

# COALBED METHANE DISCHARGE WATER INTERACTION WITH STREAM CHANNEL SEDIMENT IN THE POWDER RIVER BASIN, WYOMING<sup>1</sup>

Marji Patz, Katta J. Reddy, and Quentin D. Skinner<sup>2</sup>

**Abstract.** Extraction of methane (natural gas) from coal deposits is facilitated by pumping of aquifer water. Coalbed methane (CBM) product water, produced from pumping groundwater, is discharged into associated unlined holding ponds or downstream channels. The objective of this study was to examine the chemistry of CBM discharge water reacting with an ephemeral stream channel sediment in the Powder River Basin, Wyoming. Water samples were collected bimonthly from three CBM discharge points and seven channel locations in Burger Draw and Sue draw, and Powder River, WY. Before sample collection, pH and electrical conductivity (EC) were measured in the field. Samples were transported to the laboratory and analyzed for alkalinity, major cations and anions, and trace elements. Results suggest that pH of CBM discharge water ranged between 7 and 7.1 and EC ranged between 4.25 and 4.35 dS/m. CBM discharge water within the Burger Draw watershed contains high sodium (Na) and alkalinity. The pH of CBM discharge water increased in downstream channels of Burger Draw and Sue Draw. However, pH of the channel sediment water interface (2cm) was decreased. In addition, dissolved calcium ( $\text{Ca}^{2+}$ ) concentrations of CBM discharge water decreased significantly in the downstream channel water, which increased sodium adsorption ratio (SAR). Dissolved iron (Fe) and manganese (Mn) concentrations decreased, while dissolved arsenic (As) and selenium (Se) concentrations increased in the downstream channel. The only significant difference in water chemistry above and below of the confluence of Burger Draw with the Powder River was pH, which increased from 8.36 to 8.52. Overall, the significant increase in SAR values of CBM discharge water in Burger Draw and Sue Draw tributaries suggest further monitoring is needed to evaluate the buffering capacity of receiving streams and rivers in the Powder River Basin of Wyoming.

Additional Keywords: water quality, water chemistry, salinity, sodicity, trace elements, ephemeral stream, semi-arid environment

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## **Introduction**

Although coalbed methane (CBM) has been developed and used elsewhere in the world, exploration and extraction of methane from coalbed deposits of Wyoming, Montana, Colorado, New Mexico, and to some extent Utah of the United States is rapidly occurring (Hill et al., 2000).

It is estimated that there are 31.7 trillion cubic feet of recoverable CBM in Wyoming with approximately 90% of this occurring in the The Powder River Basin of Wyoming. Coalbed methane, present in the lattice structure of coal, is held in place by water pressure within confined coalbed aquifers. To release and retrieve methane, aquifer pressure must be reduced by bringing water to the surface through individual extraction wells, which creates cones of depression within coalbed aquifers. CBM collects in these depression zones and is then retrieved through the water extraction wells (Reddy et al., 2001). The pumped aquifer water (CBM discharge water) must be either stored in reservoirs, released in stream channel systems, spread on surface landscapes, or re-injected as ground water storage.

It is estimated that a single CBM well in the Powder River Basin may discharge from 8 to 80 L of water per minute, but this amount varies with aquifer that is being pumped and the density of the wells (McBeth et al., 2003a). At present, more than 16,000 wells are under production in the Powder River Basin and this number is expected to increase to at least 30,000 (McBeth et al., 2003a). Based on information provided by the Wyoming Geological Survey, approximately 3 trillion L of groundwater will eventually be discharged from CBM extraction in Wyoming. (DeBruin et al., 2000).

Mullins and Hajek (1998) found that CBM discharge water produced in Alabama coalbed aquifers were saline and sodic, with minor occurrences of high concentrations of trace elements, similar to CBM discharge water found in the Powder River Basin (Rice et al., 2000). The variability of water chemistry produced by CBM wells in the Powder River Basin is not clearly understood. Recent studies by Rice et al., (2000) suggest that moving from north and west toward deeper coal seams within the Powder River Basin produces saline and alkaline water.

