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COALBED METHANE PRODUCT WATER CHEMISTRY IN THREE WYOMING WATERSHEDS[1]

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ABSTRACT: The Powder River Basin in Wyoming has become one of the most active areas of coalbed methane (CBM) development in the western United States. Extraction of methane from coalbeds requires pumping of aquifer water, which is called product water. Two to ten extraction wells are manifolded into one discharge point and product water is released into nearby unlined holding ponds. The objective of this study was to evaluate the chemistry, salinity, and sodicity of CBM product water at discharge points and associated holding ponds as a function of watershed. The product water samples from the discharge points and associated holding ponds were collected from the Cheyenne River (CHR), Belle Fourche River (BFR), and Little Powder River (LPR) watersheds during the summers of 1999 and 2000. These samples were analyzed for pH, electrical conductivity (EC), total dissolved solids (TDS), alkalinity, sodium (Na), calcium (Ca), magnesium (Mg), potassium (K), sulfate (SO_4^{2-}), and chloride (Cl^-). From the chemical data, practical sodium adsorption ratio (SAR*p*) and true sodium adsorption ratio (SAR*t*) were calculated for the CBM discharge water and pond water. The pH, EC, TDS, alkalinity, Na, Ca, Mg, K, SAR*p*, and SAR*t* of CBM discharge water increased significantly moving north from the CHR watershed to the LPR watershed. CBM discharge water in associated holding ponds showed significant increases in EC, TDS, alkalinity, Na, K, SAR*p*, and SAR*t* moving north from the CHR to the LPR watershed. Within watersheds, the only significant change was an increase in pH from 7.21 to 8.26 between discharge points and holding ponds in the LPR watershed. However, the LPR and BFR exhibited larger changes in mean chemistry values in pH, salinity (EC, TDS), and sodicity (SAR) between CBM product water discharges and associated holding ponds than the CHR watershed. For instance, the mean EC and TDS of CBM product water in LPR increased from 1.93 to 2.09 dS/m, and from1,232 to 1,336 mg/L, respectively, between discharge and pond waters. The CHR exhibited no change in EC, TDS, Na, or SAR between discharge water and pond water. Also, while not statistically significant, mean alkalinity of CBM product water in BFR and LPR watersheds decreased from 9.81 to 8.01 meq/L and from 19.87 to 18.14 meq/L, respectively, between discharge and pond waters. The results of this study suggest that release of CBM product water onto the rangelands of BFR and LPR watersheds may precipitate calcium carbonate ($CaCO_3$) in soils, which in turn may decrease infiltration and increase runoff and erosion. Thus, use of CBM product water for irrigation in LPR and BFR watersheds may require careful planning based on water pH, EC, alkalinity, Na, and SAR, as well as local soil physical and chemical properties.
(KEY TERMS: water management; irrigation; erosion; arid watershed management; water chemistry.)

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INTRODUCTION

Demand for natural gas (methane) is increasing rapidly because it is an abundant and clean burning fuel (SRI, 2000). Many countries are now producing or plan to extract methane from coal deposits. In the United States, because of energy shortages, Colorado, Wyoming, Montana, Utah, and New Mexico are now exploring the option of extraction of methane from their coal resources. It is estimated that there are 26 trillion cubic feet of recoverable CBM (coalbed methane) in the Powder River Basin, Wyoming (Figure 1) and this basin is now one of the most active areas of CBM development in the western United States (Nelson, 1999; Hill *et al.,* 2000; Reddy *et al.,* 2001).

Most CBM development in Wyoming is occurring on the eastern portion of the Powder River Basin (Figure 1), which is a semiarid basin with average annual precipitation ranging from 30 to 60 cm. This basin (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) is generally high plains with elevations from 1,640 to 1,800

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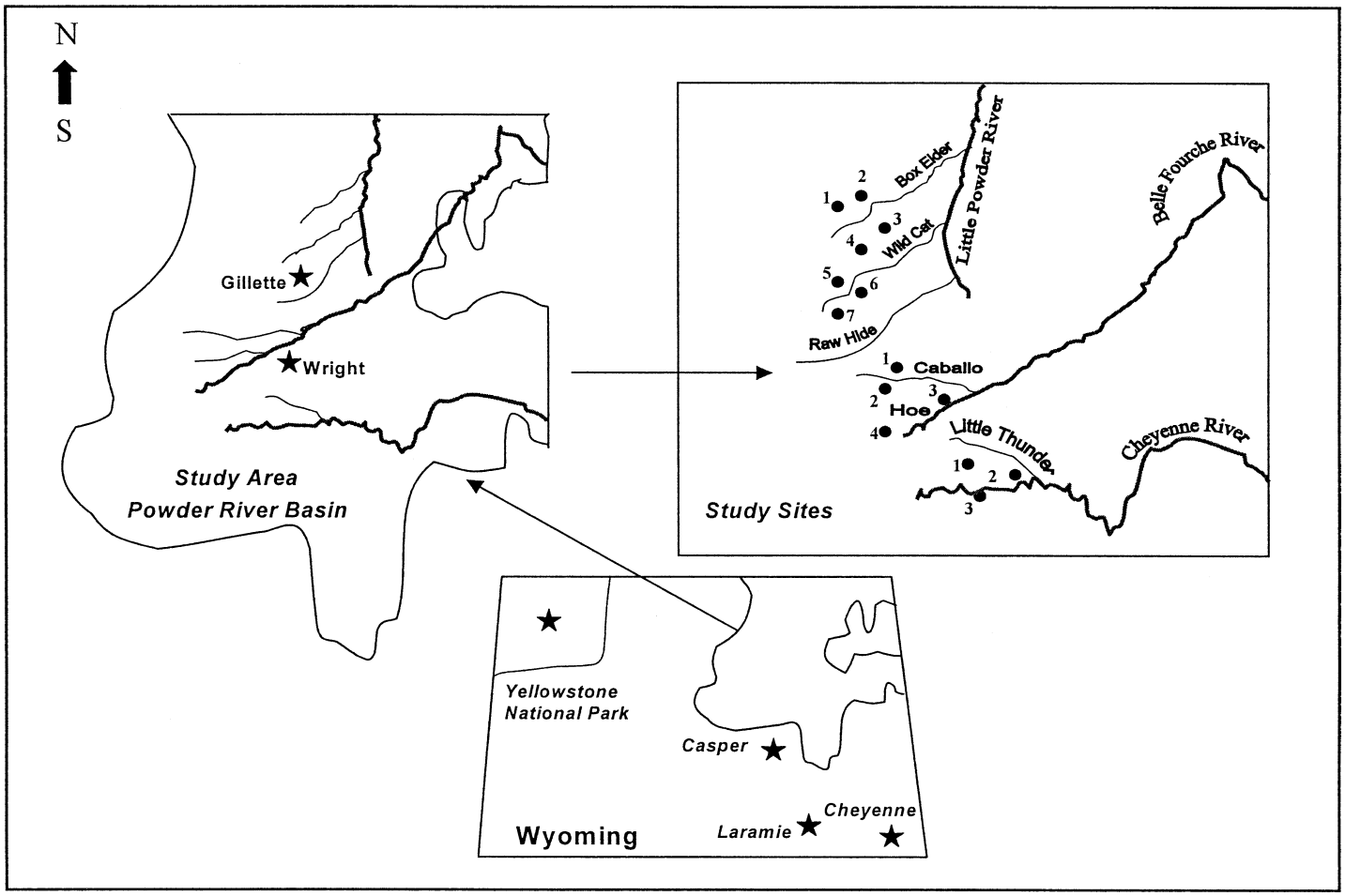

