

The geochemical evolution of water coproduced with coalbed natural gas in the Powder River Basin, Wyoming

Elizabeth L. Brinck, James I. Drever, and Carol D. Frost

ABSTRACT

Water produced with coalbed natural gas (CBNG) attains its characteristic sodium-bicarbonate composition through a series of processes, including dissolution of salts, precipitation of salts, pyrite oxidation, ion exchange, sulfate reduction, and methanogenesis. After CBNG-produced water is discharged to the surface, interaction with the atmosphere will initiate the precipitation of calcite, iron hydroxide, and barite among other minerals. The interaction of CBNG-produced waters with semiarid Powder River Basin soils can mobilize accumulated salts, which, through infiltration, can then reach the water table, potentially affecting the quality of the groundwater. The mobilization of the soil-based salts may render the composition of the water recharging the near-surface groundwater very different from the initial chemical composition of the CBNG-produced water. Additionally, prolonged exposure to CBNG-produced water can cause the salinization and sodification of soils surrounding CBNG-produced water ponds and streams carrying CBNG-produced water. This can impact the quantity of biomass and the species composition of the vegetation in proximity to CBNG-produced water discharge locations. The high sodium to calcium and magnesium ratio in CBNG-produced water requires careful management to prevent sodification of irrigated soils when it is used as an irrigation source. In many instances, irrigation with CBNG-produced water requires the addition of soil amendments such as gypsum and sulfur to maintain the fertility and physical qualities of the soil. An understanding of the geochemical evolution of CBNG-produced water is necessary to anticipate and address these potential environmental issues associated with production of CBNG.

INTRODUCTION

Coalbed natural gas (CBNG) production is the process of extracting natural gas from coal beds by depressurizing the coal through the

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removal of the coal aquifer water. The lower pressure allows the natural gas, almost entirely composed of methane, to desorb from the coal and to be collected and used as an energy source (DeBruin et al., 2004). The increasing rate of CBNG production over the last 20 yr has had important influences on Wyoming's economy and environment. One area undergoing intensive CBNG production is the Powder River Basin in northeast Wyoming (approximate latitude 43–46° north and longitude 105–107° west). The Powder River Basin is a semiarid geologic structural and hydraulic basin bounded on the south by the Laramie Mountains, the west by the Big-horn Mountains, and on the northeast by the Black Hills. The Paleocene Fort Union Formation is the target of much of the CBNG production in this area (Bartos and Ogle, 2002).

In 2005, more than 17,000 CBNG wells were in place in the Powder River Basin (Wyoming Oil and Gas Conservation Commission) and more than 3000 more wells planned to be installed by 2010 (DeBruin et al., 2004). During 2005 in the Powder River Basin, 88.62 billion liters of water was produced during CBNG production (Wyoming Oil and Gas Conservation Commission) with an estimated 7 trillion liters of water expected to be produced over the lifetime of the development (DeBruin et al., 2004). How this water is managed subsequent to production has varied through time by producer, by environment, and by regulation. Presently, CBNG-produced water in the Powder River Basin is disposed into surface drainages, on-channel impoundments, off-channel impoundments; dispersed into the air by sprayers; used for surface and subsurface irrigation; re-injected; and treated (Wheaton and Donato, 2004). Depending on the disposal method, CBNG-produced water has the potential to impact groundwater, surface water, and soil quality.

The addition of approximately 7 trillion liters of water to a semiarid watershed such as the Powder River Basin has the potential to impact the ecology and environment. However, the nature and magnitude of these impacts are not clearly understood and accordingly have been the focus of numerous studies over the last decade. This article summarizes Powder River Basin CBNG-produced water research and describes the geochemical evolution of CBNG-produced water from recharge to production, surface discharge, and uptake into the shallow subsurface aquifers, soil, and vegetation. Throughout this process, the chemical composition of the water is dynamic.

