MONITORING OF GROUNDWATER CONTAMINATION BY TRACE ELEMENTS FROM CBNG DISPOSAL PONDS ACROSS THE POWDER RIVER BASIN, WYOMING[1]

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Abstract. The demand for natural gas is increasing due to the global energy crisis. Due to the demand for natural gas there have been major explorations in the Rocky Mountain States. One of the largest areas for natural gas extraction is the Powder River Basin, Wyoming. The process of extracting natural gas involves pumping water from coal seam aquifers that is mixed with the natural gas. Once the water and gas reach the surface they are separated and product water is disposed into a nearby disposal pond. The objectives of this study were to monitor water quality components, model the components in a water quality model, and monitor trace metals in the sediments of the disposal ponds. Samples were collected and analyzed for major cations, anions, and trace metals. Results from one year of sampling suggest wide ranges in pH, oxidation reduction potential, electrical conductivity, temperature, and dissolved oxygen. Concentrations for sodium were high when compared with the concentrations of the other major cations. Practical sodium adsorption ratios calculated from the concentrations of sodium, magnesium, and calcium ranged from 6.3 to 51.86. True sodium adsorption ration calculated from the activities of sodium, magnesium and calcium ranged from 7.07 to 88.05. The highest concentration of trace metals in both wells and disposal ponds were barium and boron. Sediment samples were also collected and a Toxic Characteristic Leaching Procedure was preformed to determine leachability and toxicity of trace metals. The two trace metals detected in sediment leachates were barium and manganese. When compared to groundwater drinking water standards both barium and boron concentrations in sediment leachates were above the limits.

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Introduction

The demand for natural gas (methane) in the United States has been increasing at an exponential rate due to the economical incentives for gas companies and its appealing properties (Bank & Kuuskraa 2006). With this high demand for natural gas, exploration is at an all time high in the western states of Wyoming, Colorado, Utah, Montana, and New Mexico. One specific example of coalbed natural gas (CBNG) exploration is in the Powder River Basin (PRB) of Wyoming where as of 2004, 18,400 CBNG wells have been drilled (Bank & Kuuskraa 2006). The estimated total number of wells in the PRB peaks at 139,000 in 30 years (U.S. BLM 2003).

The increasing CBNG production in the state of Wyoming has raised concerns about the amount of water being produced and quality of the water. These concerns have lead to a series of studies on the produced water in the PRB. These studies have shown that the CBNG produced water quality is different for each watershed in the PRB depending on the depth of the coal seam. They have also shown that salt concentrations as well as trace metal concentrations increase from discharge well to disposal pond and are able to infiltrate into shallow aquifers. Trace metals in CBNG disposal ponds could become bioavailable to the organisms in and around the ponds. Some disposal ponds are created on channel and CBNG produced water can move into the stream channels (Frost and Brink 2005, McBeth et al. 2003ab, Patz et al 2003, Jackson and Reddy 2006a).

Recent studies by Jackson and Reddy (2006b) shows that trace metal concentrations in CBNG produced water disposal ponds increase as a function of time and watershed characteristics in the PRB. For example arsenic has been shown to steadily increase year to year. Overall, arsenic (As) has increased from 0.75-1.50 µg/L in discharge well and 1.50-9.74 µg/L in disposal ponds. Therefore, it is important to continue monitoring the quality of CBNG produced water to determine the fate of trace metals in the disposal ponds. In addition, none of the previous CBNG studies examined the trace metal toxicity in the sediments in the disposal ponds. Such information is vital in reclamation of CBNG ponds after CBNG production has ceased. Since water quality of CBNG produced water in disposal ponds changes as a function of time, it is important to continue to monitor disposal ponds to determine if the designated uses for these water bodies could change. Thus, objectives of this two year study were to monitor water quality components including pH, dissolved oxygen (DO), oxidation reduction potential (ORP), electrical conductivity (EC), total dissolved solids (TDS), temperature (ºC), Na adsorption ratio (SAR), alkalinity, cations (Ca, Mg, Na, K, Fe, Al, Mn, Pb, Cu, Zn, Cd, and Ba), anions (Cr, As, Se, Mo, B, Cl, NO_3, PO_4, SO_4), and dissolved organic carbon of CBNG produced water from well head to disposal pond in the PRB. The sampling sites in the PRB consists of Tongue River Basin (TRB), Powder River Basin (PRB), Little Powder River Basin (LPR), Belle Fourche River Basin (BFR), and Cheyenne River Basin (CRB), which make up the Powder River Basin. Other objectives were to model water chemistry using MINTEQA2 to determine geochemical processes, monitor trace metal (As, Ba, Cr, Se, Cu, Mo, B, and Mn) concentrations in sediments of disposal ponds, and analyze and determine if there were any significant differences between CBNG well head and disposal pond, between watersheds, and years for water samples. We also determined the toxicity of sediment samples using the Toxicity Characteristic Leaching Procedure (TCLP). However, in this report we discuss results from one year of sampling.

