Trace Element Chemistry of Coal Bed Natural Gas Produced Water in the Powder River Basin, Wyoming

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Coal bed natural gas (CBNG) produced water is usually disposed into nearby constructed disposal ponds. Geochemistry of produced water, particularly trace elements interacting with a semiarid environment, is not clearly understood. The objective of this study was to collect produced water samples at outfalls and corresponding disposal ponds and monitor pH, iron (Fe), aluminum (Al), chromium (Cr), manganese (Mn), lead (Pb), copper (Cu), zinc (Zn), arsenic (As), boron (B), selenium (Se), molybdenum (Mo), cadmium (Cd), and barium (Ba). Outfalls and corresponding disposal ponds were sampled from five different watersheds including Cheyenne River (CHR), Belle Fourche River (BFR), Little Powder River (LPR), Powder River (PR), and Tongue River (TR) within the Powder River Basin (PRB), Wyoming from 2003 to 2005. Paired *t* tests were conducted between CBNG outfalls and corresponding disposal ponds for each watershed. Results suggest that produced water from CBNG outfalls is chemically different from the produced water from corresponding disposal ponds. Most trace metal concentrations in the produced water increased from outfall to disposal pond except for Ba. In disposal ponds, Ba, As, and B concentrations increased from 2003 to 2005. Geochemical modeling predicted precipitation and dissolution reactions as controlling processes for Al, Cu, and Ba concentrations in CBNG produced water. Adsorption and desorption reactions appear to control As, Mo, and B concentrations in CBNG water in disposal ponds. Overall, results of this study will be important to determine beneficial uses (e.g., irrigation, livestock/wildlife water, and aquatic life) for CBNG produced water in the PRB, Wyoming.

Introduction

Several western states within the United States (e.g., Wyoming, Colorado, Montana, North Dakota, New Mexico, and Utah) are exploring natural gas extraction from coal resources to meet the nation's energy demands. Coal bed natural gas (CBNG) is formed in confined coal bed aquifers through complex biogeophysical processes and remains trapped by aquifer pressure. Natural gas extraction is facilitated by pumping water from the aquifer. This water is commonly referred to as CBNG produced water. A single CBNG extraction well in the Powder River Basin (PRB) can discharge 8−80 L of produced water per minute, but this water production varies between aquifers and well density (*1*). The Wyoming State Geological Survey predicts 2−3 billion m^3 of produced water will eventually be discharged from CBNG extraction in Wyoming (*1*). Commonly, 2−10 CBNG extraction wells are combined together at a single outfall to discharge produced water and release it into constructed disposal ponds, stream channels, or re-inject into shallow groundwater aquifers. However, the majority of CBNG-produced water is discharged into unlined disposal ponds.

CBNG produced water can have high concentrations of soluble salts, and when confined in disposal ponds, can have increased concentrations of trace elements (*2*−*7*). These trace elements can be essential or toxic to plants and animals depending on their ionic species and concentrations. Geochemical processes such as mineral dissolution, precipitation, and ion adsorption/desorption control trace metal bioavailability and subsequent toxicity (*8*, *9*).

The Wyoming Department of Environmental Quality (WYDEQ) considers CBNG produced waters as surface water of the state with Class 4C designation, allowing for agricultural, industrial, wildlife, and recreational uses (*10*). This water classification has raised concerns from landowners due to potential harmful effects CBNG produced water could have on surrounding soils, vegetation, wildlife, and livestock. Beneficial uses proposed for CBNG produced water include irrigation, livestock and wildlife drinking water, aquatic life, and human drinking water (*10*). However, any potential beneficial use of produced water depends on its water quality.

A few studies have examined the quality of CBNG produced water and associated disposal ponds in the PRB (*3*, *4*). For example, McBeth et al., (*3*) monitored CBNG produced water quality at outfalls and associated disposal ponds on the western edge of the PRB. These studies established seven sites in the Little Powder River Basin, four sites in the Belle Fourche River Basin, and three sites in the Cheyenne River Basin and monitored water quality during the summers of 1999 and 2000. McBeth et al., (*3*) found that concentrations of dissolved Ba, Mn, and Cr decreased while concentrations of dissolved Al, Fe, As, and Se increased in disposal ponds. Our study is similar to McBeth et al. (*3*); however, in our study several sites from two different watersheds were added. Furthermore, CBNG outfalls and disposal ponds were monitored for 3 years, and geochemical changes over time were reported. Studies conducted by Rice et al. (*4*) examined the chemistry of CBNG discharge water from the well head at forty seven locations throughout the central PRB and found that trace elements were at or below the detection limits. Overall, both Rice et al. (*4*) and McBeth et al. (*3*) studies found that dissolved concentrations of most trace elements from CBNG well heads, outfalls and disposal pond waters were very low (below the EPA primary drinking water's maximum contaminant levels) (*11*). In these studies, no statistical analyses were conducted to determine changes in the concentration or distribution of trace elements from outfall to corresponding disposal pond.

In conjunction with CBNG energy development, there is a need to protect the environment. Potential water quality problems from CBNG-produced water disposal could affect energy extraction, impacting the nation's current energy crisis. To effectively manage CBNG produced water, there is a need to understand geochemical changes that occur in CBNG disposal ponds. Management decisions could be made from this information to identify beneficial uses for CBNG produced water such as irrigation and livestock/wildlife use, and prevent ecological problems such as trace metal contamination of water and soils, and subsequent toxicity to plants and animals. The objective of this study was to collect and monitor Al, As, Ba, B, Fe, Cd, Cu, Cr, Mn, Mo, Se, Pb, and Zn from CBNG produced water samples at outfalls

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and associated disposal ponds from 2003 to 2005. From the monitoring data, we conducted paired *t* tests to identify statistical differences between outfalls and associated disposal ponds by individual watershed. Geochemical modeling was used to identify mineral precipitation/dissolution processes affecting water quality in these CBNG produced waters; likewise, CBNG produced water quality parameters were compared to common water use criteria to determine possible beneficial uses. Major anion (alkalinity, SO_4^{2-}, Cl^-, F^-, NO_3^-, and PO_4^{3-}) and cation (Ca, Mg, Na, and K) concentrations were also monitored (in Table S3), and their results were reported by Jackson and Reddy (*6*).

