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Composite Geochemical Database for Coalbed Methane Produced Water Quality in the Rocky Mountain Region

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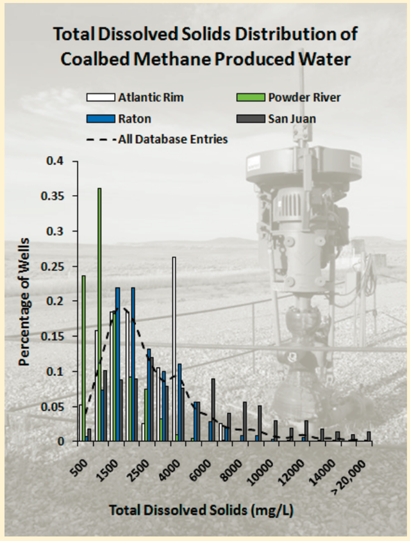
S *Supporting Information*

ABSTRACT: Coalbed methane (CBM) or coalbed natural gas (CBNG) is an unconventional natural gas resource with large reserves in the United States (US) and worldwide. Production is limited by challenges in the management of large volumes of produced water. Due to salinity of CBM produced water, it is commonly reinjected into the subsurface for disposal. Utilization of this nontraditional water source is hindered by limited knowledge of water quality. A composite geochemical database was created with 3255 CBM wellhead entries, covering four basins in the Rocky Mountain region, and resulting in information on 64 parameters and constituents. Database water composition is dominated by sodium bicarbonate and sodium chloride type waters with total dissolved solids concentrations of 150 to 39,260 mg/L. Constituents commonly exceeding standards for drinking, livestock, and irrigation water applications were total dissolved solids (TDS), sodium adsorption ratio (SAR), temperature, iron, and fluoride. Chemical trends in the basins are linked to the type of coal deposits, the rank of the coal deposits, and the proximity of the well to fresh water recharge. These water composition trends based on basin geology, hydrogeology, and methane generation pathway are relevant to predicting water quality compositions for beneficial use applications in CBM-producing basins worldwide.



INTRODUCTION

Coalbed methane is an unconventional natural gas resource with large reserves in the United States (US) and worldwide. To produce gas, water is removed in large volumes from wells to reduce hydrostatic pressure in the aquifer allowing methane to desorb from the coal.[1] The water produced as a byproduct to gas production is termed produced water, product water, or coproduced water. Produced water represents the largest waste stream volume associated with gas production.[2] New Mexico, Colorado, and Alabama contain 75% of proven CBM resources in the US and greater than 80% of current US production occurs in the Rocky Mountain region.[3] Much of this region has an arid to semiarid climate and is faced with water scarcity from overallocated freshwater sources.

CBM produced water exhibits lower total dissolved solid (TDS) concentrations than conventional oil and gas produced water, with TDS concentrations in Rocky Mountain basins ranging from 370 to 43,000 mg/L as compared to 1000 to 400,000 mg/L for conventional oil and gas resources.[4] Lower TDS concentrations suggest a greater likelihood for this type of produced water to be utilized as an alternative water resource. Utilization of this nontraditional water source for irrigation, streamflow enhancement, and drinking water augmentation is hindered by limited knowledge of water solute composition and ranges of expected constituent concentrations.

The goal of this study is to assess the geochemical signature of CBM produced water in four of the major CBM basins in the Rocky Mountain region through the creation of a composite geochemical database. The database is used to compare CBM produced water quality to suggested constituent concentrations for beneficial use applications. The database is also used to determine the influence of specific basin attributes, such as coal depositional environments, proximity to freshwater recharge, and methane formation pathway, on water compositions that impact suitability for beneficial use applications.

MATERIALS AND METHODS

Database Focus Area and Assimilation. This study focused on major CBM basins in the Rocky Mountain region that include the Atlantic Rim portion of the Greater Green River, Powder River,

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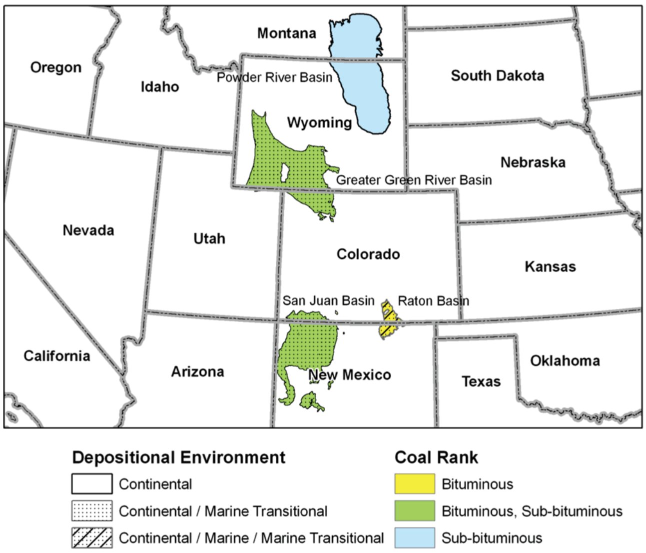

Figure 1. Coalbed methane study basins in the Rocky Mountain region.

Raton, and San Juan (Figure 1). Water quality data were limited to produced water sampled at the wellhead to standardize data collection. Database entries were collected from public entities including the United States Geological Survey (USGS), the Colorado Oil and Gas Conservation Commission (COGCC), and the Wyoming Oil and Gas Conservation Commission (WOGCC).[5−7] Nonpublic historical water quality analyses were contributed by producers in each basin.