Materials and Methods

Water and sediment samples were collected during the month of July of 2006. Before collecting water samples, field measurements of pH, DO, ORP, EC, and temperature were taken at discharge well and in discharge pond using the Thermo Five-Star Field Probe. Water samples were taken using QA/QC protocols (WYDEQ 2001) and transported to the University of Wyoming Water Quality Laboratory in a cooler. Samples were then filtered using a 0.45µm filter and subdivided. Half of the sample was acidified to pH of 2 with HNO_3. The other half remained unacidified. Unacidified samples were analyzed for total alkalinity by acid titration method and also analyzed by Ion Chromatography (IC) for SO_4, Cl, F, NO_3, and PO_4 . Acidified samples were then 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).

Once water analysis data was received, it was put into MINTEQA2 to determine charge balance, ionic strength, and activities of ions. From Ca, Mg, and Na measurements, practical sodium adsorption ratio (SARp) based on concentrations was calculated. SARt is the Na adsorption ratio calculated based on the activities that were calculated in MINTEQA2.

Sediment samples were collected according to the procedures of the TCLP as described in the SW-846 manual (U.S. E.P.A 2005). The sediment samples were also brought back to University of Wyoming Water Quality Lab in a cooler. The sediment samples were then taken to Paragon Analytics in Ft. Collins, CO where the TCLP test was conducted on the samples. In this procedure 8 trace metals including As, Ba, Cr, Se, Cu, Mo, B, and Mn were analyzed.

Results and Discussion

The pH, DO, temperature, alkalinity, ORP, and EC are shown in Table 1. The pH of wells and ponds ranged from 7.14 to 10.06. This is expected since the PRB is an alkaline system that leads to basic pH. The consistently higher pH measurements tended to be in TRB and PR, except for one of the disposal ponds in CHR. Temperature ranged from 18.1 to 31.7ºC. There was no clear pattern of temperatures changes across the PRB. The DO ranged from 0.05 to 15.19 mg/L. The observed large range suggests that each pond is influenced by the environmental factors. This can also be an indicator of how much submerged aquatic vegetation (SAV) is present in the ponds. Higher DO concentrations suggest a greater probability of having more pond SAV, which can be used as a health indicator. ORP ranged from -220 to 151.1 mV. The distinct patterns in the ORP measurements are that the highly reduced measurements are coming from the well water. This is expected since the water that is coming out of the wells is from deep aquifers. The disposal ponds had the measurements that were positive ORP indicating that the water in the disposal ponds is oxidized. This is important to help determine the species of the elements present in both the wells and ponds. Alkalinity ranged from 306 to 2358 mg/L CaCO3. The highest alkalinities were observed in the PR and TR when compared with CHR, BFR, and LPR.

The major elements of calcium, magnesium, sodium, and potassium, as well as SARp and SARt are shown in Table 2. Sodium ranged from 120.3 to 1123.5 mg/L. The lowest concentration was found in BFR well 174. The highest concentration was found in PR pond 179. Magnesium concentrations ranged from 1.4 to 22.6 mg/L. The lowest concentration was found in PR 182 well. The highest concentration was found in LPR 165 well. Potassium concentrations ranged from 2.1 to 35.3 mg/L. The lowest and highest concentrations were found both in the PR. The SARp ranged from 6.3 to 51.86. The SARp is an important component to determine if water can be used for irrigation. However, high amounts of Na in irrigation water can cause soil structure break down. The SARt ranged from 7.07 to 88.05. These results suggest that when concentrations are low the SARp and SARt are similar. However, when concentrations are high, for example PR 179 pond, the SARp is much lower than SARt. This is due to ionic interactions and ionic complexation at high concentrations.

