclear</td>
<td>2,2 Dibromo-3-nitrilopropionamide (95–100% by weight)</td>
<td>10222-01-2</td>
</tr>
<tr>
<td></td>
<td>X-Cide</td>
<td>2,2-Dibromo-3-nitrilopropionamide (60–100% by weight)</td>
<td>10222-01-2</td>
</tr>
<tr>
<td></td>
<td>X-Cide 5009</td>
<td>2-Bromo-2-nitropropene-1,3-propanediol (60–100% by weight)</td>
<td>52-51-7</td>
</tr>
<tr>
<td>Post-2010</td>
<td>M-100H</td>
<td>Live microorganisms and nutrients in a liquid medium that degrade hydrocarbons, PAHs, and polychlorinated biphenyls (PCBs)</td>
<td>Biological product</td>
</tr>
<tr>
<td></td>
<td>Corroso-Bac</td>
<td>Facultative bacteria that produce ketones and organic acids that inhibit corrosion by neutralizing the metal</td>
<td>Biological product</td>
</tr>
<tr>
<td></td>
<td>Litho-Bac</td>
<td>Facultative bacteria that produce alcohols, ketones, organic acids, and biosurfactants that sequester and chelate cations (calcium, magnesium, barium) and inhibit scale formation</td>
<td>Biological product</td>
</tr>
<tr>
<td></td>
<td>Para-Bac</td>
<td>Facultative bacteria that produce biosurfactants, organic acids, ketones, and alcohols that disperse, dissolve and prevent deposition of paraffin chains of C16 to C60 +</td>
<td>Biological product</td>
</tr>
</tbody>
</table>
Figure 2 | Boxplot comparison of total dissolved solids (TDS), dominant anions (alkalinity, chloride and sulfate), and dominant cations (sodium, calcium, magnesium and potassium) for produced water (CBM), groundwater (GW) and surface water (SW) in the central Raton Basin of Colorado. Based on composite data from 1995-2012.

Figure 3 | Relationship between sodium and chloride in central Raton Basin CBM Wells (CBM), groundwater wells (GW) and surface water sampling sites (SW).
The SAR is calculated as:

$$\text{SAR, (mmol/L)}^{0.5} = \frac{[\text{Na}^+]}{\sqrt{[\text{Ca}^{2+}] + [\text{Mg}^{2+}]}}$$

where the concentrations of sodium, calcium, and magnesium are expressed in mmol/L (Hounslow 1995).

The SAR was calculated for over 2100 CBM wells in the central Raton Basin, and ranged from less than 1 to over 100 with a median value of 76. In general, SAR values below about 10 are considered to be acceptable for irrigation, depending on the soil characteristics, type of crop, and the potential salinity hazard. The SAR reflects the potential sodium hazard associated with using water for irrigation, depending on the soil characteristics. Irrigation water that contains SAR levels over 25 can affect the soil structure, particularly for clay soils. The salt tolerance of specific crops is also an important consideration. In general, only salt-tolerant crops can be supported when TDS concentrations are above about 1,000 ppm. There were about 35 CBM wells in the central Raton Basin with calculated SAR values below 30 and about 130 CBM wells with SAR values between 30 and 50, as shown in Figure 4. However, the produced water from over 90% of the CBM wells in the central Raton Basin has SAR and TDS levels that are unacceptable for direct irrigation without additional precautions such as the use of soil amendments, alternating sources, blending, or treatment. Other water quality parameters also affect the suitability of using water for irrigation including boron, dissolved metals, and organics. Boron is an essential element for plant growth, but can be toxic for boron-sensitive crops at levels ranging from 1–15 ppm. The boron levels in the produced water from over 2200 CBM wells ranged from less than 0.2 ppb to over 1 ppm with a median value of 240 ppb, well below the levels that are considered to be problematic for plant growth.