Wellhead Sampling. To supplement limited constituent information, field samples were collected from each basin. Wellhead locations were chosen to include wells from various producing coal formations and represent a geographic spread across the basin. Wellhead samples were collected between October of 2008 and August of 2010. Twenty samples were collected from the Atlantic Rim, 31 samples from the Powder River Basin, 40 samples from the Raton Basin, and 20 samples from the San Juan Basin. At each wellhead, samples were collected for on-site field analyses that included pH (Fisher Scientific Accumet pH meter), temperature, dissolved oxygen (DO), and conductivity (YSI 85 multiprobe meter). Additional samples were collected for laboratory analyses. Two unpreserved 1-L samples were collected in amber glass bottles for analysis of TDS and total suspended solids (TSS), alkalinity, nonmetal analyses, turbidity, total and dissolved organic carbon (TOC/DOC), ultraviolet (UV) absorbance at 254 nm, and total recoverable petroleum hydrocarbons (TRPH). One 100 mL acidified sample for metals analyses and two preserved 40 mL samples for benzene, toluene, ethylbenzene, and xylene (BTEX) were also collected. Water quality analyses including methods and instrumentation are provided in Supporting Information, Table 1.

Database Quality Assurance and Quality Control. To ensure the highest quality of data collected for input into the database, a number of criteria were utilized to reject data of insufficient quality (Supporting Information, Table 2). The first criterion assured that all data entries were from CBM wells and was evaluated using well drilling permits, state well records, and American Petroleum Institute (API) numbers. Wells were matched with public records to ensure the listed producing formation was a coal gas formation based on the WOGCC and COGCC state definitions. Finally, data source information was utilized to eliminate samples collected from locations other than the wellhead, for instance at a separator, outfall, discharge point, or an impoundment.

The second criterion included four specific methods modified from Hitchon and Brulotte (1994) for eliminating data based on acceptable chemical analyses.[8] These methods were applied to each well head entry and included (1) absence of expected constituents; (2) evidence of improper sample preservation; (3) drilling contamination; and (4) overall data quality through an ionic balance within ±15%.

Statistical outliers were determined for each constituent based on the overall database values and if identified resulted in the elimination of the entire well entry. Outliers were defined as exceeding three standard deviations from the database average and representing a singular anomaly, less than 1% of the entries exceeding the 99% confidence interval in each basin. The singular anomaly criterion allowed inclusion of grouped entries to avoid the removal of a statistical confidence eclipse. This third criterion was important, as the database spans multiple regions and clustered data entries may exist for certain constituents.

Finally, sampled well entries from similar locations were compared to ensure data source quality. Sampled wells, private data, and public entries were compared through the use of a two sample *t test*. Using $P = 0.05$, TDS entries, and the three most common ions in CBM produced water (sodium, bicarbonate, and chloride) were compared in each data set to justify similarity. The two sample *t test* was chosen for the fourth criterion, because it is conservative and robust against nonnormality.[9]

Comparison to Beneficial Use Applications. The completed database was compared to suggested constituent levels for drinking water, livestock water, and irrigation water. All individual well entries in the database were compared to suggested constituent levels and tallied to determine the percentage of wells in each basin exceeding specific standards. Not all well analyses included complete constituent information; therefore, parameters and constituents were compared to beneficial use standards only when reported. The percentage of wells exceeding a standard is based on the total number of wells reporting. For instances where comparing a calculated value to standards, the value is only calculated for wells reporting all of the required input parameters.

RESULTS

The resulting geochemical database contains 3255 well entries, 1% of which are in the Atlantic Rim area of the Greater Green River, 14% in the Powder River, 65% in the Raton, and 20% in the San Juan. The database in final form contains 64 parameters and constituents. The average, minimum, and maximum concentrations for each constituent by basin are provided in Table 1. Quality assurance and control (QA/QC) criteria of acceptable chemical analysis eliminated 40% of the original 5489 well entries. Database QA/QC resulted in the elimination of 33% of well entries from public sources, 65% from private producer data, and 2% from the study well sampling campaign. Of the data remaining, 67% represents sources outside the public domain.

CBM produced water is expected to exhibit lower TDS on average than conventional produced water sources because organic material forming coal deposits are more commonly limnic than marine.[10] Database TDS distributions revealed that a majority of wells fall in the lower portion of the observed TDS range of 150 to 39,260 mg/L. Over 16% of the database TDS values are at or below 1000 mg/L and 85% have TDS values less than 5000 mg/L. Analysis of the TDS composition reveals that