Very little information is available regarding the chemistry of CBM discharge water in the Powder River Basin, Wyoming. For example, McBeth et al., (2003 ab) reported CBM discharge water chemistry at wellhead and in pond storage as a function of watershed soils in the Cheyenne

River, Belle Fourche River, and Little Powder River Basins of Wyoming. In other study Hulin et al., (2002) reported laboratory data on CBM discharge water chemistry changes as influenced by the Dead Horse Creek channel sediment in the Powder River Basin. However, to our knowledge no information is available on the chemistry of CBM discharge water released to the upland channel systems that support ephemeral stream. Such information needed by local landowners, citizens, downstream water users, and state and federal water quality agencies to properly manage CBM discharge water in the Powder River Basin, Wyoming. The overall objective of this study was to examine CBM discharge water chemistry from wellhead to subsequent travel down gradient of uplands and within ephemeral stream channels.

### **Materials and Methods**

#### **Study Area**

This study was conducted within the Burger Draw watershed, Powder River Basin, WY. The Burger Draw supports an ephemeral stream channel and is located in the Powder River Basin west of Gillette, Wyoming. Burger Draw watershed contains Sue Draw tributary. The Sue Draw joins Burger Draw downstream before Burger Draw confluences with the Powder River (Fig. 1).

The average precipitation in the study area ranges from 254 to 356 mm, of which 10% falls as snow in winter and between 30% and 40% as rain from June to August (U.S. Department of Interior Bureau of Land Management, 1999). The Big George coal seam lies within the deep Paleocene Fort Union Formation and is covered by Eocene Wasatch Formation which contains several shallower coal seams (DeBruin et al., 2000). The mineralogy of study area consists of inter-bedded sandstones, silt stones, shales, clay stones, and coal within the Fort Union formation, and arkosic sandstones, silt stones, shales, and conglomerate lenses within the Wasatch Formation (U.S. Department of Interior Bureau of Land Management, 1999). The landscape comprises loams, silty clays, fine sandy loams, and sandy loam soils, with shale and sandstone outcrops. Soils in the study area are classified as moderate to well drained.

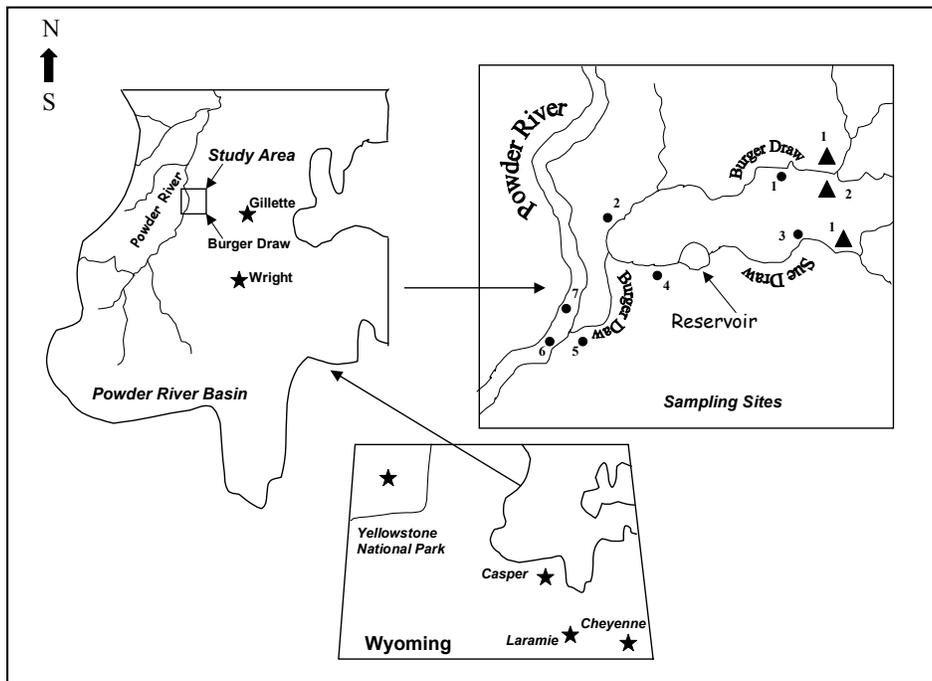


Figure 1. Map showing the Burger Draw study area with sampling sites in reference to the Powder River, Wyoming.