Materials and Methods

Study Area Description. Most CBNG development in Wyoming occurs in the eastern portion of the PRB. This basin is part of the Great Plains Missouri Plateau. The PRB is semiarid with average annual precipitation ranging from 30 to 60 cm. The basin is bounded by the Black Hills on the east, the Hartville Uplift to the south, the Big Horn Mountains on the west, and the Yellowstone River to the north (*12*). The PRB generally consists of high plains with elevations from 1640−1800 m above sea level with rolling hills capped with clinker (*12*).

Major coal formations in the PRB include the Tertiary Wasatch Formation and the Tertiary Tongue River Member of the Fort Union Formation (*5*). Soils in the PRB are dominated by Ustic Haplargids (clay loam), Ustic Calciargids (fine loamy), and Ustic Torriorthents (loamy) (*5*). The major river systems in the PRB include the Cheyenne River, Belle Fourche River, Little Powder River, Powder River, and Tongue River. The Cheyenne River drains the southeast portion of the PRB; the Belle Fourche River drains the eastern portion of the basin; the Little Powder River and Powder River drain the northern portion of the basin; and the Tongue River drains the northwestern portion of the basin. These are perennial rivers and tributaries of the Missouri River.

Surface streams that contribute to CHR, BFR, LPR, PR, and TR have intermittent or ephemeral flows based on snowmelt or storm events. Major land uses in the PRB include ranching, livestock production, coal and uranium extraction, and natural gas extraction (*5*). Discharge of CBNG produced water increases overall flow of receiving tributaries, which drain through local soils and plant communities. Subsequently, these processes influence the quality of the receiving water.

Site Selection. Site selection was based on geographic location and extensive CBNG development in the Tongue River, Powder River, and Little Powder River watersheds. Twenty-six sites were selected within the five Wyoming watersheds to obtain CBNG produced water discharge points and associated disposal pond samples. Figure 1 identifies sampling locations that include seven sites each within the LPR and PR watersheds, three sites from the CHR watershed, four sites from the BFR watershed, and five sites from the TR watershed.

Sample Collection and Analysis. *Sampling.* CBNG water samples from each outfall and corresponding disposal pond were collected during the summers of 2003, 2004, and 2005. Before sample collection, field measurements including pH, conductivity, temperature, oxidation and reduction potential (ORP), and dissolved oxygen were taken from each CBNG outfall and associated disposal pond with an Orion model 1230 Multi-Probe. Exact locations for pond measurements were taken from within the disposal pond directly away from the outfall, at the point where disposal pond pH stabilized (typically 2−3 meters into the disposal pond). The disposal pond water samples and field measurements were collected far from any sediment disturbances caused by movement in the disposal pond.

Chemical Analysis. Duplicate water samples from outfalls and disposal ponds were taken from each site. Samples were transported in ice coolers (2 °C) to the University of Wyoming Water Quality Laboratory. Each sample was filtered through a 0.45 μm filter and subdivided: half were acidified to a pH of 2.0 with HNO_3, and half were left unacidified. Acidified samples were analyzed for Ca, Na, Mg, K, Fe, Al, Cr, Mn, Pb, Cu, Zn, As, Se, Mo, Cd, Ba, and B by inductively coupled plasma-mass spectrometry (ICP−MS), and unacidified samples were analyzed for SO_4^{2-}, Cl^-, F^-, NO_3^-, and PO_4^{3-} using ion chromatography (IC). Total alkalinity of unacidified samples was determined by the acid titration method.

Geochemical Modeling. The geochemical model MINTEQA2 was used to verify analytical data accuracy and predict ion activities and saturation indices (*13*). This model used chemical data, pH, ORP, alkalinity, and redox couples to calculate ion speciation, ion activities, ion complexes, and saturation indices.

Quality Control. The quality control/quality assurances protocols such as duplicate sampling and analysis, trip blanks, and known concentrations of reference standards were included. Standard laboratory procedures were used for all analytical analyses including pH, electrical conductivity, and alkalinity measurements. All analyses were performed following the EPA Code of Federal Regulations (CFR) 40, Part 1, Chapter 36 procedures (*14*).

Statistical Analysis. Due to a "natural pairing" of the outfall and an associated disposal pond, paired *t* tests were used to identify these differences between water types (outfalls vs associated disposal ponds) which were separated by individual watershed (alpha = 0.05) (*15*). Residual normality was obtained for all measured parameters except Se, Cd, and Mn, which were removed from statistical analysis.

Results and Discussion

Samples from outfalls and corresponding disposal ponds varied in pH and ORP throughout the watersheds (Figure 2). The pH of outfall samples ranged from 7.1 to 7.5 among all watersheds, while samples from disposal ponds ranged from 8.1 to 9.4. Though some individual CBNG water sample pH ranges overlapped, outfalls typically had lower pH than their corresponding disposal ponds. Outfall water pH was stable and controlled by the geologic formation and the concentration of dissolved CO_2 confined in the aquifer, whereas the disposal pond water pH was varied because of the degassing of CO_2 from the produced water and its interaction with local soils (*2*). The ORP followed a trend similar to that of pH, in that the ORP samples from outfalls typically were lower (−109 to 161 mV) than the ORP of samples from disposal ponds (−17 to 121 mV). These results were expected due to a reduced environment where CBNG is produced, and the relative oxidized environment in the disposal ponds.