Table 1. Water Quality Database Constituent Information by Producing Basin (Average, Minimum, and Maximum)[c]

composite water quality database constituents/parameters	Greater Green River/Atlantic:Rim avg.	Greater Green River/Atlantic:Rim min. - max.	Powder River avg.	Powder River min. - max.	Raton avg.	Raton min. - max.	San Juan avg.	San Juan min. - max.	total entries
Physicochemical Parameters									
pH (S.U.)	7.93	6.97 - 9.25	7.71	6.86 - 9.16	8.19	6.90 - 9.31	7.82	5.40 - 9.26	3255
temperature (°C)	24.4	15.1 - 29.5	22.6	10 - 28.5	45.3	13.5 - 100.0	28.6	17.9 - 42.7	238
dissolved oxygen (DO) (mg/L)	0.29	0.03 - 1.70	1.07	0.11 - 3.48	0.39	0.01 - 3.52	0.51	0.04 - 1.69	73
conductivity (μS/cm)	3552	1010 - 10,600	1598	413 - 4420	3199	742 - 11,550	5308	232 - 18,066	901
total dissolved solids (TDS) (mg/L)	2148	610 - 6230	997	252 - 2768	2512	244 - 14,800	4693	150 - 39,260	3219
total suspended solids (TSS) (mg/L)	6.3	BDL - 24.8	11.0	1.4 - 72.7	32.3	1.0 - 580.0	47.2	1.4 - 236.0	1402
turbidity (NTU)	11.9	0.5 - 69.0	8.2	0.7 - 57.0	4.5	0.3 - 25.0	61.6	0.8 - 810.0	81
sodium adsorption ratio (SAR)[a]	51.6	12.8 - 88.1	16.2	0.2 - 78.9	72.2	6.1 - 152.9	68.3	1.1 - 452.8	3169
Organic Parameters									
dissolved organic carbon (DOC) (mg/L)	1.16	0.55 - 2.36	3.18	1.09 - 8.04	1.26	0.30 - 8.54	3.21	0.89 - 11.41	81
total organic carbon (TOC) (mg/L)	1.18	0.45 - 2.35	3.52	2.07 - 6.57	1.74	0.25 - 13.00	2.91	0.95 - 9.36	82
specific ultraviolet absorbance (SUVA) (L/mg-m)[b]	1.09	0.31 - 2.18	1.12	0.46 - 1.83	2.67	0.00 - 10.70	3.32	0.00 - 25.23	81
ultraviolet absorbance (UVA) at 254 nm (L/cm)	0.012	0.004 - 0.030	0.038	0.005 - 0.110	0.029	0.000 - 0.197	0.110	0.000 - 1.404	81
UVA at 272 nm (L/cm)	0.009	0.002 - 0.025	0.026	0.003 - 0.070	0.024	0.000 - 0.175	0.085	0.000 - 1.098	81
UVA at 436 nm (L/cm)	0.001	0.000 - 0.008	0.001	0.000 - 0.003	0.001	0.000 - 0.020	0.010	0.000 - 0.163	81
oil and grease (mg/L)	5.32	1.00 - 11.0	n/a	n/a - n/a	9.10	0.60 - 17.6	n/a	n/a - n/a	51
total recoverable petroleum hydrocarbon (TRPH) (mg/L)	0.75	BDL - 3.00	BDL	BDL - BDL	BDL	BDL - BDL	2.55	BDL - 10.00	16
benzene (μg/L)	n/a	BDL - BDL	n/a	n/a - n/a	4.7	BDL - 220.0	149.7	BDL - 500.0	947
ethylbenzene (μg/L)	n/a	BDL - BDL	n/a	n/a - n/a	0.8	BDL - 18.0	10.5	BDL - 24.0	35
toluene (μg/L)	n/a	BDL - BDL	n/a	n/a - n/a	4.7	BDL - 78.0	1.7	BDL - 6.2	926
xylenes (total) (μg/L)	n/a	BDL - BDL	n/a	n/a - n/a	9.9	BDL - 190.0	121.2	BDL - 327.0	64
Radionuclides									
gross alpha (pCi/L)	n/a	n/a - n/a	n/a	n/a - n/a	10.6	0.2 - 46.1	n/a	n/a - n/a	30
gross beta (pCi/L)	n/a	n/a - n/a	n/a	n/a - n/a	15.6	0.7 - 122.0	n/a	n/a - n/a	38
radium-226 + radium-228 (pCi/L)	4.29	0.20 - 17.0	0.88	BDL - 2.70	0.44	BDL - 5.00	n/a	n/a - n/a	449
radon 222 (pCi/L)	n/a	n/a - n/a	n/a	n/a - n/a	34.2	0.30 - 139	n/a	n/a - n/a	134
uranium (mg/L)	0.03	BDL - 0.17	BDL	BDL - BDL	0.34	BDL - 2.50	0.08	BDL - 0.65	83
Inorganic Parameters									
alkalinity (as $CaCO_3$) (mg/L)	1488	524 - 2792	1384	653 - 2672	1107	130 - 2160	3181	51 - 11,400	2347
aluminum (Al) (mg/L)	0.014	BDL - 0.068	0.018	BDL - 0.124	0.193	BDL - 2.900	0.069	BDL - 0.546	163
antimony (Sb) (mg/L)	BDL	BDL - BDL	BDL	BDL - BDL	BDL	BDL - BDL	BDL	BDL - BDL	11
arsenic (As) (mg/L)	0.027	BDL - 0.300	0.001	BDL - 0.004	0.010	BDL - 0.060	0.001	BDL - 0.020	308
barium (Ba) (mg/L)	1.31	0.05 - 6.95	0.61	0.14 - 2.47	1.67	BDL - 27.40	10.80	BDL - 74.0	619
beryllium (Be) (mg/L)	BDL	BDL - BDL	BDL	BDL BDL	BDL	BDL - BDL	BDL	BDL - BDL	81
bicarbonate (HCO_3) (mg/L)	1630	524 - 2870	1080	236 - 3080	1124	127 - 2640	3380	117 - 13,900	3255
boron (B) (mg/L)	1.15	0.30 - 2.21	0.17	BDL - 0.39	0.36	BDL - 4.70	1.30	0.21 - 3.45	1771
bromide (Br) (mg/L)	0.72	BDL - 2.26	0.09	BDL - 0.26	4.86	0.04 - 69.60	9.77	BDL - 43.48	1073
cadmium (Cd) (mg/L)	BDL	BDL - BDL	BDL	BDL - 0.002	0.002	BDL - 0.003	0.002	BDL - 0.006	18
calcium (Ca) (mg/L)	12.73	1.50 - 51.2	32.09	2.00 - 154.0	14.47	0.81 - 269.0	53.29	1.00 - 5530	3239
carbonate (CO_3) (mg/L)	n/a	n/a - n/a	2.17	0.00 - 139.0	51.30	1.30 - 316.33	40.17	0.00 - 1178	1848
chloride (Cl) (mg/L)	336	4.5 - 2190	21	BDL 282	787	4.8 - 8310	624	BDL - 20,100	3135
chromium, total (Cr) (mg/L)	0.002	BDL - 0.021	0.012	BDL - 0.250	0.105	BDL - 3.710	0.002	BDL - 0.023	495
cobalt (Co) (mg/L)	BDL	BDL - BDL	BDL	BDL BDL	0.001	BDL - 0.018	0.001	BDL - 0.017	81
copper (Cu) (mg/L)	0.005	BDL - 0.087	0.078	BDL - 1.505	0.091	BDL - 4.600	0.058	BDL - 0.706	748
cyanide, free (CN) (mg/L)	0.005	0.005 - 0.009	n/a	n/a n/a	0.366	BDL - 3.000	n/a	n/a - n/a	88