### Sampling Sites

Three discharge wells and seven sampling sites were established within the stream channel to monitor the chemistry of CBM discharge water at the wellhead, below discharge points, above and below reservoir storage in Sue Draw, before and after confluence of Sue and Burger Draw discharges, and above and below the confluence of Burger Draw with Powder River (Fig. 1). Sampling sites were marked by wooden stakes set above the high water line to facilitate sampling replication.

### Water Sampling

Water samples were collected four times at bimonthly intervals, from May to November, 2001. All samples were collected within three consecutive days for each sampling period from the seven sampling sites (Fig. 1). All samples were collected in sequence from downstream to the upstream discharge sites. Samples were taken while facing upstream so channel flow disturbance would be

flushed away from the sample bottle and stream flow interface. Sterile sample bottles (250 mL) were rinsed with stream water and used for collecting samples. A second water sample at each site was then collected using a clean and rinsed 7.5 L open mouth plastic container to measure pH and electrical conductivity. These analysis were made using field portable Hannah Instruments. All laboratory samples were preserved, sealed, labeled, and immediately placed on ice and transported to the laboratory for further analysis. Sample collection, preservation, and analysis were done following the protocols of Wyoming Department of Environmental Quality Water Quality Division (1999).

### Chemical Analysis

Samples were filtered using 0.45 millipore filters and the clear filtrates were analyzed for calcium (Ca), magnesium (Mg), sodium (Na), potassium (K), iron (Fe), manganese (Mn), total alkalinity, boron (B), sulfate ( $\text{SO}_4^{2-}$ ), chloride ( $\text{Cl}^-$ ), fluoride ( $\text{F}^-$ ), arsenic (As), and selenium (Se). The Ca, Mg, K, Fe, Mn, B, As, and Se were analyzed with the ELAN 6100 series of Inductively Coupled Plasma - Mass Spectrometers (ICP-MS). Sodium was determined using the Atomic Absorption Spectrophotometric Method. Sulfate ( $\text{SO}_4^{2-}$ ), chloride ( $\text{Cl}^-$ ), and fluoride ( $\text{F}^-$ ) were determined using the DX500 Ion Chromatographic Method using AS-3500 auto sampler. Total alkalinity was determined with acid titration method. All analyses were performed in accordance with standard laboratory quality assurance/quality control procedures (Greenberg et al., 1992).

From Ca, Mg, and Na measurements, sodium adsorption ratio (SAR) was calculated (Hanson et al., 1993). The SAR was calculated in two ways following the procedures of Sposito and Mattigod (1977). The first method was based on total dissolved concentrations, practical SAR (SAR<sub>p</sub>) is uncorrected for ion pairs, complexes, and activity coefficients. The second method, true SAR (SAR<sub>t</sub>) was based on free ion activities as predicted by the model MINTEQA2 (Allison and Brown, 1992). This model uses pH, total alkalinity, and total dissolved concentrations of different elements and calculates free ion activity after correcting for ion complexes, ion pairs, and activity coefficients.

### Quality Assurance

Duplicates, blanks, quality control check samples, standard reference samples, spike recovery analyses, and calculations of upper and lower control limits for the method were completed to meet quality assurance. Concentration of analyzed cations and anions were checked for charge balance to determine the accuracy of the analytical data.

### Statistical Analysis

The SAS statistical package was used to determine and establish the number and sets of duplicates to be collected at each site within a random design (SAS Inc., 1999). Differences in water chemistry data from different sites were determined by one-way analysis of variance (ANOVA) procedures using SPSS for Windows 10.0. An alpha level of 0.05 was used to determine differences within a 95% confidence interval. The Levene test was used to determine homogeneity of variances; homogeneity was achieved in skewed data with a weighted analysis using the inverse of the standard deviation.