Environmental concerns have the potential to slow the production of CBNG in the Powder River Basin in Wyoming and Montana. The Montana Board of Envi-

ronmental Review adopted rules in early 2006 that prohibit the degradation of surface water flowing from Wyoming to Montana. This includes the Powder River, the Little Powder River, and the Tongue River, watersheds undergoing intense CBNG development in Wyoming (Buccino and Jones, 2004; Neary, 2006). Understanding the geochemical evolution of CBNG-produced water throughout the whole cycle is key to drafting appropriate regulations, preventing environmental degradation, and anticipating potential remediation after cessation of CBNG production. Currently, most regulation is based on the initial chemical composition of the CBNG-produced water (Buccino and Jones, 2004). This article, however, demonstrates that, in most situations, the subsequent changes to the water caused by its interaction with the atmosphere and local soils will ultimately determine the impact on the environment of the Powder River Basin.

Several previous studies summarize the geochemical evolution of groundwater in Powder River Basin aquifers like those accessed during CBNG production (Lee, 1981; Van Voast and Reiten, 1988; Clark, 1995; Van Voast, 2003; Wheaton and Donato, 2004). These articles document how water recharging coal aquifers metamorphoses into the sodium-bicarbonate-dominated water which is associated with CBNG-produced water. We expand on the theories presented in these articles and present an alternative to the commonly expressed process of cation exchange to explain sodium concentrations. Extensive data from the Powder River Basin are presented to illustrate geochemical changes. The present article then extends these studies by describing the geochemical changes in CBNG-produced water throughout the entire hydrologic cycle from the initial recharge of coal aquifers to the reintroduction of the produced waters into near-surface aquifers. In summarizing the geochemical changes of CBNG-produced water that occurs after the water is discharged to the surface, we have integrated a wide variety of research in water and soil chemistry. Research investigating the fate of the CBNG-produced water is important because it is the ultimate composition of the water and the geochemical interactions that occur that must be taken into account when regulating discharge or attempting to prevent environmental degradation caused by CBNG-produced water.

EVOLUTION OF WATER CHEMISTRY IN THE POWDER RIVER BASIN

Groundwater evolution within the coal aquifers of the Powder River Basin can be considered in four stages