Mean trace metal concentrations and standard errors for water samples from CBNG outfalls and disposal ponds, separated by watershed, are presented in Table 1. Iron (1.28−8.27 μM/L), Al (6.71−67.35 μM/L), Ba (0.95−4.47 μM/L), and B (5.89−15.20 μM/L) were the major constituents of trace metal concentrations, while Cd and Pb concentrations were the lowest at <0.01 μM/L for both elements. Most trace elements increased in concentration from the CBNG outfall to the disposal pond. Barium was an exception because it significantly decreased from the outfall to the disposal pond in all watersheds (Figure 3). Though most trace elements increased in disposal ponds, only Al, Cu, Ba, As, Mo, and B were statistically different from outfalls to disposal ponds (alpha 0.05) and will be discussed in the subsequent sections. Yearly mean concentrations of Al, Cu, Ba, As, Mo, and B are presented in Table S1. Of those trace elements (Al, Cu, Ba, As, Mo, and B), Al and Cu concentrations decreased between years in disposal ponds, while Ba, As, and B concentrations

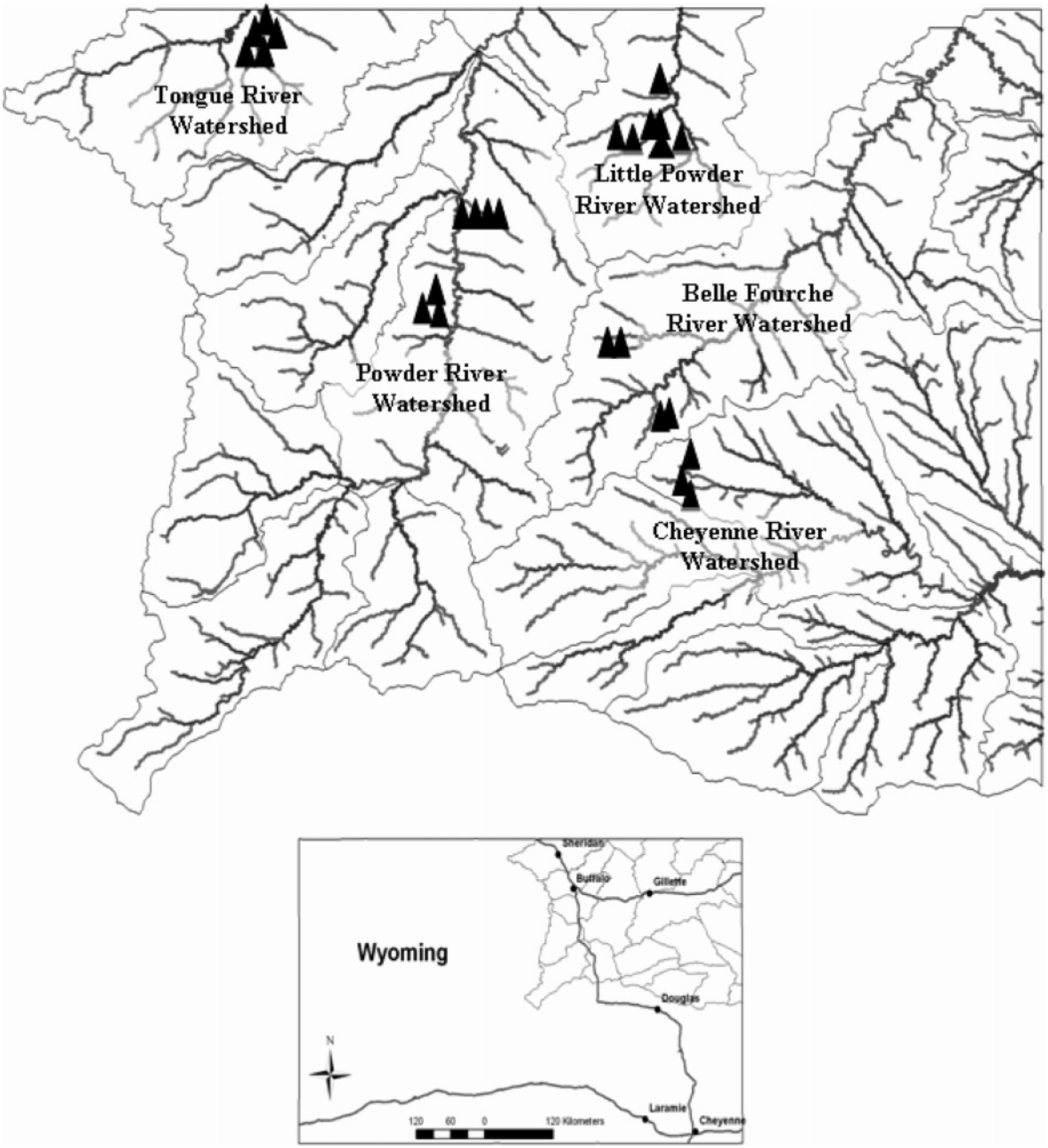

FIGURE 1. Sample site locations in the Powder River Basin, Wyoming.

increased between years; however, Mo concentrations remained the same in most watersheds.

Aluminum. Aluminum concentrations varied between outfalls and disposal ponds across watersheds (Figure 3). The BFR, LPR, and PR Al concentrations were significantly different between outfalls and disposal ponds (*t* test *p*-values 0.05, 0.02, and 0.02). In the BFR, Al concentrations tended to be higher in outfalls than in disposal ponds (18.83−10.72 μM/L), but in the LPR and PR, disposal ponds had higher Al concentrations (LPR 11.27−21.24 μM/L and PR 6.71−9.29 μM/L).