## **Results and Discussion**

### Chemistry of CBM Discharge Water at Wellhead and Downstream Channel

The analytical data of CBM discharge water and downstream sampling sites in Burger Draw and Sue Draw before the confluence with the Powder River is presented in Table 1. The results suggest that CBM discharge water in Burger Draw watershed is saline and dominated by alkalinity and Na. Similarly, CBM discharge water in downstream channels of Burger Draw and Sue Draw is dominated by alkalinity and Na. The analytical data of CBM discharge water after the confluence of the Sue Draw with the Burger Draw and above and below the confluence of Burger Draw with the Powder River are presented in Table 2. The results suggest that Powder River water data above and below the confluence of the Burger Draw CBM discharge water are dominated by the  $\text{SO}_4^{2-}$ , Na, Cl, Ca, and Mg.

Table 1. Analytical data of CBM discharge water at wellhead and in downstream in Burger Draw and Sue Draw. DC = Discharge Sites

	pH	EC dS/m	Alk meq/L	Ca	Mg	Na	K	Cl <sup>-1</sup>	SO <sub>4</sub> <sup>2-</sup>	SARp			
				----- mg/L -----									
Burger Draw													
DC 1*	Mean		7.13	4.25	45.20	47.85	29.90	892.10	43.80	32.76	0.04	24.58	
	<i>CI 95%</i> <sup>2</sup>	0.06	0.06	1.49	2.98	2.17	24.14	1.03	2.14	1.29	1.06		
DC 2	Mean		7.04	4.35	45.80	47.70	32.75	955.00	43.95	29.90	0.04	25.71	
	<i>CI 95%</i> <sup>2</sup>	0.06	0.06	1.49	2.98	2.17	24.14	1.03	2.14	1.29	1.06		
Site 1	Mean		8.39	4.14	46.56	30.80	38.32	979.40	49.00	22.94	17.24	27.55	
	<i>CI 95%</i> <sup>2</sup>	0.07	0.07	1.88	3.77	2.75	30.53	1.30	2.71	1.64	1.34		
Site 2	Mean		8.51	4.21	47.23	29.56	38.62	970.80	48.76	25.34	15.90	27.40	
	<i>CI 95%</i> <sup>2</sup>	0.07	0.07	1.88	3.77	2.75	30.53	1.30	2.71	1.64	1.33		
Sue Draw													
DC 1*	Mean		7.13	4.30	47.56	51.55	33.50	942.35	44.80	29.26	0.08	24.76	
	<i>CI 95%</i> <sup>2</sup>	0.06	0.06	1.49	2.98	2.17	24.14	1.03	2.14	1.29	1.06		
Site 3	Mean		8.54	4.20	48.12	28.66	36.62	1028.6	49.10	22.51	0.04	29.74	
	<i>CI 95%</i> <sup>2</sup>	0.07	0.07	1.88	3.77	2.75	30.53	1.30	2.71	1.64	1.34		
Site 4	Mean		9.15	4.27	49.20	13.40	37.80	1039.6	51.04	22.58	3.41	32.46	
	<i>CI 95%</i> <sup>2</sup>	0.07	0.07	1.88	3.77	2.75	30.53	1.30	2.71	1.64	1.34		

\*n = 8 for all discharge site statistics; n = 5 for all site stats  
<sup>2</sup>standard deviations

The pH of CBM discharge water at Burger and Sue Draw ranged between 7.04 and 7.13. However, in channel flow pH increased to 8.39 and 8.54 in Burger and Sue Draws, respectively. Sue Draw water pH was 8.54 above Sue Reservoir but increased to 9.15 after retention storage (Table 1). After Sue Draw flow mixed with Burger Draw's, pH decreased to 8.84 (Table 2). The storage of CBM product water in reservoirs within the Cheyenne River, Belle Fourche River, and

Little Powder River drainages provided similar results; pH was 6.99 to 7.21 at discharge and increased from 7.79 to 8.26 in storage (McBeth et al., 2002a).

Salinity of CBM discharge water is considered high, ranging from 4.25 and 4.35 dS/m for Burger Draw and 4.30 dS/m for Sue Draw. However, we observed only slight salinity changes in the downstream flow, 4.14 to 4.21 and 4.20 to 4.27 within Burger and Sue draws. Similar to EC, total alkalinity appears to increase in downstream flow but this increase was minimal. Discharge concentrations of alkalinity in Burger Draw were 45.20 and 45.80 meq/L whereas in Sue Draw it was 47.56 meq/L. Alkalinity in the downstream flow in Burger Draw was 46.56 and 47.23 meq/L and in Sue Draw 48.12 meq/L before reservoir storage. After storage, alkalinity increased to 49.20 meq/L in Sue Draw (Table 1).