Figure 1. Map of Powder River Basin, Wyoming, and Sampling Sites for CHR, BFR, and LPR Watersheds (not to scale).

m above sea level. Eastern portions of the basin are typically high plains dominated by grass/sagebrush communities, but the central and western portions contain the Powder River Breaks and have a more diversified landscape setting and associated flora. For a detailed description of the geology and flora of the Powder River Basin see Knight (1994), Ellis *et al.* (1998), and Flores and Bader (1999).

Methane is produced deep within confined coalbeds through biogeophysical processes and remain trapped in the coalbed by the aquifer water pressure. Recovery of methane from coalbeds is accomplished with extraction wells. As shown in the Figure 2, extraction of methane requires that some of the coalbed aquifer's water be removed to depressurize a zone around the bottom of the well. This extracted water is called coalbed methane product water. It is estimated that a single CBM well in the Powder River Basin may produce approximately 8 to 80 L of product water per minute, but this amount varies upon the aquifer system pumped. At present, more than 16,000 wells are under production in the Powder River Basin and this number is expected to increase to 30,000 or more. Estimates are that approximately 30 trillion L of product water will be produced from CBM extraction in Wyoming.

Currently, two to ten extraction wells are manifolded together into one discharge point and released into constructed unlined holding ponds or onto rangelands. Rice *et al.* (2000) examined the chemical data of CBM product water at the wellhead. These studies reported that TDS (total dissolved solids) in CBM product water at wellheads increased from south to north and from east to west in the Powder River Basin. In another study, McBeth *et al.* (2001) examined the chemistry of trace elements of CBM product water both at the wellheads and associated holding ponds in the Powder River Basin. The dissolved concentration of trace elements in the CBM product water increased in the discharge water and in associated pond water moving from south to north and from east to west in the Powder River Basin.

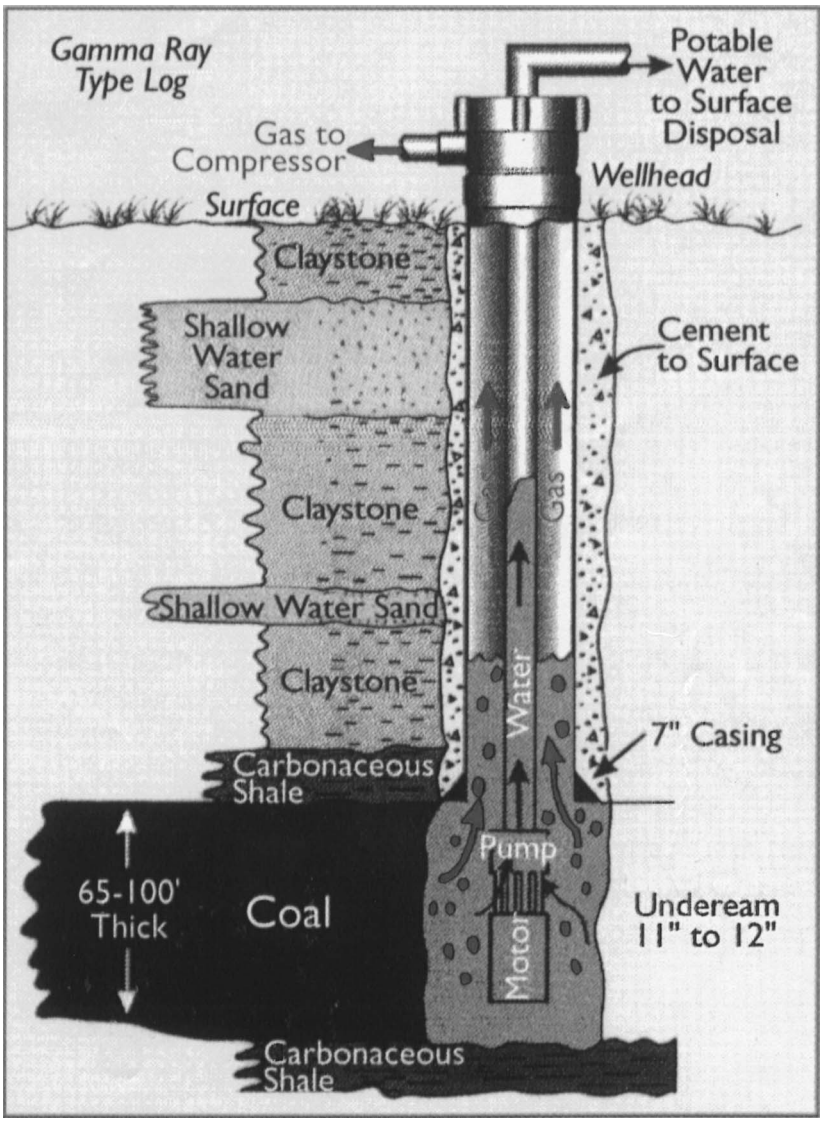

Figure 2. CBM Extraction Well Schematic (courtesy of Barrett Resources Corporation).

Different options, including irrigation, are proposed for the management of this new supply of CBM product water in the Powder River Basin. However, the potential use of CBM product water for irrigation in arid and semiarid watersheds requires careful evaluation of chemistry (pH and major elements), salinity (EC, electrical conductivity), and sodicity (SAR, sodium adsorption ratio). To our knowledge, very limited data on the chemistry of CBM product water in the Powder River Basin are available. In addition, information on how the chemistry of CBM product water changes when it reacts with local soils of associated holding ponds is lacking. More information on the chemistry, salinity, and sodicity of CBM product water at the discharge points and in associated holding ponds is needed in the Powder River Basin. Such information is useful to federal and state agencies, landowners, and industry personnel in making reliable decisions on how to properly manage this new supply of water, particularly for irrigation in arid and semiarid watersheds of the western United States.