Disposal pond Al concentrations tended to decrease from 2003 to 2005 in most watersheds. In BFR, LPR, PR, and TR disposal ponds, overall Al concentrations decreased. For example, in LPR disposal ponds, Al concentrations decreased from 2003 to 2004 from 49.16 to 10.70 μM/L, and decreased to 0.97 μM/L in 2005. It is interesting to observe that disposal pond Al concentrations in CHR did not follow the other four watersheds' decreasing Al trend, but increased in concentration from 10.53 μM/L in 2003 to 35.08 μM/L in 2005.

Dominant Al species data in outfalls and disposal ponds across all watersheds are presented in Tables 2 and 3. For all produced water sampled, $Al(OH)_4^-$ was the dominant dissolved ionic species. McBeth et al. (*3*) found similar results in CBNG produced waters in CHR, BFR, and LPR watersheds, and Stumm and Morgan (*9*) also predicted $Al(OH)_4^-$ as a dominant species in natural waters.

The CHR and TR Al concentrations were not significantly different between outfalls and disposal ponds (*t* test *p*-values 0.22 and 0.42), but Al mean concentrations in TR outfalls were much higher (67.35 μM/L) than all other watersheds. The unusually high Al concentrations can be attributed to a common remediation technique used by CBNG producers in the TR that acidifies the produced water with sulfuric acid. This process is used to lower the sodium adsorption ratio (SAR), but it also affects many other trace elements, such as Al, causing them to become soluble and mobile (*8*, *9*). MINTEQA2 results from TR suggest that $AlSO_4^+$ is the dominant species in sulfuric acid treated produced waters, but $Al(OH)_4^-$ is dominant in outfalls and disposal pond waters

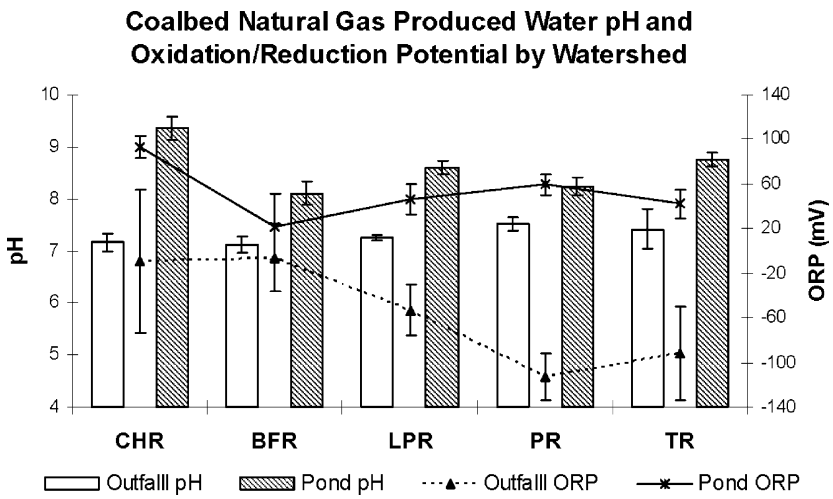

FIGURE 2. The pH and oxidation/reduction potential (ORP) measured in millivolts (mV) of coal bed natural gas (CBNG) produced waters in Cheyenne (CHR), Belle Fourche (BFR), Little Powder (LPR), Powder (PR), and Tongue River (TR) watersheds. Error bars denote one standard error of the mean.

before and after the acid treatment. The geochemical model suggests that when sulfuric acid treated produced water enters disposal ponds, $AlSO_4^+$ is the dominant Al species. As the disposal ponds equilibrate, $Al(OH)_4^-$ becomes the dominant ionic species.

Copper. Mean copper concentrations are given in Figure 3. The results indicate a significant increase from outfalls to disposal ponds across all watersheds except in TR watershed (*t* test *p*-value 0.08). Outfall concentrations across all watersheds ranged from 0.11 to 0.17 μM/L, and the disposal ponds ranged between 0.18 and 0.31 μM/L. Overall copper concentrations in disposal ponds tended to decrease between 2003 and 2005 in all watersheds. For instance, in CHR, Cu concentrations slightly increased from 2003 to 2004 from 0.39 to 0.43 μM/L, and then decreased to 0.11 μM/L in 2005.

MINTEQA2 predicted $CuCO_3^0$ as the dominant Cu species in CBNG outfalls (Table 2). The geochemical prediction for the dominant Cu species in CBNG disposal ponds varied between $Cu(CO_3)_2^{-2}$ and $CuCO_3^0$ equally. Based on a thermodynamic approach, Strumm and Morgan also predicted $CuCO_3^0$ and $Cu(CO_3)_2^{-2}$ as a predominant dissolved Cu species in natural waters with a near neutral to alkaline pH (*9*).

MINTEQA2 analyses further suggested that dissolved Cu concentrations across all watershed outfalls were close to the solubility of chalcocite (Cu_2O) and cuprite (Cu_2S), while dissolved Cu concentrations in disposal ponds were close to the solubility of tenorite (CuO). This finding is expected due to the highly reduced environment of the CBNG outfalls (ORP of most outfalls is between −240 and −4 mV) and the somewhat oxidized environment of the ponds (ORP of most ponds is between 6 and 158 mV).

Barium. Unlike the previous elements, Ba concentrations significantly decreased from outfall to disposal pond across all watersheds (*t* test *p*-values: CHR 0.03, BFR 0.02, LPR <0.01, PR <0.01, and TR <0.01) (Figure 3). McBeth et al. (*3*) reported similar results in CBNG produced waters in CHR, BFR, and LPR watersheds. Mean discharge well concentrations ranged from 1.97 to 4.47 μM/L, and disposal ponds ranged from 0.95 to 2.43 μM/L. In disposal ponds, Ba concentrations tend to increase in BFR, LPR, PR, and TR between years; however, Ba decreased in CHR disposal ponds. MINTEQA2 results suggested that the dominant Ba dissolved species in outfalls and disposal ponds was Ba^{+2} (Table 2 and 3), and dissolved Ba concentrations were near the solubility of Barite ($BaSO_4$). Increased pH in disposal ponds (8.1−9.4) may result in Barite mineral precipitation and an overall decrease in Ba concentrations within disposal ponds (*3*).