Change in Ca in downstream flow was significant. Well discharge for Burger Draw was 47.85 and 47.70 mg/L. Calcium decreased to 30.80 mg/L in channel flow. Decrease also occurred in Sue Draw where well discharge water was 51.55 but decreased to 28.66 mg/L before storage and again to 13.40 mg/L after storage. This sharp decrease in Ca in both channels may be attributed to the precipitation of calcium carbonates. There was little change in Mg and Na concentrations in either Burger or Sue Draws. Discharge of Mg in both Burger and Sue Draws was between 29.90 and 33.50 mg/L and 892.10 to 955.00 mg/L for Na. Magnesium increased to between 36.62 and 38.62 mg/L in channel flow of both streams. Na concentration was higher in Sue than Burger Draw. Sue Draw was 1028.60 before and 1039.60 mg/L after reservoir storage. Concentration of Na in Burger Draw flow was 970.80 mg/l before it mixed with water from Sue Draw. Just prior to confluence with the Powder River Mg and Na concentrations increased to 37.32 mg/L and 991.40 mg/L, respectively (Table 1 and 2).

We believe important changes in water quality in flow of Burger and Sue Draws were: a) the increase in pH of CBM product water, and b) the decrease in the concentration of Ca in CBM product water after flowing through channels and pond storage. These changes should influence the SAR values of CBM product water in Burger Draw and Sue Draw and the Powder River. The SAR<sub>p</sub> values (Table 1) for the CBM discharge water at the wellhead (24.58, 25.71, 24.76) were high in Burger and Sue Draws and also increased as the CBM discharge water moved downstream and through the reservoir storage (27.40 and 32.46).

Table 2. Analytical data of CBM discharge water after the confluence of Burger Draw and Sue Draw and Powder River above and below the confluence of Burger.

	pH	EC dS/m	Alk meq/L	Ca	Mg ----- mg/L	Na	K ----- mg/L	Cl <sup>-1</sup>	SO <sub>4</sub> <sup>2-</sup>	SARp
<b>Burger Draw After Sue Draw Confluence</b>										
<b>Site 5</b>										
Mean		8.84	4.10	46.53	20.52	37.32	991.40	48.78	22.97	14.58 29.81
CI 95% <sup>2</sup>		0.07	0.07	1.88	3.77	2.75	30.53	1.30	2.71	1.64 1.34
<b>Powder River</b>										
<b>Site 6 (above Burger Draw Confluence)</b>										
Mean		8.36	2.73	3.16	195.02	69.14	372.00	11.65	240.51	962.74 5.82
CI 95% <sup>2</sup>		0.09	1.00	2.54	91.85	15.69	189.80	5.94	120.62	331.78 2.85
<b>Site 7* (below Burger Draw Confluence)</b>										
Mean		8.52	2.92	5.60	180.38	66.47	428.83	14.16	222.77	818.72 6.97
CI 95% <sup>2</sup>		0.08	0.91	2.32	83.85	14.32	173.26	5.42	120.62	331.78 2.61

n = 8 for all discharge site statistics; \*n = 6  
<sup>2</sup>95% confidence intervals

Other chemical attributes associated with salinity and sodicity in channel water were potassium, chloride, and sulfate. Although of minor circumstance in our discharge water, it appears that channel flow did contribute to changes in concentration (Table 1). Chloride concentrations decreased from 32.76 to 22.51 mg/L and potassium and sulfate concentrations increased from 44.80 to 51.04 and from 0.04 to 17.24 mg/L, respectively.