The objective of this study was to evaluate the chemistry, salinity, and sodicity of CBM product water for irrigation in the Powder River Basin, Wyoming. The study focused on evaluating the chemical changes in CBM product water at discharge points and after this water is placed in associated ponds in three different watersheds of the Powder River Basin, to help evaluate the current practice of managing point source well discharge water in semiarid environments. CBM product water samples were collected from both sources within each watershed during the

summers of 1999 and 2000. Samples were analyzed for pH, TDS, EC, alkalinity, SAR, and dissolved concentration of major elements (sodium, calcium, magnesium, potassium, sulfate, and chloride) to determine changes in the chemistry, salinity, and sodicity of CBM product water.

MATERIALS AND METHODS

Study Site

Project study sites in the eastern portion of the Powder River Basin extend from the south to northwest and include the Cheyenne River (CHR), Belle Fourche River (BFR), and Little Powder River (LPR) watersheds (Figure 1). The CHR drains the southeastern portions of the Powder River Basin. The BFR drains the eastern parts of the Powder River Basin and the LPR drains the northern portion of the Powder River Basin. These are perennial rivers and tributaries of the Missouri River. Major coal formations in the Powder River Basin include the Tertiary White River Formation and Tertiary Tongue River Member of the Fort Union Formation.

Soils in the CHR watershed are dominated by Ustic Haplargids (clay loam). The upper 0 to 11 cm of these soils contain a neutral pH of 7.2 with 1 percent organic carbon. These soils are well drained with slow permeability and have low to high runoff. The BFR watershed soils are Ustic Calciargids (fine loamy). These soils also are well drained with moderate permeability and have low or medium runoff. The upper 0 to 11 cm of these soils have a neutral pH of 7.2 with 1.2 percent organic carbon. The LPR watersheds soils are Ustic Torriorthents (loamy). The upper 0 to 11 cm contain 0.85 percent organic carbon with a pH of 8.0. These soils are well drained with moderate permeability and have medium or high runoff depending upon slope (NRCS, 2002).

Water Sampling

Three sites from the CHR watershed, four sites from the BFR watershed, and eight sites from the LPR watershed were selected for sampling (Figure 1). More sites from the LPR watershed were included because of the extensive CBM development in that area. For each site, a product water discharge point and its associated holding pond were identified. One site in the LPR watershed was excluded since it was not possible to locate the associated holding pond. The typical management practice is to allow product water from the CBM well discharge point to flow into a nearby constructed holding pond. These ponds are typically within a few meters of the discharge point. Many holding ponds are constructed concurrently with initial well installation and probably six to seven years old. The CBM product water samples from all discharge points and associated holding ponds were collected during the summers of 1999 and 2000.

Discharge water samples were collected directly from the wellhead by filling clean acid washed polyethylene bottles. The pH was measured at the discharge point in the field using a portable Hanna Instrument (HI 8314) unit prior to sample collection. The pH meter was calibrated using standard buffer solutions. Prior to the collection of samples, bottles were rinsed with discharge water three times. Similarly, holding pond water samples corresponding to discharge points were collected nearby the discharge point. Before sample collection, pH was measured with a portable Hanna Instrument (HI 8314) unit. Again, samples were collected in acid washed polyethylene bottles that had been rinsed three times with pond water. All samples were placed in a cooler and transported to the Water Quality Laboratory, University of Wyoming, Laramie, Wyoming, for further analysis. Each sample was filtered through a 0.45μ millipore filter and then were subjected to further chemical analysis.

Each filtered sample was divided into two subsamples. One subsample was acidified to pH 2.0 with HNO_3 while the other subsample was left unacidified. Acidified samples were analyzed for calcium, magnesium, sodium, and potassium. Unacidified samples were analyzed for pH, total dissolved solids (TDS), total alkalinity, sulfate, and chloride. Quality control procedures included analysis of blank samples as controls and NBS standards for every 15 to 20 samples.

Procedures

The pH was measured with a combination pH electrode. Total dissolved solids were analyzed by drying samples to a constant weight at 180°C. From the TDS (mg/L) measurement, EC (dS/m) was calculated by dividing by a factor of 640. This factor is recommended for water with EC less than 5 (dS/m) (Hanson *et al.,* 1993). Total alkalinity was determined with the acid titration method. Calcium, magnesium, and potassium were analyzed with inductively coupled plasma mass spectrometry (ICP-MS, ELAN 6100). Sodium was measured with atomic absorption (AA). Sulfate and chloride were analyzed with DX 500 Dionex ion chromatography (IC). All analyses were performed following standard procedures (American

Public Health Association, 1992). From sodium, calcium, and magnesium measurements (meq/L), the SAR was calculated (Hanson *et al.,* 1993). The SAR was calculated in two ways. The first method, practical SAR (SAR*p*) was based on total dissolved concentrations which is uncorrected for ion pairs, complexes, and activity coefficients. The second method, true SAR (SAR*t*), was based on free ion activities, which is corrected for ion pairs, complexes, and activity coefficients. The free ion activities were calculated using the geochemical model MINTEQA2 (Allison and Brown, 1992). This model uses pH, total alkalinity, and total dissolved concentrations of major ions to calculate free ion activities after correcting for ion pairs, complexes, activity coefficients, and charge balance. Outputs from this model also verify the accuracy of analytical data.

Data Analysis

Statistical relationships within individual watersheds between discharge and pond waters were accomplished with two tailed T-tests at a 95 percent confidence interval. Bonferroni corrections were calculated to give an alpha level of 0.001 (Ramsey and Schafer, 1997). Relationships among the three watersheds were performed using analysis of variance (ANOVA), with Tukey's pairwise comparisons at a 95 percent confidence interval for an alpha level of 0.05. The results presented meet the assumptions of equal variances and normal distribution of residuals. Tables 1, 2, and 3 show descriptive statistics, mean (M), standard deviation (SD), and sample size (n) for all parameters across all watersheds.