Arsenic. Mean As concentrations in water samples from outfalls and from disposal ponds across watersheds are presented in Figure 4. Results suggest that As concentration increases from the outfalls to the disposal ponds. Arsenic was statistically higher in samples from the disposal ponds in all watersheds (*t* test *p*-values: CHR 0.01, LPR >0.01, PR 0.01, and TR 0.04) except BFR (*t* test *p*-value 0.07). Outfall sample concentrations ranged from 0.01 to 0.02 μM/L, whereas disposal pond sample concentrations ranged from 0.02 to 0.13 μM/L.

Recently, As has been identified as a major contaminant of groundwater resources and a public health concern. Further investigation of As concentrations in water samples from disposal ponds revealed an incremental increase from year to year across all watersheds. For example, As increased in CHR disposal ponds from 2003 to 2005 from 0.03 to 0.12 uM/L. Many studies have identified that As solubility is directly related to adsorption and desorption processes of metal oxides and hydroxides (*9*, *16*). In semi-arid alkaline environments, mineral oxides and hydroxides tend to have a negative surface charge. In nature, As is an anion, thus it is expected to be soluble and mobile in these watersheds and increase in concentration over time in disposal ponds.

Molybdenum. Mean Mo concentrations are presented in Figure 4. Though all concentrations were low, across all watersheds, Mo increased from outfalls to disposal ponds. Outfall sample concentrations were ≤0.01 μM/L and disposal pond sample concentrations ranged from 0.02 to 0.03 μM/L. Statistically, only water samples from BFR and TR outfalls and disposal ponds were significantly different (*t* test *p*-values 0.04), while there was little difference in Mo concentrations between years. Like As, Mo solubility is directly related to adsorption and desorption processes of metal oxides and hydroxides and its concentration increases in disposal ponds (*9*). There is a positive correlation between CBNG discharge pond concentrations of Mo and Fe. Reddy et al., (*17*) found similar correlations between dissolved Mo and Fe in soil solutions.

Boron. Outfall and disposal pond sample B concentrations are presented in Figure 4. Boron concentrations increase in samples from outfalls to ponds across all watersheds, but were only statically significant in TR (*t* test *p*-value 0.04). Outfall sample concentrations ranged from 5.89 to 13.08 μM/L, and disposal pond sample concentrations ranged from 7.72 to 15.20 μM/L. Boron concentrations in disposal ponds increased overall between years across all watersheds. For example, disposal pond B concentrations in CHR increased from 6.03 to 10.68 μM/L from 2003 to 2004, then slightly

TABLE 1. Mean Element Concentrations (μM/L) with One Standard Error of the Mean for Coal Bed Natural Gas (CBNG)-Produced Waters in Cheyenne (CHR), Belle Fourche (BFR), Little Powder (LPR), Powder (PR), and Tongue River (TR) Watersheds

	CHR		BFR		LPR		PR		TR	
	outfalls	disposal ponds	outfalls	disposal ponds	outfalls	disposal Ponds	outfalls	disposal ponds	outfalls	disposal ponds
iron (Fe)	2.05± 0.23	5.88 ± 2.09	2.04 ± 0.46	8.27 ± 2.66	2.22 ± 0.20	3.88 ± 1.91	1.45 ± 0.24	3.64 ± 1.61	1.28 ± 0.61	2.60 ± 0.83
aluminum (Al)	8.07 ± 6.09	19.84 ± 8.99	18.83 ± 13.39	10.72 ± 5.13	11.27 ± 4.89	21.24 ± 9.87	6.71 ± 2.99	9.29 ± 3.52	67.35 ± 43.52	13.37 ± 6.01
chromium (Cr)	0.10 ± 0.03	0.13 ± 0.03	0.09 ± 0.01	0.10 ± 0.02	0.17 ± 0.02	0.17 ± 0.03	0.23 ± 0.05	0.22 ± 0.03	0.16 ± 0.03	0.18 ± 0.03
manganese (Mn)	0.09 ± 0.03	0.19 ± 0.09	0.47 ± 0.32	1.19 ± 0.79	0.23 ± 0.07	0.21 ± 0.15	0.15 ± 0.04	0.06 ± 0.02	0.14 ± 0.05	0.13 ± 0.04
lead (Pb)	<0.01 ± 0.01	<0.01 ± 0.01	<0.01 ± 0.01	<0.01 ± 0.01	<0.01 ± 0.01	<0.01 ± 0.01	<0.01 ± 0.01	<0.01 ± 0.01	<0.01 ± 0.01	<0.01 ± 0.01
copper (Cu)	0.11 ± 0.03	0.31 ± 0.06	0.12 ± 0.03	0.18 ± 0.05	0.17 ± 0.02	0.30 ± 0.07	0.12 ± 0.04	0.31 ± 0.03	0.17 ± 0.03	0.27 ± 0.03
zinc (Zn)	0.13 ± 0.05	0.17 ± 0.05	0.16 ± 0.05	0.13 ± 0.04	0.12 ± 0.03	0.14 ± 0.03	0.11 ± 0.03	0.16 ± 0.05	0.16 ± 0.06	0.28 ± 0.08
arsenic (As)	0.02 ± 0.01	0.07 ± 0.02	0.01 ± 0.01	0.05 ± 0.02	0.01 ± 0.01	0.13 ± 0.09	0.01 ± 0.01	0.05 ± 0.01	0.01 ± 0.01	0.02 ± 0.01
selenium (Se)	0.01 ± 0.01	0.01 ± 0.01	0.01 ± 0.01	0.01 ± 0.01	0.02 ± 0.01	0.02 ± 0.01	0.02 ± 0.01	0.03 ± 0.01	0.01 ± 0.01	0.01 ± 0.01
molybdenum (Mo)	<0.01 ± 0.01	0.02 ± 0.01	0.01 ± 0.01	0.02 ± 0.01	<0.01 ± 0.01	0.03 ± 0.02	0.01 ± 0.003	0.02 ± 0.01	<0.01 ± 0.01	0.02 ± 0.01
cadmium (Cd)	<0.01 ± 0.01	<0.01 ± 0.01	<0.01 ± 0.01	<0.01 ± 0.01	<0.01 ± 0.01	<0.01 ± 0.01	<0.01 ± 0.01	<0.01 ± 0.01	<0.01 ± 0.01	<0.01 ± 0.01
barium (Ba)	2.46 ± 0.16	1.23 ± 0.25	2.55 ± 0.17	1.71 ± 0.31	4.47 ± 0.36	2.43 ± 0.26	3.74 ± 0.72	2.07 ± 0.45	1.97 ± 0.19	0.95 ± 0.17
boron (B)	5.89 ± 0.27	8.36 ± 0.83	6.45 ± 0.42	7.72 ± 0.63	9.19 ± 0.44	11.66 ± 1.78	13.08 ± 1.99	15.20 ± 1.14	10.08 ± 0.63	11.44 ± 0.62