It is important to understand changes in trace metal concentrations from wells to disposal ponds. Often, studies have shown that trace metals bioaccumulate in aquatic systems and cause severe health issues. However, the range between essential and toxic trace metal concentrations is very small. The trace metals examined in this study are listed in Table 3. Barium had the highest concentration (718.4 µg/L) when compared to other trace metals. Boron had the next highest concentrations (309.5 µg/L). Chromium, Mn, Cu, As, Se, Mo, and Zn were all at lower concentrations when compared to Ba and B. However, Cd and Pb were detected in only a few samples.

Table 1. Field Measurements of CBNG wells and disposal ponds for sampling year one.

Site	Location	Type	Temp	pH	DO	ORP	EC	Alkalinity
CHR	171	Well	20.4	7.16	4.01	-84	650	332
CHR	171	Pond	24.3	10.06	9.79	55.9	877	423
CHR	170	Well	19.1	7.26	0.28	-101.6	612	316
CHR	170	Pond	24.5	8.8	0.09	83	1626	843
BFR	174	Well	15.5	7.41	0.34	-35.2	614	306
BFR	174	Pond	31.7	9.16	12.36	66.6	744	345
BFR	173	Well	19.4	7.34	0.23	-2.1	650	321
BFR	173	Pond	25.1	9.61	15.19	56	782	348
LPR	162	Pond	19.2	9.46	5.79	74.7	1983	1273
LPR	163	Well	18.1	7.46	0.13	-143.1	1432	748
LPR	163	Pond	18.2	8.49	3.9	42.5	1439	742
LPR	164	Well	20.9	7.26	1.98	-63.4	1573	838
LPR	164	Pond	22.3	9.19	5.06	110.8	1578	909
LPR	165	Well	20.3	7.14	0.93	-62.5	1613	839
LPR	165	Pond	20.8	7.33	1.45	-29.1	1628	863
LPR	167	Well	25	7.31	0.04	-210.7	1046	542
LPR	167	Pond	26	7.49	0.67	37.1	1106	539
PR	180	Well	19.8	8.81	9.42	62.6	1158	615
PR	182	Well	15.2	8.46	0.66	-220	997	507
PR	182	Pond	28.6	9.14	5.15	74.7	3350	1929
PR	183	Pond	27.2	9.23	7.36	132.4	2661	1544
PR	181	Pond	25.4	9.45	0.09	108	3700	2358
PR	179	Pond	25.7	9.29	0.06	104.7	3800	2297
TR	184	Pond	23.7	9.41	5.62	151.1	1731	1020
TR	186	Well	18.6	8.1	0.68	-161	1764	893
TR	186	Pond	22.6	8.15	0.05	56.7	1769	1068
TR	185	Pond	21.7	8.59	7.12	24.2	1611	1085
TR	187	Pond	21.4	8.86	7.23	62.4	2661	1297

Table 2. Major Cations, SARp, and SARt. All major cations are in mg/L.

Site	Location	Type	Na	Mg	K	Ca	SARp	SARt
BFR	173	Pond	171.4	5.5	6.5	6.9	11.80	16.30
BFR	173	Well	133.4	6.0	6.2	17.3	7.05	7.90
BFR	174	Pond	166.7	6.3	8.7	12.2	9.66	12.67
BFR	174	Well	120.3	5.9	6.1	16.5	6.47	7.22
CHR	170	Pond	420.8	10.7	15.5	20.7	18.71	24.85
CHR	170	Well	137.5	4.0	4.2	11.7	8.87	9.90
CHR	171	Pond	216.2	5.7	6.1	5.6	15.33	23.78
CHR	171	Well	128.1	8.6	5.3	17.2	6.30	7.07
LPR	162	Pond	535.2	17.3	16.0	10.5	23.62	36.63
LPR	163	Pond	315.5	14.8	9.7	22.6	12.67	13.70
LPR	163	Well	316.7	15.2	9.7	33.7	11.37	13.52
LPR	164	Pond	383.6	20.2	12.5	6.7	16.69	23.17
LPR	164	Well	325.6	19.9	11.0	42.7	10.31	12.38
LPR	165	Pond	353.2	22.3	10.4	40.7	11.05	13.31
LPR	165	Well	326.1	22.6	9.9	47.2	9.78	11.72
LPR	167	Pond	212.6	9.4	6.1	10.7	11.45	13.39
LPR	167	Well	233.6	10.2	6.0	23.2	10.16	11.90
PR	179	Pond	1123.5	18.2	35.3	5.5	51.86	87.68
PR	180	Well	290.6	1.7	2.3	6.4	26.38	33.35
PR	181	Pond	1051.2	16.6	14.3	7.5	49.06	88.05
PR	182	Pond	924.3	13.8	15.8	9.4	44.86	73.70
PR	182	Well	256.9	1.4	2.1	5.4	25.47	30.27
PR	183	Pond	778.8	12.3	11.4	7.7	40.60	64.75
TR	184	Pond	575.4	4.7	5.2	5.5	43.40	68.25
TR	185	Pond	557.1	6.1	4.8	6.7	37.45	49.27
TR	186	Pond	558.4	3.9	4.7	6.5	42.73	54.36
TR	186	Well	467.2	2.0	3.9	4.9	44.97	55.60
TR	187	Pond	774.7	5.7	5.8	8.1	51.13	72.19