RESULTS AND DISCUSSION

The complete water chemistry data of CBM product water and associated holding pond water for summer 1999 and summer 2000 for three watersheds across the Powder River Basin, Wyoming, are presented in Tables 1, 2, and 3. The CBM product water chemistry at discharge points is dominated by TDS, alkalinity, and sodium. The CBM product water chemistry in holding ponds is dominated by TDS, alkalinity, sodium, and sulfate. The pH, EC, TDS, and alkalinity of CBM product water discharge points increased moving from CHR to LPR, whereas CBM pond water increased in EC, TDS, and alkalinity moving from CHR to LPR. The pH of discharge water increased between the CHR and LPR from 6.99 to 7.21 ($p < 0.001$, df = 27). Whereas the pH of corresponding pond water did not significantly change among watersheds; however, the difference in means between CHR and LPR pond waters suggests that a larger sample size might provide significance (7.79 and 8.26). Only the LPR watershed showed a significant pH increase from 7.21 to 8.26 between discharge water and pond water ($p < 0.001$, df = 13). These results suggest that LPR watershed soils are more alkaline and calcareous than BFR and CHR watershed soils.

The measurement of EC is an important parameter to determine the salinity hazards of a given water. This information also helps develop appropriate irrigation management schemes using product water on crops based on soil physical and chemical properties. The EC of CBM product water at both discharge points and holding ponds increased from the CHR watershed to the LPR watershed. From CHR to LPR, the EC of discharge water increased from 0.80 to 1.93 dS/m ($p < 0.001$, df = 27), and pond water increased from 0.82 to 2.09 dS/m ($p = 0.002$, df = 27). Within watersheds there was no statistically significant change in EC between discharge and pond waters. But, within the BFR and LPR watersheds the mean EC values for discharge and pond waters increased from 1.18 to 1.50 dS/m and from 1.93 to 2.09 dS/m, respectively. While this change is not significant, these mean EC values are important because all of these values approach or are within the range of high saline water, 1.2 to 2.25 dS/m. Studies by Keren (2000) suggest that use of high saline water for salt sensitive crops and soils with restricted drainage may be detrimental. Thus, application of CBM product water for irrigation, particularly in LPR and BFR watersheds, may require careful planning based on CBM water chemistry and soil chemical and physical properties.

The mean TDS values of CBM discharge water increased from 511.7 to 1,232 mg/L ($p < 0.001$, df = 27) between the CHR and LPR watersheds. The TDS values of corresponding pond water increased from 523.5 to 1,336 mg/L ($p = 0.002$, df = 27) from the CHR to the LPR watersheds. There was no significant change within any of the watersheds in the concentration of TDS between discharge and pond waters. However, the BFR and LPR watersheds did show larger mean TDS values in pond waters than discharge waters. Mean TDS values changed, although not significantly, from 752.8 to 957.0 mg/L and from 1232 to 1336 mg/L, between discharge and pond waters in the BFR and LPR watersheds, respectively. The TDS and EC values for CBM discharge waters presented in this study are in agreement with the data reported by Rice *et al.* (2000). These authors also observed an increase in TDS and EC of CBM product water at discharge

TABLE 1. The pH, EC, TDS, Alkalinity, Na, Ca, Mg, K, SO_4^{2-}, and Cl^- Values and Descriptive Statistics for the Little Powder River Watershed, Wyoming. D, P, M, SD, and n are discharge, pond, mean, standard deviation, and sample size, respectively.

LITTLE POWDER RIVER WATERSHED																				
	pH		EC (dS/m)		TDS (mg/L)		Alk. (meq/L)		Na (mg/L)		Ca (mg/L)		Mg (mg/L)		K (mg/L)		SO_4^{2-} (mg/L)		Cl^- (mg/L)	
Site	D	P	D	P	D	P	D	P	D	P	D	P	D	P	D	P	D	P	D	P
1999																				
1	7.24	8.16	0.94	1.46	600	933	17.94	18.34	351.0	347.8	26.60	14.52	22.70	20.61	10.80	11.13	1.24	1.93	7.94	7.74
2	7.27	7.95	1.56	1.67	1000	1067	21.88	21.23	384.0	410.0	10.70	20.35	24.90	25.17	11.40	12.33	0.55	6.14	7.13	7.71
3	7.19	8.15	1.46	1.67	933	1067	16.86	20.61	348.0	373.6	8.50	13.36	29.00	26.87	15.70	13.03	0.33	2.03	5.64	6.29
4	7.08	7.71	1.46	2.40	933	1533	19.52	3.19	373.2	270.5	17.43	118.8	28.62	69.35	13.22	8.72	0.42	798	5.91	39.67
5	7.16	7.71	1.56	2.40	1000	1533	20.49	3.19	379.3	260.1	37.76	109.6	29.07	66.42	13.00	8.14	0.43	814	5.96	53.05
6	7.27	8.09	2.40	2.50	1533	1600	21.73	21.17	409.6	403.0	32.72	28.60	26.29	25.21	13.45	10.95	1.57	2.54	7.53	7.49
7	7.39	7.96	2.31	2.74	1476	1751	20.48	19.07	404.1	383.3	8.39	8.60	21.87	20.79	17.47	15.74	0.44	0.38	14.37	12.10
2000																				
1	7.24	8.26	2.50	2.34	1600	1500	18.64	18.64	363.2	357.9	56.34	30.75	21.69	23.36	11.53	12.86	1.62	1.85	7.17	7.34
2	7.16	8.61	2.34	2.34	1500	1500	19.39	21.20	390.1	387.3	58.67	26.58	26.66	28.00	13.60	15.27	0.39	1.04	6.16	6.24
3	7.14	9.58	2.63	3.21	1684	2054	19.81	25.95	349.6	527.2	57.64	6.50	27.41	23.62	16.38	18.71	0.75	7.19	5.88	9.24
4	7.11	8.19	1.67	1.26	1069	808	20.47	19.58	367.9	368.6	57.98	56.89	25.87	28.60	11.41	12.41	0.17	12.10	6.29	7.09
5	7.18	8.19	1.95	1.26	1250	808	20.22	19.58	375.9	368.6	56.22	56.89	27.36	28.60	12.01	12.41	2.60	12.97	6.32	7.79
6	7.31	8.26	1.58	2.43	1014	1557	20.30	20.88	393.2	404.1	55.26	32.05	22.78	26.90	10.26	13.28	2.32	2.99	9.15	8.06
7	7.20	8.85	2.59	1.56	1656	998	20.46	21.36	399.1	421.3	48.33	12.41	21.06	20.91	15.22	19.40	1.97	3.30	14.31	15.95
Descriptive Statistics																				
M	7.21	8.26	1.93	2.09	1232	1336	19.87	18.14	377.7	377.4	38.04	38.28	25.38	31.03	13.25	13.17	1.06	119.0	7.84	13.98
SD	0.083	0.486	0.531	0.600	339.9	384.0	1.357	6.590	20.22	64.20	20.30	35.79	2.865	15.87	2.218	3.243	0.819	291.1	2.919	14.20
n	14	14	14	14	14	14	14	14	14	14	14	14	14	14	14	14	14	14	14	14

TABLE 2. The pH, EC, TDS, Alkalinity, Na, Ca, Mg, K, SO_4^{2-}, and Cl^- Values and Descriptive Statistics for the Belle Fourche River Watershed, Wyoming. D, P, M, SD, and n are discharge, pond, mean, standard deviation, and sample size, respectively.