The presence/absence of metals and metalloids, concentrations, and co-occurrence in produced water provides additional insight into biogeochemical reactions. Summary data are provided in the Supplemental Materials (available in the online version of this paper). Boron, iron, and manganese were detected in all produced water samples (over 1800 CBM wells), while copper was detected in 36% of the samples (700 CBM wells) and chromium was detected in 22% of the samples (430 CBM wells). Arsenic and selenium were detected in less than 2% of the over 1940 CBM wells that were monitored for these metalloids and they co-occurred in 4 wells. Mercury was not detected in any of the over 800 CBM wells where it was monitored. Trace metals were monitored in a subset of 110–145 CBM wells; barium and lithium were detected in most of the monitored wells (110–123 CBM wells) while antimony, beryllium, cadmium, cobalt, nickel, and thallium were not detected in any of the monitored wells. Aluminum and zinc were detected in 40–50 CBM wells and molybdenum and lead were detected in about 12–13% of the CBM wells that were monitored (16–17 CBM wells). Silver was detected in 8% of the monitored CBM wells. It is important to note
that care must be taken when discussing the frequency of detection analytes across datasets with varying detection limits. While the detection frequency would change if all the data had similar detection limits, the relative frequency would not (e.g. copper and chromium would be more frequently detected than arsenic and selenium). While parallel data are not available for water wells, these trends provide a reference point that might be useful for identifying potential sources of contamination.

**Dissolved methane**

The concentrations of dissolved methane in water wells ranged from non-detectable to over 30 mg/L with a median value of about 2 mg/L, while the median dissolved methane concentration in produced water was 6 mg/L. Results of stable isotope testing of CBM wells, monitoring wells, and landowner wells across the central Raton Basin are shown in Figure 5. In general, the isotope signatures from samples from CBM wells reveal a combination of thermogenic and biogenic activity. The methane isotopic signature (hydrogen and carbon) for the water well samples is more variable and there is some overlap with the CBM wells (Figure 5(a)). The overlap with CBM wells may be due to the depth of the water well and connections with coal seams, especially in cases where the water wells have been drilled into coal seams or coal mines. In addition, the use of un-cased or open-hole completions for water wells can provide a migration pathway for methane or other gases that is unrelated to CBM development. When the carbon isotope signatures for carbon dioxide and methane are compared (Figure 5(b)), there is more of a clear separation between the domain of the water wells and the CBM wells. The isotope data are a useful tool for investigating the sources of dissolved methane and identifying potential connections to CBM wells. Interpretation of the data can be complicated in cases where water wells are drilled into coal seams.

**Chemical fingerprinting**

Interpretation of data on hydrocarbons is of particular relevance to evaluation of potential impacts of CBM on water resources. In general, hydrocarbons originate from petroleum sources but can also include runoff from roads, commonly used commercial products, synthetic polymers, vegetation, macro- or micro-biological sources, and a wide range of other sources. The most generic measurement is total petroleum hydrocarbons (TPH), which can include thousands of unresolved hydrocarbon compounds, ranging from small, volatile, short-chained aliphatic or aromatic compounds to large, non-volatile, long-chained, branched or aromatic compounds. Subsets of TPH include gas range organics (GRO), diesel range organics (DRO), and residual range organics (RRO). Additionally, the most common volatile organic compounds measured are BTEX compounds. While often used in environmental assessments, TPH and BTEX concentrations alone can be problematic as they do not provide any information about the source of hydrocarbons. The
analyses of other classes of hydrocarbons, such as the parent and alkyl-homologue PAHs and PIANO compounds, as well as the qualitative interpretation of the GC/FID chromatogram provide insight into the source of hydrocarbons and the nature of the material contributing to measured TPH concentrations (Stout et al. 2002; Stout & Emsbo-Mattingly 2008).

Hydrocarbons, PAHs, and other organic constituents have been monitored periodically in the central Raton Basin CBM wells. Summary data are provided in the Supplemental Materials (available in the online version of this paper). BTEX compounds were detected in 10 to 44% of the samples from over 2300 CBM wells, with average concentrations ranging from 4 to 14 ppb. Chlorobenzenes were monitored in about 160 CBM wells with periodic detections of 1,4 dichlorobenzene (13% of wells; median value 14 ppb) and 1,2 dichlorobenzene (4% of wells; median value 1.7 ppb). Naphthalene was the only PAH that was detected in the subset of 134 wells that were evaluated and it was detected in 5% of the samples (median concentration of 5 ppb). None of the compounds associated with HF fluids were detected in the produced water or any of the water well samples. Alkylphenols were not detected in any of the samples.