Table 3. Trace metals in CBNG product water (μg/L).

Site	Location	Type	B	Cr	Mn	Cu	As	Se	Mo	Ba	Zn	Cd	Pb
CHR	171	Well	50.9	0.8	7.4	11.3	2.1	0.6	0.0	282.5	5.6	U	U
CHR	171	Pond	118.4	2.8	11.7	15.8	7.5	0.8	2.9	108.4	7.2	U	1.1
CHR	170	Well	39.5	1.3	6.7	4.7	0.9	0.4	0.1	161.6	3.9	U	U
CHR	170	Pond	205.4	2.7	3.2	41.0	10.8	1.5	12.5	219.7	20.1	0.1	0.4
BFR	174	Well	51.2	0.7	4.7	4.3	0.4	0.6	U	306.4	4.6	U	U
BFR	174	Pond	143.2	1.7	2.0	19.5	4.6	0.5	5.1	82.2	3.6	U	0.4
BFR	173	Well	52.1	1.2	4.9	6.3	0.6	0.2	U	285.9	3.5	U	U
BFR	173	Pond	85.2	2.3	5.7	11.0	2.3	0.4	0.9	71.0	4.6	U	0.6
LPR	162	Pond	245.0	3.4	2.3	20.6	7.8	1.0	4.0	113.2	3.1	U	0.6
LPR	163	Well	88.6	4.9	6.5	5.2	0.1	0.1	0.1	505.4	3.4	U	U
LPR	163	Pond	98.0	2.9	0.2	6.3	0.5	0.2	0.1	379.7	1.4	U	U
LPR	164	Well	88.5	5.0	8.8	3.8	0.1	U	U	703.8	2.2	U	U
LPR	164	Pond	99.8	2.5	1.1	11.9	2.0	0.6	0.5	360.9	5.5	U	0.1
LPR	165	Well	72.8	3.6	22.1	6.9	0.4	1.3	U	718.4	2.9	U	U
LPR	165	Pond	99.1	3.7	0.3	6.3	0.1	0.3	U	630.3	1.6	U	0.1
LPR	167	Well	115.6	2.6	17.2	4.2	0.1	0.2	0.2	319.9	3.5	U	U
LPR	167	Pond	128.4	0.6	1.3	5.0	0.6	1.5	0.1	244.1	7.4	U	0.2
PR	180	Well	77.1	3.1	2.2	6.2	0.1	0.1	0.5	190.5	2.7	U	0.2
PR	182	Well	59.7	1.8	9.2	33.3	0.1	0.3	1.4	114.6	12.9	U	0.5
PR	182	Pond	172.0	26.8	1.6	12.7	8.1	1.0	4.9	122.9	1.6	U	0.2
PR	183	Pond	173.0	4.1	0.7	13.1	4.3	0.7	1.4	177.0	1.1	U	0.1
PR	181	Pond	195.3	29.1	1.6	25.4	8.8	1.3	7.9	105.5	1.2	U	0.1
PR	179	Pond	309.5	40.4	0.5	14.4	6.8	1.8	1.7	322.1	0.7	U	0.1
TR	184	Pond	134.6	2.8	1.7	10.8	1.5	0.8	1.1	93.0	2.4	U	0.2
TR	186	Well	106.7	3.1	2.7	6.7	0.1	0.3	0.1	222.8	1.7	U	U
TR	186	Pond	137.2	4.5	1.6	10.4	1.3	0.9	1.0	98.4	5.4	U	0.2
TR	185	Pond	136.2	3.6	0.7	11.3	0.6	0.8	0.5	127.2	1.7	U	0.2
TR	187	Pond	174.7	4.8	31.9	29.0	3.7	1.8	7.8	22.8	4.6	0.1	2.2