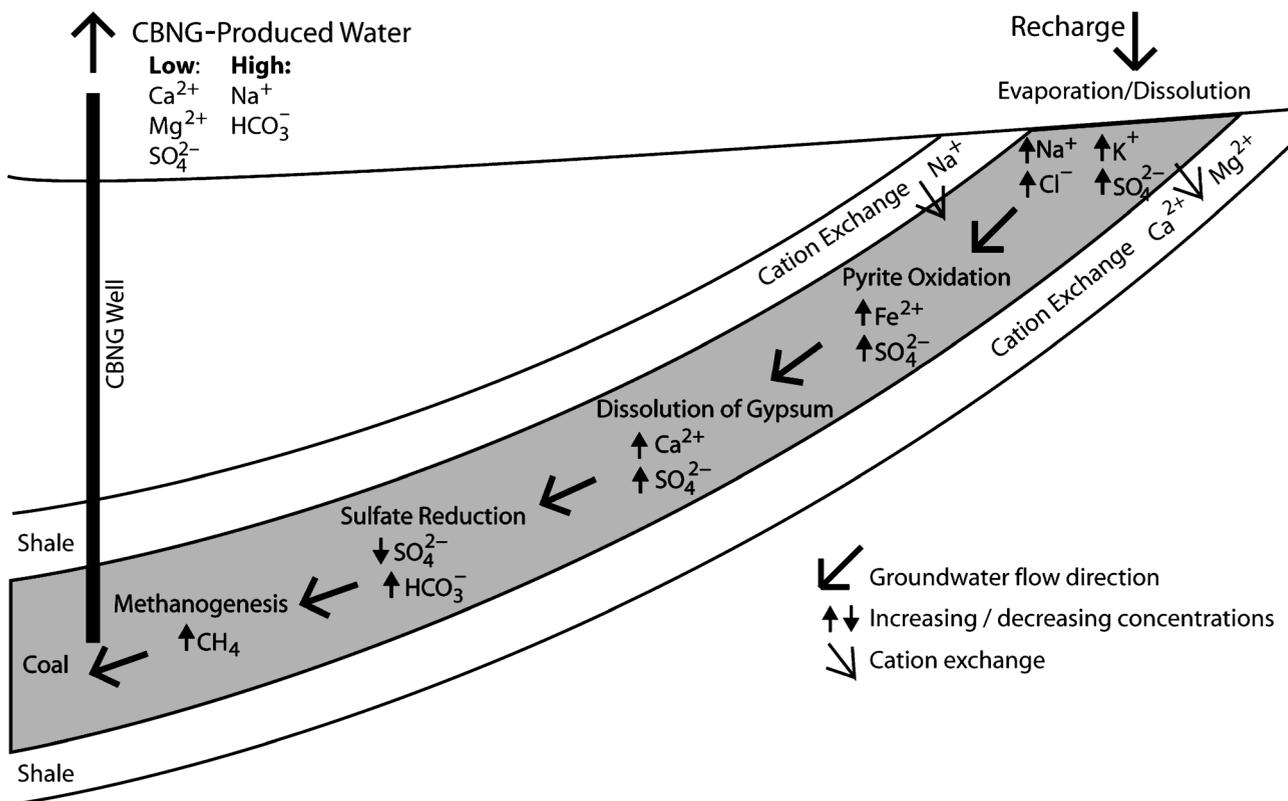


Figure 1. Summary of geochemical processes occurring in coal aquifers used for coalbed natural gas (CBNG) production.

(Figure 1). First is the redissolution of salts that have accumulated in the unsaturated, semiarid soils of the basin such as gypsum, calcite, thenardite, and possibly epsomite (Harris, 1987; Natural Resources Conservation Service [NRCS], 2004). Next, the water dissolves gypsum and salts in the aquifer and incorporates products of pyrite oxidation. Third, sulfate reduction consumes sulfate and generates bicarbonate: this increase in bicarbonate causes the precipitation of calcite, reducing calcium in solution. Lastly, methanogenesis occurs with the generation of methane.

Recharge of Coal Aquifers and Initial Dissolution Reactions

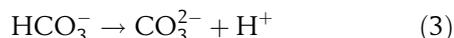
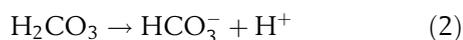
The Powder River Basin extends more than 55,000 km² (21,236 mi²) in Wyoming and Montana within the unglaciated part of the Missouri Plateau of the northern Great Plains. The Powder River Basin was formed during the Laramide orogeny during the Paleocene and Eocene (Hunter, 1999), and is bounded by the Bighorn Mountains and the Casper arch to the west, the Laramie Mountains to the south, the Black Hills to the east, and the Miles City arch to the north. In Wyoming, the axis of this asymmetrical basin trends north-northwest and is

west of the basin center, creating shallowly dipping beds on the eastern margin (approximately 0.5–5°) and steeply dipping beds on the western edge (approximately 20–25°) (Denson et al., 1980; Flores and Bader, 1999). The recharge of Fort Union coal aquifers occurs mainly along the margins of the basin where the coals are exposed at the surface. Clinker beds, baked and hardened sedimentary rocks that are formed by burning of underlying coalbeds, crop out extensively, particularly along the margins of the basin. The rock is highly fractured and permeable and is considered to be a major source of recharge in the Powder River Basin coals (Heffern and Coates, 1999).