BELLE FOURCHE RIVER WATERSHED																				
	pH		EC (dS/m)		TDS (mg/L)		Alk. (meq/L)		Na (mg/L)		Ca (mg/L)		Mg (mg/L)		K (mg/L)		SO_4^{2-} (mg/L)		Cl^- (mg/L)	
Site	D	P	D	P	D	P	D	P	D	P	D	P	D	P	D	P	D	P	D	P
1999																				
1	7.16	8.13	1.41	1.41	900	900	11.94	11.25	200.8	203.5	20.49	25.75	15.75	13.91	12.22	9.27	0.24	0.58	8.20	8.10
2	7.29	8.09	1.41	0.63	900	400	11.71	6.47	212.2	211.3	10.49	26.30	17.61	16.28	14.11	11.42	0.66	0.78	8.46	8.02
3	7.19	7.32	1.25	1.46	800	933	8.17	7.65	149.8	151.2	21.42	20.76	8.25	8.45	7.77	7.55	14.17	14.53	9.21	9.12
4	7.02	7.57	1.15	1.41	736	902	8.59	8.28	166.3	165.7	8.92	23.75	10.00	9.86	9.09	9.40	5.18	9.55	10.48	10.46
2000																				
1	7.18	9.51	1.07	3.79	686	2426	10.59	3.46	191.1	554.6	31.88	43.66	13.71	106.5	8.15	24.85	0.33	1379	8.27	17.00
2	7.21	8.07	1.02	1.45	652	929	10.88	10.88	194.3	202.3	26.47	15.72	14.33	14.08	9.82	10.66	3.11	0.70	8.46	8.69
3	7.15	7.31	0.85	0.99	546	632	8.04	8.00	155.5	155.5	22.67	22.45	9.09	9.33	7.45	7.53	39.72	40.90	8.95	8.96
4	7.16	7.70	1.25	0.83	802	533	8.54	8.09	149.5	142.5	21.35	18.05	8.64	8.32	7.47	7.31	1.90	2.28	9.36	9.72
Descriptive Statistics																				
M	7.17	7.96	1.18	1.50	752.8	957.0	9.81	8.01	177.4	223.4	20.46	24.56	12.17	23.30	9.51	11.00	8.16	181.0	8.92	10.01
SD	0.075	0.708	0.194	0.981	122.9	628.0	1.640	2.450	24.96	136.6	7.610	8.530	3.610	33.70	2.451	5.800	13.55	484.0	0.763	2.940
n	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8

TABLE 3. The pH, EC, TDS, Alkalinity, Na, Ca, Mg, K, SO_4^{2-}, and Cl^- Values and Descriptive Statistics for the Cheyenne River Watershed, Wyoming. D, P, M, SD, and n are discharge, pond, mean, standard deviation, and sample size, respectively.

CHEYENNE RIVER WATERSHED																				
	pH		EC (dS/m)		TDS (mg/L)		Alk. (meq/L)		Na (mg/L)		Ca (mg/L)		Mg (mg/L)		K (mg/L)		SO_4^{2-} (mg/L)		Cl^- (mg/L)	
Site	D	P	D	P	D	P	D	P	D	P	D	P	D	P	D	P	D	P	D	P
1999																				
1	6.91	7.31	0.52	0.94	333	600	5.68	5.73	109.9	114.5	10.14	9.55	4.70	4.75	4.57	4.80	0.29	0.19	8.17	8.74
2	6.86	8.07	0.83	1.25	533	800	8.11	8.05	141.4	143.5	22.09	20.01	10.94	10.70	6.44	6.63	0.80	0.61	9.69	8.79
3	6.89	7.29	1.15	1.04	733	667	8.15	8.14	138.0	137.8	23.44	22.91	12.18	11.57	7.12	6.97	0.75	0.78	8.52	8.31
2000																				
1	7.10	8.12	0.50	0.74	322	474	5.85	6.06	114.5	116.1	10.12	9.70	5.06	5.12	4.62	4.55	0.28	0.55	7.53	7.63
2	7.09	7.91	1.00	0.45	640	291	7.94	8.22	139.3	147.2	20.51	16.13	9.88	9.97	6.05	6.18	0.67	0.73	9.36	9.74
3	7.09	8.06	0.80	0.48	509	309	9.04	9.02	146.9	148.5	26.60	25.72	12.92	11.88	7.44	7.30	0.38	1.12	6.95	7.09
Descriptive Statistics																				
M	6.99	7.79	0.80	0.82	511.7	523.5	7.46	7.54	131.7	134.5	18.82	17.34	9.28	9.00	6.04	6.07	0.53	0.66	8.37	8.38
SD	0.114	0.389	0.258	0.318	163.6	202.7	1.370	1.322	15.25	15.51	7.020	6.770	3.570	3.220	1.222	1.146	0.238	0.305	1.049	0.936
n	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6

points moving south to north from the CHR to the LPR watershed.

The alkalinity of discharge water increased moving from south to north with a rise from 7.46 to 19.87 meq/L between the CHR and LPR watersheds ($p < 0.001$, df = 27). Likewise, pond water alkalinity increased from 7.54 to 18.14 meq/L between the CHR and LPR watersheds ($p < 0.001$, df = 27). There were no significant differences in alkalinity within any of the watersheds between discharge and pond water. However, examining the mean alkalinity values for both LPR and BFR shows a slight, although not statistically significant, decrease from 19.87 to 18.14 meq/L for LPR and from 9.81 to 8.01 meq/L for BFR between discharge and pond waters. This decrease is probably due to the precipitation of carbonate minerals in holding ponds. The increased pH values in holding ponds are within the buffering process of calcite (Reddy *et al.,* 1990). Both BFR and LPR soils contain significant amounts of calcite, particularly the LPR watershed soils. These results suggest that release of CBM product water onto the rangelands of LPR watersheds may precipitate calcium carbonate in soils. These results are consistent with soil properties discussed earlier, suggesting that LPR watershed soils are more alkaline and calcareous than BFR or CHR watershed soils. For example, the upper 0 to 11 cm of LPR watershed soils have a more alkaline pH, 8.0 versus 7.2, than the BFR or CHR watershed soils.