**U=Undetectable*

The sediment that is in the disposal ponds comes in to contact with the CBNG product water. Through geochemical processes the trace metals that are in the disposal pond water can interact with the sediments. Once they interact with the sediments the trace metals in the product water can leach out of the disposal ponds. Therefore, it is important to determine leachability of the trace metals from the disposal ponds and possibly into the groundwater. The TCLP test is intended to determine both leachability and toxicity of trace metals. This has implications on reclamation practices once the disposal ponds are no longer needed.

The sediment analysis showed that there were two main trace metals (Ba and Mn) detected in the sediments within the disposal ponds. These results are shown in Table 4. The highest concentration of Ba in any sediment leachate was 17 mg/L found in the Little Power River Basin. The highest concentration of Mn in any pond sediment leachate was 8.6 mg/L found in the Belle Fourche River Basin. These Ba and Mn concentrations exceed the groundwater drinking water standards of 1.0 mg/L and 0.05 mg/L, respectively (WYDEQ, 2001).

Conclusions

The first year of sampling results suggest a wide range of pH, temperature, ORP, EC, Alkalinity, and DO in wells and disposal ponds. The major cations were all low except for sodium which exceeded 1000 mg/L. This would lead to higher SAR values in both wells and disposal ponds. However, use of high SAR water for irrigation this could cause the physical breakdown of the soil structure. The two trace metals in the CBNG product water that had high concentrations were Ba and B. They were higher than all of the other trace metals examined in this study. Cadmium and lead were only detected in a few samples. Trace metals in the sediment leachate that were detected were Ba and Mn. Concentrations of Ba and Mn in sediments leachates exceeded the groundwater standards for domestic use.

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Table 4. Trace Metals in Disposal Pond Sediment Leachate (mg/L).

Location	Type	Year	As	Site	Ba	B	Cr	Cu	Mn	Mo	Se
162	Sediment	2006	U*	LPR	14	U	U	U	5.4	U	U
163	Sediment	2006	U	LPR	6.3	U	U	U	2.4	U	U
164	Sediment	2006	U	LPR	17	U	U	U	2.9	U	U
165	Sediment	2006	U	LPR	3.7	U	U	U	0.91	U	0.057
166	Sediment	2006	U	LPR	3.5	U	U	U	2.6	U	U
167	Sediment	2006	U	LPR	3	U	U	U	2.7	U	U
169	Sediment	2006	U	BFR	0	U	U	U	2.4	U	U
170	Sediment	2006	U	CHR	3	U	U	U	1.5	U	U
171	Sediment	2006	U	CHR	6	U	U	U	2.3	U	U
173	Sediment	2006	U	BFR	2.4	U	U	U	8.6	U	U
174	Sediment	2006	U	BFR	1.8	U	U	U	2.3	U	U
179	Sediment	2006	U	PR	6.5	U	U	U	4.3	U	U
180	Sediment	2006	U	PR	1.9	U	U	U	5.8	U	U
181	Sediment	2006	U	PR	2	U	U	U	6.5	U	U
182	Sediment	2006	U	PR	2.4	U	U	U	4.2	U	U
183	Sediment	2006	U	PR	6.4	U	U	U	4.2	U	U
184	Sediment	2006	U	TR	1.9	U	U	U	6.4	U	U
185	Sediment	2006	U	TR	2.6	U	U	U	4.8	U	U
186	Sediment	2006	U	TR	3	U	U	U	3.1	U	U
187	Sediment	2006	U	TR	2.4	U	U	U	12	U	U
188	Sediment	2006	U	TR	0	U	U	U	2.2	U	U

**U-Undetectable*

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