Table 1. Continued

composite water quality database constituents/parameters	Greater Green River/Atlantic:Rim avg.	Greater Green River/Atlantic:Rim min. - max.	Powder River avg.	Powder River min. - max.	Raton avg.	Raton min. - max.	San Juan avg.	San Juan min. - max.	total entries
fluoride (F) (mg/L)	4.92	1.20 - 17.50	1.57	0.40 - 4.00	4.27	0.59 - 20.00	1.76	0.58 - 10.00	135
hydrogen sulfide (H_2S) (mg/L)	n/a	n/a - n/a	n/a	n/a - n/a	4.41	BDL - 190.0	23.00	23.00 - 23.00	574
iron (Fe) (mg/L)	1.33	0.03 - 11.69	1.55	BDL - 190.0	7.18	0.09 - 95.90	6.20	BDL - 258.0	2689
lead (Pb) (mg/L)	0.003	BDL - 0.058	BDL	BDL BDL	0.023	BDL - 0.233	0.023	BDL - 0.390	124
lithium (Li) (mg/L)	0.16	0.05 - 0.34	0.13	BDL - 0.34	0.32	0.01 - 1.00	1.61	0.21 - 4.73	249
magnesium (Mg) (mg/L)	7.32	0.60 - 33.95	14.66	BDL - 95.00	3.31	0.10 - 56.10	15.45	BDL - 511.0	3191
manganese (Mn) (mg/L)	0.04	BDL - 0.43	0.02	BDL - 0.16	0.11	0.01 - 2.00	0.19	BDL - 1.34	1845
molybdenum (Mo) (mg/L)	0.023	BDL - 0.049	0.005	BDL - 0.029	0.002	BDL - 0.035	0.020	BDL - 0.040	81
nickel (Ni) (mg/L)	0.005	BDL - 0.01	0.141	BDL - 2.61	0.015	0.004 - 0.11	0.020	BDL - 0.13	99
phosphate (PO_4) (mg/L)	0.08	BDL - 0.68	BDL	BDL BDL	0.04	BDL - 1.00	1.89	BDL - 9.42	239
potassium (K) (mg/L)	30.29	1.70 - 484.0	11.95	BDL - 44.00	6.37	BDL - 29.40	26.99	BDL - 970.0	1475
selenium (Se) (mg/L)	0.009	BDL - 0.119	0.006	BDL - 0.046	0.017	BDL - 0.100	0.018	BDL - 0.067	164
silica (SiO_2) (mg/L)	5.04	4.11 - 5.69	6.46	4.40 - 12.79	7.05	4.86 - 10.56	12.37	3.62 - 37.75	81
silver (Ag) (mg/L)	0.003	0.003 - 0.003	0.003	0.003 - 0.003	0.015	BDL - 0.140	BDL	BDL - BDL	108
sodium (Na) (mg/L)	824	240 - 2400	356	12 - 1170	989	95 - 5260	1610	36 - 7834	3255
strontium (Sr) (mg/L)	0.04	0.01 - 0.15	0.60	0.10 - 1.83	5.87	BDL - 47.90	5.36	BDL - 27.00	145
sulfate (SO_4) (mg/L)	0.45	BDL - 7.62	5.64	BDL - 300.0	14.75	BDL - 253.00	25.73	BDL - 1800	1174
tin (Sn) (mg/L)	0.008	BDL - 0.022	0.006	BDL - 0.028	0.008	BDL - 0.021	0.017	BDL - 0.039	81
titanium (Ti) (mg/L)	BDL	BDL - BDL	BDL	BDL - 0.002	BDL	BDL - 0.002	0.004	BDL - 0.020	81
total nitrogen (TN) (as mg/L N)	0.04	0.03 - 0.11	0.48	BDL - 4.70	2.61	BDL - 26.10	0.46	BDL - 3.76	369
vanadium (V) (mg/L)	BDL	BDL - BDL	BDL	BDL - BDL	0.001	BDL - 0.013	BDL	BDL - BDL	8
zinc (Zn) (mg/L)	0.014	BDL - 0.136	0.063	BDL - 0.390	0.083	0.010 - 3.900	0.047	0.005 - 0.263	219