We suggest chemical changes observed in downstream sampling sites can be explained by channel and pond sediment interactions with CBM product water. Hulin et al., (2002) demonstrated in laboratory studies that channel sediments of a stream approximately 9 km north of Burger Draw reacted with a single CBM discharge water to alter and increase salinity and sodicity after 5 and 10-

day pond contact with saturated sediment profiles. Hulin's studies further supported McBeth et al., (2002 a) who found much lower SAR values in CBM discharge (SARp between 6.24 and 11.7) but also observed that SAR significantly increases after pond storage within rangeland soils or sediments of constructed reservoirs in two of three different watersheds just to the east of Burger Draw. Although the discharge water SARp (14.65 and 17.49) of Hulin et al., (2002) was less than those observed in our study of Burger Draw, they did demonstrate that ponding above and within sediment profiles increased SARp and EC while precipitating carbonates and salts. Providing this evidence, our significant decrease in Ca as it reacts with sediment and a rather constant release of Na in flow means that one should expect a corresponding increase in the mean SARp in flow within Burger and Sue Draws. This occurred and the increase was even more pronounced after reservoir storage in Sue Draw (Table 1). SARp values for well discharge in Burger Draw were 24.58 and 25.71. Discharge into Sue Draw was 24.76; above Sue Reservoir was 29.74 and below was 32.46. Flow SARp in Burger Draw was 27.40.

#### Practical SARp and True SART

Sposito and Mattigod (1977) found that SARp is not linearly related to SART. Also, in uses of high SAR water for irrigation, it may be necessary to calculate both to determine potential sodicity hazards to crop lands caused by higher Na concentrations. SART and SARp calculations generally followed each other in the downstream direction in flow of Burger Draw, but greater change occurred between sites when using SART values.

The SART values for Burger Draw discharge were 32.9 and 34.6, and increased to 39.7 in flow downstream. Discharge in Sue Draw was 33.5, and increased to 44.1 above and to 53.4 below reservoir storage. SART was significantly different between locations on the Burger Draw drainage ( $p = 0.001$ ) when SARp ( $p = 0.327$ ) was not. To determine the relationship between the two values for SAR, we followed Sposito and Mattigod (1977) procedures and constructed a relative relationship between SARp and SART values from Burger and Sue Draws and Powder River (Fig. 2). Similar to Sposito and Mattigod (1977) studies, we compared a representative linear 1:1 functional relationship, and obtained a deviation from this plot once SAR reached approximately 15--20. This deviation increased as SART increased by a greater factor than SARp, demonstrating that the relationship is not 1:1.

The changes in SAR in Burger and Sue Draws and the deviation in the relationship between SAR<sub>p</sub> and SAR<sub>t</sub> can be attributed to the significant decrease in Ca concentration and relatively constant concentrations of Na and Mg in the channel flow. We attribute decrease in calcium concentration in the downstream to the precipitation of calcium carbonate into the channel sediment. If calcium carbonate precipitates into the channel sediment, we expect pH of water and sediment interface within few centimeters to be lower than the pH of water interface, because precipitation of calcium carbonate releases H<sup>+</sup> ions. To test this hypothesis, we measured the pH of the water column (pH<sub>w</sub>) and also the pH of first 2 cm of sediment (pH<sub>s</sub>) at their interface. When comparisons were made between pH<sub>w</sub> and pH<sub>s</sub> there was a consistent decrease in pH<sub>s</sub> at all sites. For example at site 4 (Fig. 1) pH<sub>w</sub> was 9.13 and pH<sub>s</sub> was 9.03. Above the confluence of Burger Draw with Powder River pH<sub>w</sub> was 8.35 and pH<sub>s</sub> was 8.05. These results indicate that dissolved calcium concentrations decreased in the downstream channels due to the precipitation of calcium carbonate.

#### Confluence with the Powder River

The only significant differences in water quality above and below the confluence of Burger Draw with the Powder River was pH ( $p = 0.013$ ) (Table 2). The larger size and amount of flow of the Powder River exerts a strong dilution factor when receiving discharge of CBM product water from Burger Draw. Confluence of the two discharges initiated an increase in pH from 8.36 to 8.52. Smaller, but not significant, changes observed were increases in salinity 2.73 to 2.92 dS/m, alkalinity 3.16 to 5.60 meq/L, Na 372.00 to 428.83 mg/L, and K 11.65 to 14.16 mg/L. Smaller but not significant decreases were Ca 195.02 to 180.38 mg/L, Mg 69.14 to 66.47 mg/L, Cl 240.51 to 222.77 mg/L, and SO<sub>4</sub><sup>2-</sup> 962.74 to 818.72 mg/L. Of importance to the future management of CBM discharge water release into the Powder River, the SAR<sub>p</sub> of the Powder River was significantly lower (5.82 to 6.97) than water leaving Burger Draw 29.81 (Table 2).