Chemical fingerprinting investigations yielded insights into the distribution of hydrocarbons and also highlighted potential complications in interpreting monitoring data. The GC/FID traces of unfiltered and filtered (1 micron pore size) samples are compared to a high-volatile bituminous coal in Figure 6. For these samples, it appears that higher boiling point hydrocarbons (circled on the right side of each chromatogram) were removed by filtration. These results suggest that a portion of the reported levels of total petroleum hydrocarbons (TPH), and diesel range organics (DRO), may be associated with fine particles of coal that are mobilized during well purging and sampling. It is likely that the presence of coal outcroppings and the co-location of water-wells and coalseams may inadvertently introduce coal particles into water wells leading to potential misinterpretation of coal fines as TPH or DRO.

Figure 6 | GC/FID traces for (a) unfiltered and filtered produced water and (b) unfiltered and filtered monitoring well samples.
Exploratory testing of the presence of PAHs and the distribution of individual compounds was conducted on a subset of monitoring wells, CBM wells, and produced water discharges. None of the PIANO compounds or alkylphenols was detected in any of the samples. The PAH compounds were not detected in the majority of the monitoring wells.

PAHs and alkylated PAH homologues were measured in samples from four CBM wells and two monitoring wells. Their concentrations are compared to a high volatile bituminous coal in Figure 7. In general, the PAHs concentrations in produced waters varied, but were dominated by 2- and 3-ring compounds, consistent with a high volatile bituminous coal. The differences between the PAH signatures can be used as a screening tool to determine if there might be any direct connections between the wells. At this site, there was no evidence of hydrocarbon migration from the CBM wells to the nearby monitoring wells. The enrichment of relatively soluble PAHs such as naphthalenes compared to largely insoluble compounds, such as pyrene, reflects the level of PAH dissolution under the specific pressure, temperature, and water quality conditions within each well. However, additional sampling

Figure 7 | PAH concentrations in produced water and observation wells. The relative PAH abundance in a high volatile bituminous coal is also shown.
would be needed to more fully understand the range of PAH signatures that might be present in waters that are influenced by contact with coal seams or particulate coal. There is also a need for determining the extent to which different coal ranks and other water quality parameters affect the PAH signatures, such as high rank coals that are enriched in low molecular weight (i.e. 2- and 3-ring) PAHs (Wang et al. 2010).

CONCLUSIONS

This paper provides a snapshot of data from a meta-analysis of water quality and chemical fingerprinting data from groundwater and CBM wells in the central Raton Basin, Colorado. The absence of robust baseline data and inconsistencies in well construction and operation confound the ability to evaluate impacts from unconventional oil and gas development, however several general trends were observed. The water quality indicators that were most useful for investigating this set of wells were the dominant anions (alkalinity, sulfate, chloride), dominant cations (sodium, calcium, and magnesium), metals, dissolved gases, and stable isotopes. Differences between CBM wells and a monitoring well were identified using chemical fingerprinting to compare the number and types of PAHs that were present in the bulk water. The use of PAH fingerprinting has the potential to differentiate potential sources of contaminants due to the unique signatures of different sources of hydrocarbons. However, for samples collected from water in contact with coal-bearing formations, the presence of coal fines may affect the analytical result and complicate data interpretation, particularly for PAHs and other hydrocarbons. The geochemistry of the produced water and the types of inorganic and organic constituents that are detected provide a reference point for detailed analyses of specific CBM wells and also for comparison with water wells and surface water systems.

ACKNOWLEDGEMENTS

This research was supported by Pioneer Natural Resources USA, Inc. Chemical fingerprinting studies and data processing were conducted by Battelle Memorial Institute. Supplemental data analysis was supported through the Independent Research and Development program at the National Science Foundation. Any opinions, findings, conclusions, or recommendations are those of the authors and do not necessarily reflect the views of the National Science Foundation, Flinders University, Battelle Memorial Institute, or Pioneer Natural Resources USA, Inc.

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First received 9 February 2015; accepted in revised form 26 May 2015. Available online 11 June 2015