[a] SAR is calculated based on the following equation: SAR = $[Na^+]/\sqrt{\{0.5 \times ([Ca^{2+}] + [Mg^{2+}])\}}$, Na, Ca, and Mg are all in units of meq/L.[17] [b] SUVA is calculated based on the following equation: SUVA = (UVA @ 254/DOC) × 100, UVA @ 254 in units of 1/cm, DOC in units of mg/L.[31] [c] Constituent entries are formatted as follows: Constituent name (abbreviation/chemical symbol) (units). n/a - Data not available; BDL - entries are below detection limit (see Supporting Information, Table 1).

sodium, bicarbonate, and chloride make up greater than 95% of the total ions on average for each basin, resulting in sodium bicarbonate and sodium chloride type waters consistent with previous studies.[1,4,11−15] CBM produced water is primarily a sodium bicarbonate type, comprising 83% of database well entries. The remaining entries, primarily in both the Raton and San Juan basins, are sodium chloride type waters, with less than 1% of the wells exhibiting another composition such as sodium sulfate or magnesium chloride.

Figure 2 depicts the geochemical composition of CBM produced water in a piper diagram comparing the relative cation and anion makeup. The resulting combined signature effectively illustrates the differences between the basins. As an almost purely bicarbonate type water, the Powder River Basin samples separate from the other basins, with most wells of sodium type, but a significant number of wells spanning a range of calcium and magnesium concentrations. Conversely, the Raton Basin well entries represent mostly pure sodium type waters with low concentrations of calcium and magnesium. Unlike the Powder River samples, the Raton entries can be dominated by either bicarbonate or chloride.

Well entries from the Atlantic Rim are similar to the Raton Basin samples, with higher chloride concentration than the Powder River wells and generally lower calcium and magnesium. Finally, the San Juan Basin represents water types spanning compositional characteristics between the Powder River and Raton well types. Produced waters from the southern portion of the San Juan Basin tend to have higher chloride concentrations than the northern portion due to the hydrogeology of the San Juan Basin with freshwater recharge predominately in the northern region.[11] Freshwater mixing along the groundwater flow gradient provides support for the creation of multiple water compositions spanning the observed spatial ranges of the San Juan Basin.

Beneficial Use Applications. Given the differences in general water composition existing between basins, certain beneficial use applications may be more appropriate for each basin. In addition to the general composition, trace inorganic and organic constituents constituting less than 1% of the ions in produced water also have the potential to exceed regulatory values. Tables 2, 3, and 4 provide the results for the database comparison to suggested standards for drinking, livestock, and irrigation water, respectively.

Drinking Water. Table 2 provides results of the comparison of database to US drinking water standards. Although TDS in CBM produced water is lower than in conventional produced water, levels still exceed 500 mg/L for most wells in the database. The exception is the Powder River Basin where 24% of wells meet the drinking water TDS standard. Drinking water standards were never exceeded for beryllium and zinc in any basin and rarely exceeded pH, cadmium, copper, selenium, silver, and sulfate standards. The Powder River Basin is the most suitable for drinking water applications due to lower TDS, arsenic, barium, cadmium, chloride, lead, manganese, selenium, and silver concentrations.

Benzene is the only BTEX compound detected above the maximum contaminant level (MCL) and occurs in only 7% of the

Table 2. Percentage of Coalbed Methane Wells Exceeding Regulations for Drinking Water[d]

safe constituent levels for drinking water		coalbed methane producing basin			
constituent/parameter	regulatory level[a,b]	Atlantic Rim	Powder River	Raton	San Juan
		Drinking Water - Physicochemical Parameters			
pH[b]	6.5 - 8.5	3%	2%	15%	7%
total dissolved solids (TDS)[b]	500 mg/L	100%	76%	99%	98%
		Drinking Water - BTEX Compounds			
benzene[a]	5 μg/L	0%	n/a	23%	80%
		Drinking Water - Inorganic Parameters			
aluminum (Al)[b]	0.05/0.2 mg/L	33%/0%	27%/0%	46% /15%	100%/43%
arsenic (As)	0.010 mg/L	24%	0%	11%	25%
barium (Ba)[a]	2 mg/L	18%	1%	12%	60%
cadmium (Cd)[a]	0.005 mg/L	0%	0%	0%	11%
chloride (Cl)[b]	250 mg/L	35%	2%	56%	36%
chromium, total (Cr)[a]	0.1 mg/L	0%	50%	14%	0%
copper (Cu)[a,c]	1.3 mg/L	0%	17%	<1%	0%
fluoride (F)[b]/[a]	2.0/4.0 mg/L	94%/53%	20%/0%	80%/53%	27%/3%
iron (Fe)[b]	0.3 mg/L	71%	38%	99%	78%
lead (Pb)[a,c]	0.015 mg/L	6%	0%	23%	63%
manganese (Mn)[b]	0.05 mg/L	19%	15%	56%	55%
selenium (Se)[a]	0.05 mg/L	5%	0%	10%	29%
silver (Ag)[b]	0.10 mg/L	0%	0%	6%	0%
sulfate (SO_4)[b]	250/500 mg/L	0%/0%	1%/0%	0%/0%	1%/< 1%
		Percentage of Wells Exceeding Regulatory Levels for Drinking Water			
any regulatory standard		100%	82%	100%	99%
regulatory standards other than TDS		97%	34%	97%	75%
regulatory standards other than TDS and iron		85%	9%	79%	42%