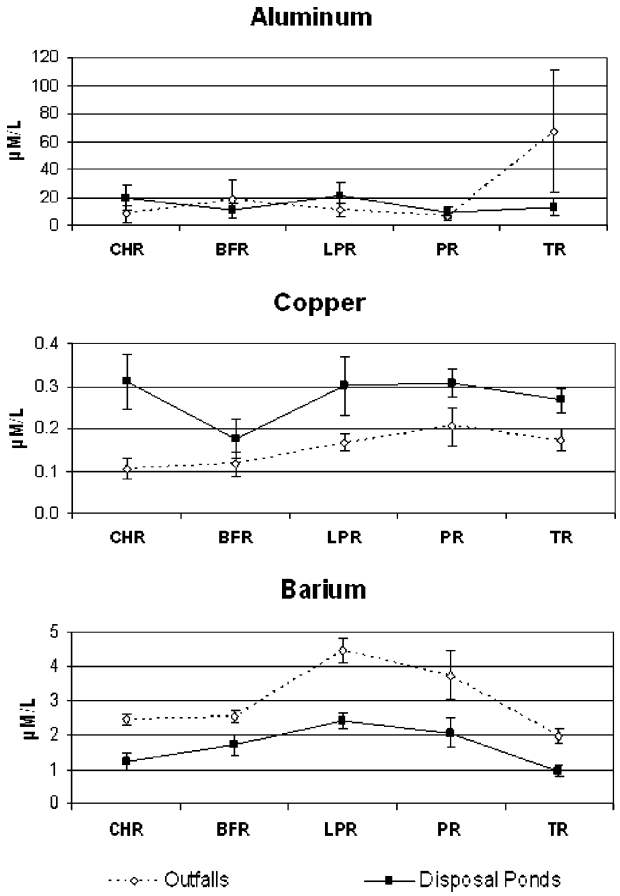

FIGURE 3. Mean aluminum, copper, and barium concentrations in coal bed natural gas (CBNG) produced waters in Cheyenne (CHR), Belle Fourche (BFR), Little Powder (LPR), Powder (PR), Tongue River (TR) watersheds. Error bars denote one standard error of the mean.

TABLE 2. Average Aluminum, Copper, Barium, and Iron Ion Percentages for Samples Collected between 2003 and 2005 in Coal Bed Natural Gas (CBNG) Outfalls Across Cheyenne (CHR), Belle Fourche (BFR), Little Powder (LPR), Powder (PR), and Tongue River (TR) Watersheds[a]

	CHR	BFR	LPR	PR	TR
	% dissolved aluminum				
$Al(OH)_4^-$	74.3	72.8	85.7	91.9	88.0
$Al_2(OH)_2CO_3^{+2}$	11.9	11.8	3.9	0.3	NA
$Al(OH)_3^0$	8.6	8.2	7.7	6.5	1.8
$AlSO_4^+$	NA	NA	NA	NA	7.5
	% dissolved copper				
$CuCO_3^0$	85.9	85.9	90.1	87.6	74.5
Cu^{+2}	8.5	8.6	3.2	1.5	6.5
$CuHCO_3^+$	2.0	2.6	1.6	1.4	1.6
$Cu(CO3)_2^{-2}$	1.9	1.5	4.3	8.2	13.8
	% dissolved barium				
Ba^{+2}	96.5	95.8	93.0	88.4	89.6
$BaHCO_3^+$	3.3	3.6	6.6	10.8	5.3
	% of dissolved iron				
$Fe(OH)_2^+$	97.6	99.2	99.0	97.8	85.5
$Fe(OH)_3^0$	1.7	0.6	0.7	1.3	2.3
$Fe(OH)_4^-$	1.2	0.1	0.2	0.9	2.6

[a] NA identifies no appreciable percentage of that species.

decreased in 2005 to 8.39 μM/L. Solubility of B is related to sorption and desorption processes (*18*). Like As and Mo, B is an anionic species and, in semiarid alkaline environments, mineral oxides and hydroxides tend to have a negative surface charge, causing B solubility and mobility to increase in these watersheds.