Measurement of dissolved concentrations of sodium, calcium, and magnesium in water is required to calculate SAR and to predict sodicity hazards. Irrigation of soils with excess sodium and high SAR, particularly clay soils, will lower water infiltration rates and increase erosion (Hanson *et al.*, 1993). A comparison of dissolved concentrations of sodium, calcium, and magnesium for three watersheds is presented in Tables 1, 2 and 3. These results show an increase in sodium, calcium, and magnesium concentrations in discharge water moving north from the CHR to the LPR watershed. The mean sodium, calcium, and magnesium concentrations increased from131.7 to 377.7 mg/L ($p < 0.001$, df = 27), from 18.82 to 38.04 mg/L ($p = 0.045$, df = 27) and from 9.28 to 25.38 mg/L ($p < 0.001$, df = 27) from the CHR to LPR watershed, respectively. However, only sodium concentrations increased in pond waters, with an increase from 134.5 to 377.4 mg/L ($p < 0.001$, df = 27) from the CHR to LPR watershed. The mean concentrations of calcium and magnesium in pond waters did, however, have mean values that followed the trend of lowest concentrations in the CHR and increasing to the north with the LPR having the highest mean values (Tables 1, 2, and 3). There were no significant changes within any of the watersheds between the discharge water and pond water in the concentrations of sodium, calcium, or magnesium. However, in the LPR watershed, the calcium concentrations in pond waters do appear to decrease from the corresponding discharge values, particularly in the 2000 sample season (Table 1). While this is not a statistically significant change, this suggests probable precipitation of calcite in pond waters, and causing higher SAR values in LPR watersheds. Also, the BFR watershed shows increases, although not significant, in the mean dissolved concentrations of sodium, calcium, and magnesium in holding ponds over the associated discharge water (Table 2).

Dissolved concentrations of potassium in CBM discharge water increased from 6.04 to 13.25 mg/L ($p < 0.001$, df = 27) from the CHR to the LPR watershed. Pond waters increased in potassium from 6.07 to13.17 mg/L ($p = 0.002$, df = 27) from the CHR to the LPR watershed, respectively. There was no change in the dissolved concentration of potassium between CBM discharge points and holding ponds in any of the watersheds. The dissolved concentration of sulfate in CBM discharge water and pond water shows no difference among any of the watersheds. There are also no significant differences between discharge and pond waters within any of the watersheds, but holding ponds in the BFR and LPR watersheds have noticeably higher mean sulfate values than associated discharges. For example, mean dissolved concentration of sulfate increased from 8.16 to 181 mg/L in the BFR watershed and from 1.06 to 119 mg/L in the LPR watershed. These large differences in means, while not statistically significant, suggest an increase in dissolved concentration of sulfate in holding ponds is due to dissolution of gypsum in soils associated with the holding ponds. Chloride does not show any changes in discharge or pond waters among watersheds, or within any watershed between discharge and pond waters.

A comparison of SAR*p* and SAR*t* values and descriptive statistics are shown in Table 4. The mean practical sodium adsorption ratio (SAR*p*) for CBM discharge water from LPR watershed (11.96) is much higher than in the BFR watershed (7.75, $p < 0.001$, df = 27) or in the CHR watershed (6.43, $p < 0.001$, df = 27). This is due to the higher dissolved concentration of sodium compared to dissolved concentration of calcium and magnesium, particularly in the LPR watershed. Dissolved sodium concentrations of 377.7 mg/L in the LPR discharge water were much higher than 177.4 mg/L in the BFR ($p < 0.001$, df = 27) or the 131.7 mg/L in the CHR ($p < 0.001$, df = 27). The SAR*p* in pond waters decreases similarly from the LPR (12.59) to the BFR (7.93, $p = 0.009$, df = 27) and to the CHR (6.76, $p = 0.003$, df = 27) watershed. There was no significant difference in SAR*p* values between CBM discharge water and holding pond water within

TABLE 4. Comparison of SAR*p* and SAR*t* of CBM Product Water and Corresponding Ponds and Descriptive Statistics Across the Powder River Basin, Wyoming. D, P, M, SD, and n are discharge, pond, mean, standard deviation, and sample size, respectively.

	Little Powder River Watershed				Belle Fourche River Watershed				Cheyenne River Watershed			
	SAR*p*		SAR*t*		SAR*p*		SAR*t*		SAR*p*		SAR*t*	
Site	**D**	**P**	**D**	**P**	**D**	**P**	**D**	**P**	**D**	**P**	**D**	**P**
					1999							
1	12.08	13.75	14.59	16.95	8.11	8.03	9.46	9.51	7.15	7.56	7.96	8.43
2	14.70	14.36	17.96	17.83	9.30	7.98	10.82	9.17*	6.15	6.44	6.99	7.42
3	12.77	13.55	15.29	16.84	6.97	7.07	7.99	8.09	5.76	5.86	6.56	6.67
4	12.78	4.88	15.49	6.63	9.08	7.21	10.37	8.30				
5	11.28	4.84	13.79	6.61								
6	12.93	13.25	15.90	16.58								
7	16.69	16.12	20.32	19.72								
					2000							
1	10.42	11.84	12.69	14.80	7.13	10.32	8.27	15.28	7.34	7.51	8.18	8.48
2	10.60	12.51	12.96	16.35	7.56	8.93	8.79	10.49	6.32	7.10	7.18	8.15
3	9.49	21.53	11.60	35.40	6.98	6.96	8.09	8.08	5.85	6.08	6.70	7.05
4	10.10	9.95	12.37	12.53	6.90	6.96	7.88	7.95				
5	10.28	9.95	12.60	12.54								
6	11.24	12.73	13.79	16.10								
7	12.06	16.94	14.79	22.92								
					Descriptive Statistics							
M	11.96	12.59	14.58	16.56	7.75	7.93	8.96	9.61	6.43	6.76	7.26	7.70
SD	1.955	4.400	2.364	7.020	0.975	1.184	1.137	2.456	0.668	0.736	0.667	0.761
n	14	14	14	14	8	8	8	8	6	6	6	6

*When speciated, this sample attained a charge imbalance of 29 percent; all other samples attained speciated charge imbalances of less than10 percent.

all three watersheds, despite the larger mean SAR*p* values for pond waters in all three watersheds (Table 4). But these comparisons all assume that dissolved concentration equals activity in the calculation of SAR*p* values. Thus, all samples were corrected for ion activities using the MINTEQA2 model and SAR*t* values were calculated from activities of sodium, calcium, and magnesium. All samples attained a charge imbalance of less than 10 percent (after ion activity calculations), except for the 1999 Site No. 2 pond sample from the BFR watershed, which had a charge imbalance of 29 percent.