[a] USEPA Primary MCL.[28] [b] USEPA Secondary MCL.[28] [c] Copper and lead action levels.[28] [d] n/a - data not available. The following constituents and parameters are reported in the database but do not exceed their respective regulatory standards: beryllium (0.004 mg/L[a]), ethylbenzene (700 μg/L[a]), toluene (1,000 μg/L[a]), xylenes (total) (10,000 μg/L[a]), and zinc (5 mg/L[b]). Antimony is included in the database but not compared to regulatory standards because the detection limit of 0.0164 mg/L is greater than the regulatory standard 0.006 mg/L[a].

wells in the total database, mostly in the Raton Basin and in four of the five wells sampled in the San Juan Basin. When considering all the wells in the database greater than 80% of the wells in all basins require treatment for drinking water use. The most commonly exceeded parameters for drinking water applications include TDS and iron. In fact, 91% of wells in the Powder River Basin and 58% of wells in the San Juan Basin meet drinking water standards for constituents other than TDS and iron. The Raton and Atlantic Rim basins contain higher fluoride concentrations exceeding the primary MCL. A majority of wells in all basins are suitable for drinking water applications if targeted treatment reduces iron, fluoride, and TDS concentrations.

Livestock Water. Results of the database wellhead comparison to suggested constituent levels for livestock water are provided in Table 3. A majority of the database wells have less than 3000 mg/L TDS, and none of the wells in the Powder River Basin exceed this level. The parameter most commonly exceeded for livestock water is temperature. Water temperatures ranged from 11.7 to 42.7 °C in sampled wells, although database entries reported temperatures up to 100 °C. Water temperature has the potential to equilibrate in ambient levels at impoundments or outfalls into aquatic environments. In addition to temperature, more than 80% of the sampled wells had DO concentrations less than 1 mg/L. Also, during field sampling most wells were noted to be effervescent. Effervescence may be due to methane saturation or, based on elevated alkalinity at the observed pH,[16] supersaturated with carbon dioxide. Although not specifically evaluated, information on these physicochemical parameters is important for protection of aquatic life at outfalls and stream discharge points.

Levels were never exceeded in any basin for aluminum, boron, cadmium, cobalt, vanadium, and zinc and were rarely exceeded for chromium, copper, lead, nickel, and sulfate. High concentrations of fluoride in the Atlantic Rim and Raton basins require removal prior to livestock water applications. Livestock water reveals a legitimate application for CBM produced water with 92% of the wells in the Powder River Basin meeting suggested standards for this application without treatment. For the other three basins, over 97% of the database is suitable for livestock water if TDS and temperature are reduced.

Irrigation Water. Results of the database wellhead comparison to suggested constituent levels for irrigation water are provided in Table 4. The sodium adsorption ratio (SAR) is used to quantify limitations of adding water with high sodium content relative to calcium and magnesium, to soils, and freshwaters. In Table 4 a SAR of less than 12 is used to identify water suitability for irrigation.[17] CBM produced water generally exhibits elevated SAR values due to the abundance of sodium and relatively lower concentrations of

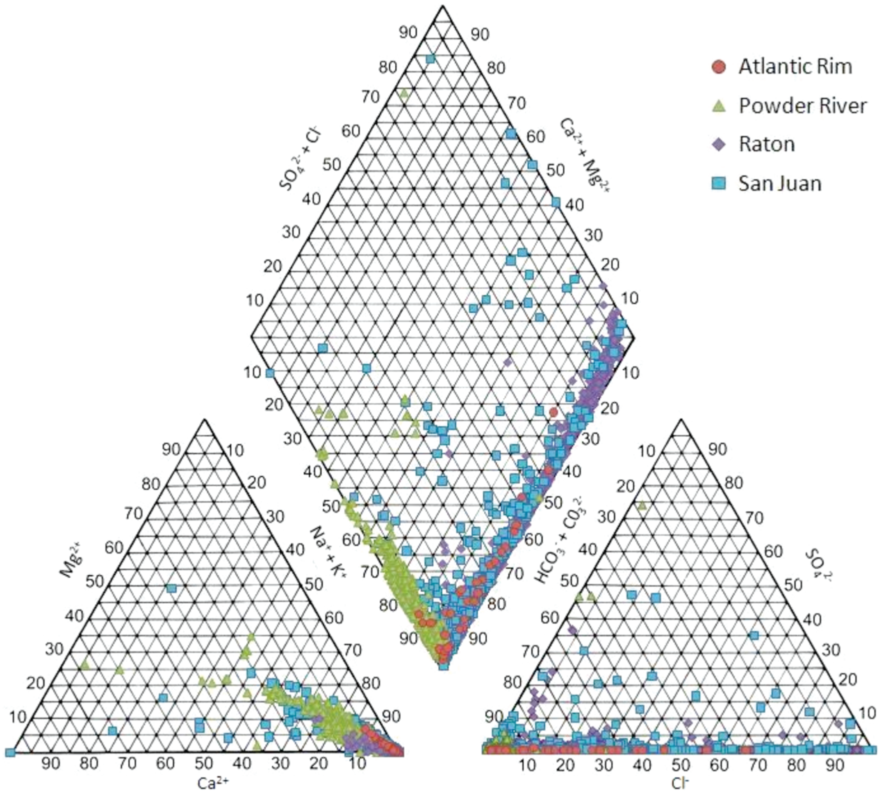

Figure 2. Piper diagram of basin specific coalbed methane geochemical water compositions.