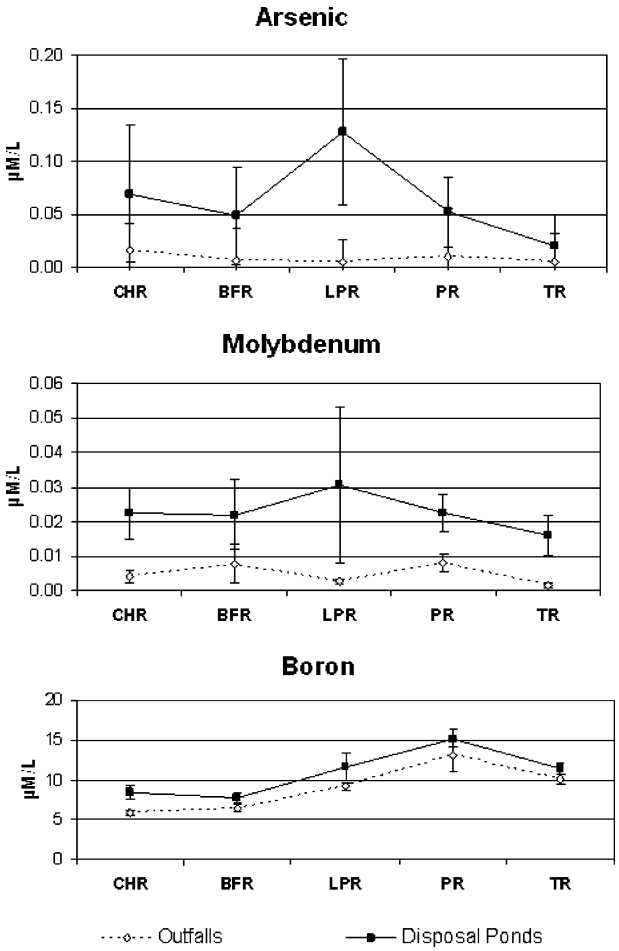

FIGURE 4. Mean arsenic, molybdenum, and boron concentrations in coal bed natural gas (CBNG) produced waters in Cheyenne (CHR), Belle Fourche (BFR), Little Powder (LPR), Powder (PR), Tongue River (TR) watersheds. Error bars denote one standard error of the mean.

TABLE 3. Average Aluminum, Copper, Barium, and Iron Ion Percentages for Samples Collected between 2003 and 2005 in Coal Bed Natural Gas (CBNG) Disposal Ponds Across Cheyenne (CHR), Belle Fourche (BFR), Little Powder (LPR), Powder (PR), and Tongue River (TR) Watersheds

	CHR	BFR	LPR	PR	TR
% dissolved aluminum					
$Al(OH)_4^-$	99.7	97.3	99.4	97.4	99.3
% dissolved copper					
$Cu(CO_3)_2^{-2}$	47.9	18.8	52.3	51.1	58.0
$CuCO_3^0$	43.4	76.4	46.5	2.2	40.6
$Cu(OH)_2^0$	5.7	0.7	0.4	45.5	0.4
% dissolved barium					
Ba^{+2}	88.5	90.7	84.8	80.0	80.4
$BaCO_3^0$	8.6	2.3	8.9	10.4	9.8
$BaHCO_3^+$	2.7	3.7	6.1	8.8	5.7
% dissolved iron					
$Fe(OH)_4^-$	82.1	24.5	55.1	46.1	63.1
$Fe(OH)_2^+$	15.3	71.3	39.9	50.8	31.8

Water Quality Standards. Existing uses for water from CBNG disposal ponds include irrigation and drinking water for livestock, wildlife, and aquatic life. Table 1 identifies trace metal concentrations in CBNG-produced waters by watershed. Table S2 identifies water quality standards for human consumption, agricultural, livestock and wildlife drinking water, and aquatic life chronic values. Comparisons with these standards suggest that many of the CBNG produced water samples contain low concentrations of trace elements. The most restrictive use, based solely on trace metal concentrations, is aquatic life. Most CBNG produced water samples exceeded the aquatic life criteria for Al and Cu. Based on secondary water quality standards, many CBNG outfall water samples are not suitable for human drinking water due to high Fe and Al concentrations. These results suggest that many of the CBNG produced waters across the PRB can be used for agriculture and livestock/wildlife drinking water.

Our studies suggest that, though trace metal concentrations were low in both CBNG outfalls and disposal ponds, a statistically significant increasing trend was observed for most trace elements between the outfalls and disposal ponds. Reactions governing the trace metal changes are precipitation/dissolution of geologic material for Al, Cu, and Ba and adsorption/desorption for As, Mo, and B. Mean concentrations of Al and Cu decreased over time in disposal ponds, whereas Ba, As, and B concentrations increased over time. Molybdenum concentrations remained the same in most watersheds. Most CBNG-produced waters examined were unsuitable for human drinking water and aquatic life, but were suitable for agricultural uses and livestock and wildlife drinking water. If the trace elements continue to increase and accumulate in CBNG disposal ponds, there may be a point in time when the concentrations of these trace elements could exceed standards for agricultural uses and livestock and wildlife drinking water. Overall, this study's results will be useful for water quality managers, industry, and landowners in properly managing and developing best uses for produced water in the PRB, Wyoming.

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Supporting Information Available

Table S1 contains yearly element concentration means for coal bed natural gas (CBNG) disposal pond waters in Cheyenne, Belle Fourche, Little Powder, Powder, and Tongue River watersheds. Maximum trace metal concentrations in water for human consumption, agricultural use, livestock and wildlife, and aquatic life values from various published water standards are presented in Table S2. Cation (Na, Ca, Mg, K) and anion (alkalinity, SO_4^{2-}, Cl^-, NO_3^-) concentrations from CBNG outfall and disposal pond waters are presented in Table S3. This material is available free of charge via the Internet at http://pubs.acs.org.

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Trace Element Chemistry of Coal Bed Natural Gas Produced Water in the Powder River Basin, Wyoming.

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Supporting information includes three tables. The first table displays yearly element concentration means for coal bed natural gas produced waters in the Powder River basin. The second table has maximum trace metal concentrations in water for human consumption, agricultural use, livestock and wildlife, and aquatic life values from various published water standards. The third and final table contains major cation and anion concentration means for coal bed natural gas produced waters in the Powder River basin. (4 Pages, 3 Tables).