Comparisons using SAR*t* between discharge waters and pond waters from different watersheds and within watersheds yielded identical results to those presented using SAR*p*. The mean SAR*t* value for LPR discharge water (14.58) is higher than discharge water in the BFR (8.96, $p < 0.001$, df = 27) and CHR watershed (7.26, $p < 0.001$, df = 27). The mean SAR*t* value for pond waters has similar results, with LPR watershed (16.56) being higher than either the BFR watershed (9.61, $p = 0.016$, df = 27) or CHR watershed (7.70, $p = 0.005$, df = 27). The SAR*t* values observed were not significantly different between discharge waters and pond waters within any watershed.

Sposito and Mattigod (1977) identified the difference between the practical sodium adsorption ratio (SAR*p*) and the true sodium adsorption ratio (SAR*t*) and suggest that the relationship between SAR*p* and SAR*t* will be nonliner in high saline and high SAR waters (SAR > 10) due to aqueous ionic interactions and complexation processes. Figure 3 shows the SAR*p* values plotted on the X-axis versus the corresponding SAR*t* values on the Y-axis for all CBM discharge and pond waters in all three watersheds. This study finds a similar relationship between SAR*p* and SAR*t*. In low salinity and low SAR waters (SAR < 10) such as the BFR and CHR watersheds the SAR*t* values for both discharge points and corresponding holding ponds compare well with SAR*p* values. There is no difference between SAR*p* and SAR*t* in BFR discharge, BFR pond, CHR discharge, or CHR pond waters. In high saline and high SAR waters such as LPR watershed the SAR*t* values predicted from free ion activities did not significantly change from the SAR*p* values. However, in the LPR there was a

noticeable difference in mean SAR*p* and SAR*t* values in both discharge waters and pond waters (Table 4). This corresponds to the notable divergence of the SAR*t* from the SAR*p* values at approximately 10 SAR (Figure 3). This is attributed to the formation of ion pairs and complexes because in high saline waters ionic interaction increases to form ion pairs and complexes. The predicted SAR*t* values for high saline waters are consistent with the results of Sposito and Mattigod (1977).

CONCLUSIONS

Analysis of CBM product water at discharge points suggests that chemical attributes including pH, EC, TDS, alkalinity, sodium, calcium, magnesium, potassium, SAR*p*, and SAR*t* all significantly increase moving from the CHR to the LPR watersheds. The CBM pond waters show significant increases in EC, TDS, alkalinity, sodium, potassium, SAR*p*, and SAR*t* moving along the same gradient from the CHR watershed to the LPR watershed. Within the three watersheds, CBM product water in the CHR watershed showed no changes in chemical attributes between discharge water and associated holding pond water. However, CBM product water from the LPR watershed showed a substantial increase in pH, with noticeable, but not significant increases in mean EC and TDS values in associated holding ponds, with the BFR watershed also showing noticeable, but not significant increases in pH, EC, and TDS in holding pond water.

Application of saline water for irrigation is of less concern in humid and well drained soils compared to arid and semi-arid environments, because rainfall is a major source of salt free water. Furthermore, water that is not consumed by plants or evapotranspiration moves rapidly through the root system. Application of salty water to arid and semiarid soils containing carbonate and clay minerals with poor drainage may accumulate salts, decrease infiltration, and increase runoff and erosion (Hanson *et al.,* 1993). A recent study (Mace and Amerhein, 2001) evaluates the effects of irrigation water with moderate SAR (< 8) on physical properties of Milham clay loam soil (Typic Haplargid) and reports that water with SAR as low as 5 will have an adverse effect on the soil structure and infiltration rates.

Overall, results of this study show that pH, EC, TDS, alkalinity, sodium, calcium, magnesium, potassium, SAR*p*, and SAR*t* of CBM product water at