calcium and magnesium. Elevated SAR is characteristic of wells that plot in Figure 2 along the lower right edge of the diamond. Although variations in SAR exist between basins, a majority of the total database wells, 90%, require treatment or chemical soil amendment to reduce the SAR to acceptable levels for irrigation applications. Acceptable TDS levels for irrigation vary with crop type, although 750 mg/L is suggested as a suitable level for most species. A majority of wells exceed this level with the exception of the Powder River Basin where only 20% of wells exceed the recommended TDS concentration.

Suggested levels were never exceeded in any basin for aluminum, beryllium, cadmium, cobalt, lead, and vanadium and rarely exceeded for arsenic, copper, lithium, manganese, nickel, and zinc. Molybdenum and boron are reported in the Atlantic Rim and San Juan basins as exceeding suggested levels in a majority of the wells. Sample information in these basins is limited to 53 entries for these constituents, a majority of which were field samples collected for this study. In Tables 2, 3 and 4, instances with high percentages of wells exceeding standards are commonly linked to the limited sample size for the constituent. If levels for rarely reported constituents, such as fluoride, mirror concentrations observed in sampled well data of this study, then these constituents would also require removal for these applications. Reduction of the TDS, SAR, and fluoride in all basins as well as boron and molybdenum in the Atlantic Rim and San Juan basins allows for a majority of the wells to be used for irrigation water.

■ DISCUSSION

Specific advantages gained from this data set as compared to previous studies include the number of well entries and number of constituents. In order to expand on the four basins studied to CBM basins worldwide, it is important to identify trends in constituents and composition as they relate to producing basin attributes. Trends in constituent occurrence for CBM produced water have been equated with a number of system attributes.[1,11] Therefore, trends in the general composition of CBM produced water were identified in conjunction with three specific system characteristics: 1) coal depositional environment, 2) methanogenesis pathway, and 3) proximity to areas of freshwater recharge.

1). Coal Depositional Environment. Coal deposits are formed 1) within inland freshwater limnic environments such as lakes, 2) within brackish environments, such as bays, deltas, lagoons, and coastal swamps, and 3) within marine environments.[10] Formation water present during coal formation commonly carries attributes of the depositional environment. Limnic or continental deposits have higher residual calcium and magnesium concentrations with lower sodium and potassium concentrations than brackish environments, while saline Na−Cl type waters with high boron content are indicative of a brackish/marine depositional environment.[10] The database confirms that continental coal deposits, such as the Powder River Basin, are Na-HCO_3 water types with lower boron concentrations similar to shallow groundwater formations of $NaHCO_3$ to Na-HCO_3−SO_4 type waters.[11,14] Brackish to marine waters exhibit increased chloride concentrations and higher average concentrations of trace elements. Cheung et al. (2009) showed that brackish/marine environments can contain up to 70 times more concentrated trace elements than the $NaHCO_3$ dominated coal formations.[14] Lower sodium and increased calcium and magnesium concentrations in combination with lower boron concentrations suggest that limnic basins are more suitable for applications requiring lower SARs and boron concentrations such as irrigation water applications.

Table 3. Percentage of Coalbed Methane Wells Exceeding Suggested Levels for Livestock Water[b]

safe constituent levels for livestock water		coalbed methane producing basin			
constituent/parameters	suggested level[a]	Atlantic Rim	Powder River	Raton	San Juan
Livestock Water - Physicochemical Parameters					
total dissolved solids (TDS)	3000 mg/L	26%	0%	24%	51%
temperature	4-18 °C	94%	93%	96%	95%
Livestock Water - Inorganic Parameters					
arsenic (As)	0.2 mg/L	24%	0%	11%	0%
chromium, total (Cr)	1 mg/L	0%	0%	2%	0%
copper (Cu)	0.5 mg/L	0%	17%	3%	8%
fluoride (F)	2 mg/L	94%	20%	80%	27%
lead (Pb)	0.05 mg/L	6%	0%	7%	25%
nickel (Ni)	1.0 mg/L	0%	13%	0%	0%
selenium (Se)	0.05 mg/L	5%	0%	10%	29%
sulfate (SO_4)	1000 mg/L	0%	0%	0%	<1%
Percentage of Wells Exceeding Suggested Levels for Livestock Water					
any suggested constituent level		97%	8%	59%	51%
suggested levels other than TDS		47%	2%	1%	2%
suggested levels other than TDS and SAR		22%	<1%	<1%	1%

[a] Suggested levels for livestock water.[29] [b] The following constituents and parameters are reported in the database but do not exceed their respective regulatory standards: aluminum (5.0 mg/L), boron (5 mg/L), cadmium (0.05 mg/L), cobalt (1.0 mg/L), vanadium (0.1 mg/L), and zinc (25 mg/L).