Location	Year	Aluminum	Copper	Barium	Arsenic	Molybdenum	Boron
CHR	2003	10.53	0.39	1.20	0.03	0.01	6.03
	2004	13.91	0.43	1.52	0.06	0.03	10.68
	2005	35.08	0.11	0.96	0.12	0.03	8.39
BFR	2003	19.57	0.18	1.45	0.04	0.01	7.38
	2004	0.64	0.27	1.89	0.02	0.02	7.01
	2005	11.94	0.08	1.80	0.09	0.04	8.76
LPR	2003	49.16	0.38	2.33	0.03	0.01	8.66
	2004	10.71	0.39	2.43	0.31	0.07	15.32
	2005	0.97	0.11	2.53	0.04	0.01	10.91
PR	2003	20.57	0.35	1.39	0.04	0.02	12.06
	2004	5.16	0.38	1.93	0.06	0.03	16.54
	2005	2.14	0.20	2.88	0.06	0.02	17.00
TR	2003	25.72	0.21	0.75	<0.01	<0.01	8.72
	2004	5.14	0.36	1.15	0.03	0.01	13.48
	2005	9.27	0.22	0.94	0.03	0.03	12.12

Table S1. Yearly mean element concentrations (µM/L) for coalbed natural gas (CBNG) disposal pond waters in Cheyenne (CHR), Belle Fourche (BFR), Little Powder (LPR), Powder (PR), and Tongue River (TR) watersheds.

Parameter	Human Drinking Water[a]	Agriculture[b]	Livestock & Wildlife[b]	Aquatic Life[c]
pH	6.5-8.5[d]	4.5-9.0	6.5-8.5	6.5-9.5
Iron	5.37[d]	89.53	NA	17.91
Aluminum	1.85-7.41[d]	185.32	185.32	3.22
Manganese	0.91[d]	3.64	NA	26.61
Lead	0.07	24.13	0.48	12.07
Copper	20.46	3.15	7.87	0.14[e]
Zinc	76.46	30.59	382.32	1.80
Arsenic	0.13	1.33	2.67	2.00
Boron	NA	69.38	462.53	NA
Selenium	0.63	0.25	0.63	0.06
Cadmium	0.04	0.09	0.44	0.02
Barium	14.57	NA	NA	36.42

Table S2. Maximum trace metal concentrations in water for human consumption, agricultural use, livestock and wildlife, and aquatic life values from various published water standards. All concentrations have been transformed into micromoles per liter (µM/L) for comparison purposes.

[a] EPA (*9*)
[b] WYDEQ ground water standards (*8*)
[c] WYDEQ surface water standards (*8*)
[d] Secondary drinking water standards (*9*)
[e] Chronic value based on water hardness (*8*)
Note: NA identifies non-existing numerical standard for that element

	CHR		BFR		LPR		PR		TR	
	Outfalls	Disposal Ponds	Outfalls	Disposal Ponds	Outfalls	Disposal Ponds	Outfalls	Disposal Ponds	Outfalls	Disposal Ponds
Sodium (Na)	2.92 ±0.14	3.39 ±0.19	3.30 ±0.26	4.03 ±0.47	6.60 ±0.32	7.93 ±0.80	11.10 ±1.57	13.88 ±1.08	9.18 ±0.45	10.30 ±0.44
Calcium (Ca)	0.70 ±0.05	0.43 ±0.06	0.83 ±0.09	0.96 ±0.18	1.09 ±0.10	0.54 ±0.06	0.60 ±0.12	0.42 ±0.05	0.21 ±0.02	0.32 ±0.06
Magnesium (Mg)	0.20 ±0.02	0.16 ±0.01	0.22 ±0.03	0.42 ±0.12	0.44 ±0.04	0.42 ±0.04	0.27 ±0.06	0.32 ±0.05	0.05 ±0.01	0.12 ±0.02
Potassium (K)	0.22 ±0.02	0.25 ±0.03	0.28 ±0.01	0.40 ±0.06	0.38 ±0.02	0.44 ±0.04	0.64 ±0.16	0.66 ±0.10	0.16 ±0.01	0.19 ±0.02
Alkalinity ($CaCO_3$)	31.89 ±1.52	29.50 ±2.85	36.63 ±2.03	36.31 ±4.69	74.13 ±3.58	81.39 ±6.13	107.83 ±14.89	131.23 ±10.01	76.10 ±6.48	79.93 ±5.99
Sulfate (SO_4^{2-})	0.02 ±0.01	0.20 ±0.08	1.18 ±1.16	8.10 ±4.55	0.33 ±0.20	0.71 ±0.34	0.85 ±0.42	1.26 ±0.81	8.97 ±6.90	13.41 ±5.94
Chloride (Cl^-)	0.55 ±0.12	0.42 ±0.05	0.57 ±0.12	0.63 ±0.10	0.42 ±0.07	0.46 ±0.06	1.33 ±0.43	0.71 ±0.15	1.09 ±0.19	1.08 ±0.16
Nitrate (NO_3^-)	<0.01 ±0.01	<0.01 ±0.01	<0.01 ±0.01	0.01 ±0.01	0.01 ±0.01	0.02 ±0.01	0.02 ±0.01	0.05 ±0.02	<0.01 ±0.01	0.05 ±0.02

Table S3. Mean element concentrations (µM/L) with one standard error of the mean for coal bed natural gas (CBNG) produced waters in Cheyenne (CHR), Belle Fourche (BFR), Little Powder (LPR), Powder (PR), and Tongue River (TR) watersheds (*6*). Fluoride and phosphate concentrations in produced waters were <0.01 µM/L for CHR, BFR, LPR, PR, and TR watersheds.