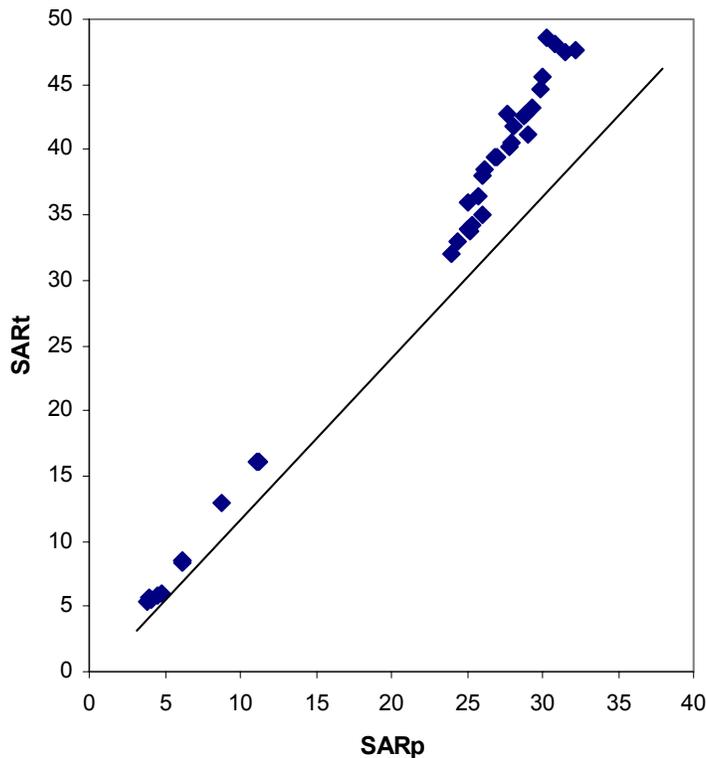


Figure 2.  
The  
relations  
hip  
between

true SAR (SARt) and practical SAR (SARp) in comparison to a 1:1 functional linear relationship (depicted by line). Squares are SARt experimental points plotted against SARp.

### Trace Elements

Trace element concentrations with travel downstream are summarized in Table 3. Significance change occurred for Fe, Mn, and As; and seasonally for B with no other significant differences observed in flow of Burger Draw. As expected, Fe precipitates at once after discharge from wells (887.90 to 738.15 ug/L) as it transforms from a reduced to an oxidized state in Burger Draw (108.00 ug/L) or Sue Draw ( 3006.15 ug/L to 92.60 ug/L). Further reduction in Fe concentration in downstream flow did not appear to occur. Manganese concentrations were similar to Fe and decreased after initial contact with the atmosphere and the channel system. Boron remained fairly constant throughout the stream channel with a slight increase after reservoir storage in Sue Draw Table 3. Trace elements data for CBM discharge water at wellhead and in downstream in Burger Draw and Sue Draw and the Powder River, units are ug/L. DC = discharge. S = sampling site.

	Fe	Mn	B	As	Se	
<b>Burger Draw</b>						
DC 1 <sup>1</sup> Mean		887.9	16.5	179.0	2.15	1.70
CI 95% <sup>2</sup>	55.0	1.97		13.68	0.53	0.73
DC 2 Mean		738.1	17.55	137.50	1.55	1.95
CI 95% <sup>2</sup>	55.0	1.97		13.68	0.53	0.731
S 1 Mean	108.00	9.83		131.20	2.18	1.13
CI 95% <sup>2</sup>	69.62	2.50		17.30	0.68	0.93
S 2 Mean	89.08	5.56		144.0	2.31	1.16
CI 95% <sup>2</sup>	69.62	2.50		17.30	0.68	0.93
<b>Sue Draw</b>						
DC 1 Mean		3006.15	45.50	159.00	3.45	1.95
CI 95% <sup>2</sup>	55.04	1.97		13.68	0.53	0.73
S 3 Mean	92.60	4.33		138.60	2.58	1.12
CI 95% <sup>2</sup>	69.62	2.50		17.30	0.68	0.93
S 4 Mean	154.20	6.05		156.40	4.48	2.16
CI 95% <sup>2</sup>	69.62	2.50		17.30	0.68	0.93
<b>Burger/Sue Confluence</b>						
S 5 Mean	114.20	6.83		143.40	3.70	2.37
CI 95% <sup>2</sup>	69.62	2.50		17.30	0.68	0.93
<b>Powder River (above Burger Draw confluence)</b>						
S 6 Mean	610.40	7.96		369.20	4.04	7.74
CI 95% <sup>2</sup>	225.22	8.40		106.67	3.92	2.25
<b>Powder River (below Burger Draw confluence)</b>						
S 7* Mean		579.17	10.35	338.00	3.84	8.16
CI 95% <sup>2</sup>	205.60	7.66		97.38	3.58	2.06