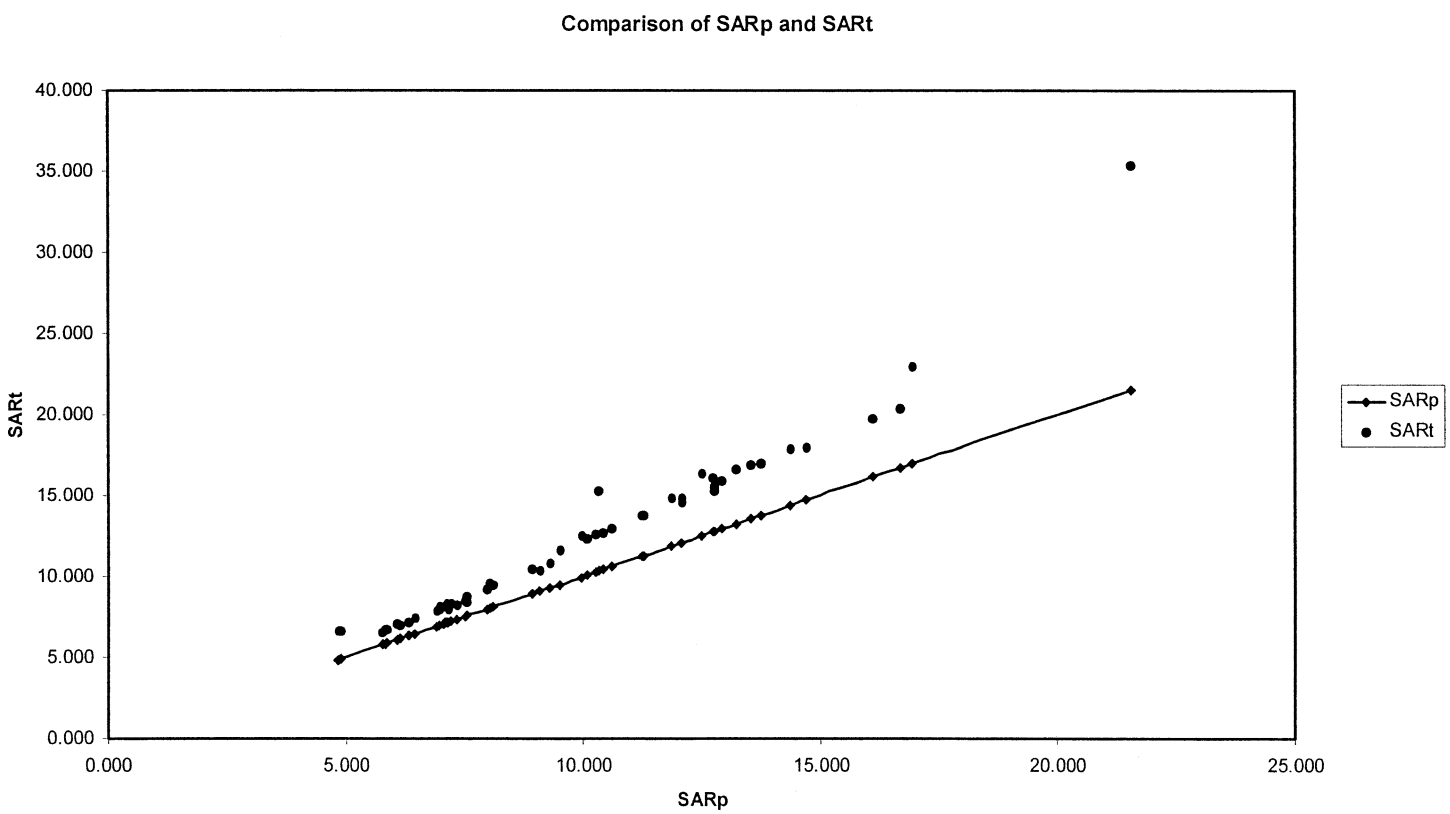

Figure 3. Plot of SAR*p* Versus SAR*t* of CBM Product Water and Corresponding Ponds Across the Powder River Basin, Wyoming. Solid line represents the 1:1 relationship where SAR*p* and SAR*t* are equal.

discharge points increases moving from the CHR watershed to the LPR watershed. The CBM pond waters show significant increases in EC, TDS, alkalinity, sodium, potassium, SAR*p*, and SAR*t* moving from the CHR watershed to the LPR watershed. The BFR watershed shows significant differences from the other two watersheds in very few cases, but has mean values for almost every parameter that are less than the LPR watershed, but greater than the CHR watershed. Our results suggest that release of CBM product water onto arid and semiarid rangelands in the LPR, and to some extent in the BFR watersheds, may cause precipitation of calcium carbonate in soils, which in turn may decrease infiltration rates and increase runoff and erosion. The data discussed in this research may help federal and state agencies, landowners, and the CBM industry in arid and semiarid areas to develop appropriate irrigation management schemes for CBM product water based on soil physical and chemical properties. Further research to determine the long term changes in the quality of CBM product water at discharge points and in corresponding holding ponds will be useful.

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LITERATURE CITED

Allison, J. D. and D. S. Brown, 1992. MINTEQA2: An Equilibrium Metal Speciation Model. Environmental Protection Agency, Environmental Research Laboratory, Athens, Georgia.

American Public Health Association, 1992. Standard Methods for the Examination of Water and Wastewater. American Public Health Association, Washington, D.C.

Ellis, M.S., G. D. Stricker, R. M. Flores, and L. R. Bader, 1998. Sulfur and Ash in Paleocene Wyodak-Anderson Coal in the Powder River Basin, Wyoming and Montana: A Non-Sequitur to Externalities Beyond 2000. Proceedings of the 23rd International Technical Conference on Coal Utilization, Clearwater, Florida.

Flores, R. M. and L. R. Bader, 1999. Fort Union Coal in the Powder River Basin, Wyoming and Montana: A Synthesis. U.S. Geological Survey Professional Paper 1625-A, Chapter PS.GRI-99/0131.

Hanson, B., S. R. Grattan, and A. Fulton, 1993. Agricultural Salinity and Drainage: A Handbook for Water Managers. University of California Irrigation Program, University of California, Davis, California.

Hill, D. G., C. R. Nelson, and C. F. Brandenburg, 2000. Changing Perceptions Regrading the Size and Production Potential of North America Coalbed Methane Resources. *Available at* www.srinstitute.com. *Accessed* March 2000.

Keren, R., 2000. Salinity. *In:* Handbook of Soil Science, M. E. Sumner (Editor). ISBN 0-8493-3136-6, CRC Press, Boca Raton, Florida.

Knight, D. H., 1994. Mountains and Plains: The Ecology of Wyoming Landscapes. Yale University Press, New Haven, Connecticut.

Mace, J. E. and C. Amerhein, 2001. Leaching and Reclamation of a Soil Irrigated With Moderate SAR Waters. Soil Science Society of America Journal 65:199-204.

McBeth, I. H., K. J. Reddy, and Q. D. Skinner, 2001. Quality of Coalbed Methane Product Water: Arsenic, Boron, Fluoride, and Selenium. *In:* Water Quality Monitoring and Modeling Proceedings, J. J. Warwick (Editor). American Water Resources Association, Middleburg, Virginia, TPS-01-1, pp. 259-264.

Nelson, C. R., 1999. Gas Research Institute North American Coalbed Methane Resource Map. GRI Report No. GRI-99/0131.

NRCS (National Resource and Conservation Service), 2002. Soils of Wyoming. *Available at* www.statelab.iastate.edu/soils/sc/wwwforms/fozzy.uwyo.edu. *Accessed* August 2002.

Ramsey, F. L. and D. W. Schafer, 1997. The Statistical Sleuth: A Course in Methods of Data Analysis. Duxbury Press, Belmont, California.

Reddy, K. J., Q. D. Skinner, and I. H. McBeth, 2001. Exploring Uses for Coalbed Methane Product Water. College of Agriculture, University of Wyoming, Laramie, Wyoming, Reflections11:22-24.

Reddy, K. J., W. L. Lindsay, S. M. Workman, and J. I. Drever, 1990. Measurement of Calcite Ion Activity Products in Soils. Soil Science Society of America Journal 54:67-71.

Rice, C. A., M. S. Ellis, and J. H. Bullock, Jr., 2000. Water Co-Produced With Coalbed Methane in the Powder River Basin, Wyoming: Preliminary Compositional Data. Open-File Report 00-372, U.S. Geological Survey, Denver, Colorado.

Sposito, S. and S. V. Mattigod, 1977. On the Chemical Foundation of the Sodium Adsorption Ratio. Soil Science Society of American Journal 41:323-329.

SRI (Strategic Research Institute), 2000. Coalbed and Coal Mine Methane: A New Energy Resource for 21st Century. *Available at* www.srinstitute.com. *Accessed* March 2000.