Table 4. Percentage of Coalbed Methane Wells Exceeding Suggested Levels for Irrigation Water[b]

safe constituent levels for irrigation water		coalbed methane producing basin			
constituent/parameter	suggested level[a]	Atlantic Rim	Powder River	Raton	San Juan
Irrigation - Physicochemical Parameters					
sodium adsorption ratio (SAR)	<13	100%	37%	100%	94%
total dissolved solids (TDS)	750 mg/L	62%	20%	70%	80%
Irrigation - Inorganic Parameters					
arsenic (As)	0.10 mg/L	24%	0%	0%	0%
boron (B)	0.75 mg/L	71%	0%	9%	63%
chloride (Cl)	350 mg/L	29%	0%	48%	32%
chromium, total (Cr)	0.1 mg/L	0%	50%	14%	0%
copper (Cu)	0.2 mg/L	0%	17%	7%	17
fluoride (F)	1.0 mg/L	100%	71%	97%	67%
iron (Fe)	5.0 mg/L	6%	3%	40%	22%
lithium (Li)	2.5 mg/L	20	0%	0%	26%
manganese (Mn)	0.2 mg/L	3%	0%	14%	18%
molybdenum (Mo)	0.01 mg/L	90%	23%	4%	85%
nickel (Ni)	0.2 mg/L	0%	25%	0%	0%
zinc (Zn)	2.0 mg/L	0%	0%	1%	0%
Percentage of Wells Exceeding Suggested Levels for Irrigation Water					
any suggested constituent level		100%	42%	99%	95%
suggested levels other than TDS		100%	38%	98%	91%
suggested levels other than TDS and SAR		100%	11%	43%	21%

[a] Suggested levels for irrigation water.[30] [b] The following constituents and parameters are reported in the database but do not exceed their respective regulatory standards: aluminum (5 mg/L), beryllium (0.10 mg/L), cadmium (0.01 mg/L), cobalt (0.05 mg/L), lead (5.0 mg/L), and vanadium (0.1 mg/L). Selenium is included in the database but not compared to regulatory standards because the detection limit of 0.0374 mg/L is greater than the regulatory standard 0.02 mg/L.

2). Methane Generation Pathway. Coalbed methane is a product of 1) anaerobic biological subsurface processes (biogenic) and 2) temperature transformations (thermogenic) associated with coal formation.[18] The Powder River Basin predominantly produces biogenic methane,[1,19] while limited isotopic information indicates methane is thermogenic in origin in the Raton Basin.[20] The San Juan Basin exhibits some thermogenic methane as well as secondary biogenic methane, potentially due to groundwater recharge, along the northern portion of the basin.[21,22] The USGS (2000) noted the Powder River Basin produces larger water volumes than the Raton and San Juan basins, consistent with characteristics of biogenic methane production in low rank coals with high porosities, high water content, and low temperature.[23] Thermogenic gas is formed when coal formations reach a specific thermal maturity, generally a high-volatile bituminous coal, and is indicative of older, higher rank coals with greater overburden. Water quality characteristics for coals of thermogenic origin can be summarized as elevated water temperatures, increased potential for hydrocarbon gases such as ethane and butane, and deeper coal depths.[1,18,24] Lower temperatures related to lower rank coals and biogenic methane production suggest that low rank coals likely harbor water of a more suitable composition beneficial use applications such as livestock watering, wetlands, or stream discharge.

3). Proximity to Areas of Freshwater Recharge. Formation waters can be diluted by groundwater flow as coal seams behave as regional aquifers when confined by shale or dense sandstone aquitards.[1] Water compositions related to freshwater recharge for this study are categorized in two groups: (1) waters near in proximity to recharge zones and (2) waters distant from recharge zones. For waters near recharge zones, water quality reflects meteoric water recharge with elevated DO, higher TOC, and lower TDS as well as subsurface mineral dissolution resulting in increased calcium, magnesium and sulfate concentrations.[18,24,25] TDS concentrations are commonly lower near recharge zones where residence time is short.[1] For waters distant from recharge zones, mineral ion exchange and precipitation reduce the calcium, magnesium, barium, and sulfate concentrations.[11,18,25] With distance from recharge zones, derived by geographic distance or depth, mixing with formation waters generally increases TDS, alkalinity, sodium, and chloride concentrations.[1,11,12,26,27] Waters in proximity to recharge zones represent the most likely candidates for drinking water applications, particularly if the wells exist in a limnic coal deposit such as the Powder River Basin.

Increased knowledge of CBM-produced water quality composition provides critical information necessary to develop regulatory standards, design treatment processes, and identify beneficial use opportunities to utilize CBM produced water as a resource rather than a waste product. Identifying the underlying basin attributes that result in suitable water compositions allow conclusions from this study to be applicable to CBM basins worldwide. Water quality trends derived from the comparison of database concentrations to standards for these three beneficial use applications provide general information on the type of basin suitable for different types of beneficial use application. Findings of this study add knowledge about the specific constituents requiring treatment for CBM produced water use in various applications and thus help define water treatment requirements to utilize produced water as a beneficial water resource.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Table 1 includes the methods and instrumentation utilized for sample analysis. Table 2 includes the QA/QC criteria utilized in the database assimilation and the results for each basin entries. Tables 3-6 include additional statistical information by basin for each constituent, such as standard deviations, 25th, 50th, and 75th percentile values. This material is available free of charge via the Internet at http://pubs.acs.org.

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