<sup>1</sup>n = 8 for all discharge statistics; n = 5 for site statistics, except asterisked (\*) where n = 6  
<sup>2</sup>95% confidence intervals

(138.60 ug/L above and 156.40 ug/L below storage). Arsenic and Se appeared to increase with downstream flow but As was significantly higher after reservoir storage in Sue Draw (2.58 ug/L

above the storage and 4.48 ug/L below the storage). These results are in agreement with the findings of McBeth et al. (2001b) and Hulin (2001) studies.

Within the grouping of trace elements in the Powder River, statistical differences were not detected above and below the confluence. Changes outside of significance were observed for Mn. Manganese increased from 7.96 to 10.35 ug/L, while B decreased from 369.20 to 338.00 ug/L. However, no differences in concentration of Fe, As, and Se were observed after above and below confluence. In addition, dissolved concentrations of As, Se, and B are below the EPA primary drinking water maximum contaminant limits (50 ug/L for As, 50 ug/L for Se, none for B) (US EPA 2001).

Iron and Mn are listed as secondary drinking water standards of 300 ug/L and 50 ug/L respectfully; they are not toxic for drinking water, but do cause cosmetic and aesthetic effects. McBeth et al., (2002b) reported that their discharge and pond water was below limits for Fe and Mn, with levels in the Little Powder River system increasing above allowed limits for Fe after reservoir storage. Hulin (2001) laboratory study reports that Fe and Mn exceeded allowable limits in surface and groundwater after ponding over saturated sediments. Results of this study suggests CBM discharge water Fe levels were above the drinking water limit, however as flow progresses downstream Fe levels quickly drop below the maximum contaminant limit for drinking water. However, we observed Fe concentrations in the Powder River were above the drinking water contaminant limit prior to and after receiving Burger Draw CBM discharge. In our study Mn remained below the maximum contaminant limit for drinking water.

Differences in concentrations between the studies presented within the Powder River Basin reflect the high variability of CBM discharge water. In general, chemistry increases with the depth of the coal seam as suggested by Mullins and Hajek (1998); to the west from the Belle Fourche (McBeth et al., 2002a); toward Dead Horse Creek (Hulin, 2001) and Burger Draw; and North from the Cheyenne River (McBeth et al., 2002a) and Burger Draw toward Dead Horse Creek (Hulin, 2001).

### **Conclusions**

The results of this research suggest the following:

- The pH of CBM discharge water increased in the downstream channel water, however the pH of sediment water interface decreased due to the precipitation of calcium carbonate. The precipitation of calcium carbonate in the downstream channel also decreased calcium concentration and increased SAR.
- The increase of SAR<sub>t</sub> was significant in downstream flow where as SAR<sub>p</sub> was not, suggesting the need to calculate both values to clearly understand the sodicity hazard in a high saline SAR system.
- CBM discharge water Fe and Mn concentrations decreased in short distances in flow and then remained about the same to the confluence of the receiving river. Arsenic and Se concentrations increased with flow downstream.
- Reservoir storage resulted in an increase in pH, EC, TDS, alkalinity, SAR, sulfate, iron, manganese, boron, arsenic, and selenium where as calcium decreased significantly.

Overall, results discussed in this research may help federal and state agencies, landowners, citizens, downstream water users, and the CBM industry in arid and semi-arid areas to develop appropriate management schemes for beneficial uses for CBM discharge water.

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