The semiarid Powder River Basin receives an average of 42 cm (16 in.) of precipitation per year (NRCS, 2004; Micale and Marrs, 2006), which makes the evaporative concentration of salts and their subsequent dissolution a dominant process in the evolution of water recharging aquifers. The redissolution of evaporite salts will cause the water to take on chemical characteristics indicative of arid basins. Evaporation and transpiration cause the salts associated with rain to accumulate in the soil. During heavy rain events or significant snowmelts, these salts will be brought into solution and reach the

water table (Drever and Smith, 1978). Additionally, mechanical weathering and oxidation of geologic material will provide an additional source of solutes that may be brought into solution (Van Voast and Reiten, 1988). Groundwater in clinker aquifers tends to be calcium-sulfate or calcium-bicarbonate type and lower in total dissolved solids (TDS) than groundwater in unburned sandstones and shales, possibly because the clinker is less reactive than unbaked sedimentary rocks and therefore less soluble (Heffern and Coates, 1999). Additionally, as a major source of recharge in this area, the clinker may be regularly flushed of soluble salts. The dominant ions in the recharge water will be biased toward those that composed the most soluble salts, particularly sodium and sulfate species (for example, thenardite) (Brinck and Frost, 2007a). Drever and Smith (1978) showed that the occasional heavy rains in arid basins will partially redissolve the salts deposited in the soil and vadose zone, and the composition of this water will be dominated by sodium and chloride then sulfate and potassium. Calcium, bicarbonate, magnesium, and silica tend to remain as solids and hence form a minor fraction of the dissolved constituents. The nonmarine origin of the Powder River Basin may be the reason that little chloride is found in the groundwater in this area (Van Voast, 2003).

In addition to the dissolution of salts, water moving through the soil will pick up carbon dioxide (CO₂) from the soil air, which is in higher concentrations than atmospheric CO₂ because of plant respiration (Chapin et al., 2002). Higher concentrations of CO₂ will decrease the pH of the water through the liberation of hydrogen ions (H⁺) (Fetter, 2001):

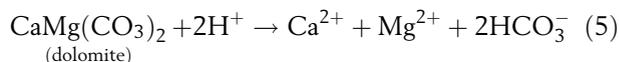
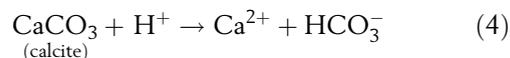


This decrease in pH promotes further dissolution reactions as described below.

Dissolution of Salts and Pyrite Oxidation

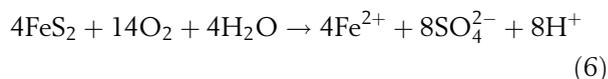
As the pH of the water decreases because of increased dissolved CO₂, phases such as calcite (CaCO₃) and dolomite (CaMg(CO₃)₂) become more soluble. The

dissolution of these phases will add calcium, magnesium, and alkalinity to the water and will raise the pH by consuming available hydrogen ions (Clark, 1995):

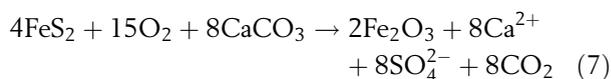


Weathering of silicates (particularly volcanic ash) may also occur in the soils of the recharge area, providing a source of dissolved sodium. Low measured Si concentrations in Powder River Basin coal aquifer water may indicate a subsequent reprecipitation of silica species.

The oxidation of pyrite (FeS₂), a mineral commonly associated with coal (Evangelou, 1998), will increase the sulfate concentration of the groundwater (Lee, 1981; Clark, 1995):

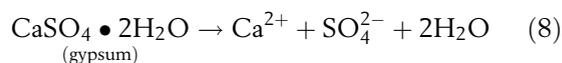


If calcite is present (and it is almost ubiquitous in soils of the Powder River Basin) (NRCS, 2004), the acidity produced by pyrite oxidation will be neutralized by calcite dissolution. The total reaction (including precipitation of iron as a ferric oxide) is summarized by



The net result is the addition of Ca²⁺ and SO₄²⁻ to the water. Significant pyrite oxidation will occur only in the vadose zone: at greater depths in the aquifer, the supply of molecular oxygen, originating with the oxygen-saturated precipitation, will be limited by both chemical and biological consumption.

The dissolution of gypsum will add both calcium and sulfate ions to the water. Dissolution may occur at any point in the aquifer because it is not affected by the availability of oxygen or by the pH of the water:



By adding calcium ions to the water, the dissolution of gypsum can drive the precipitation of calcite. Gypsum,

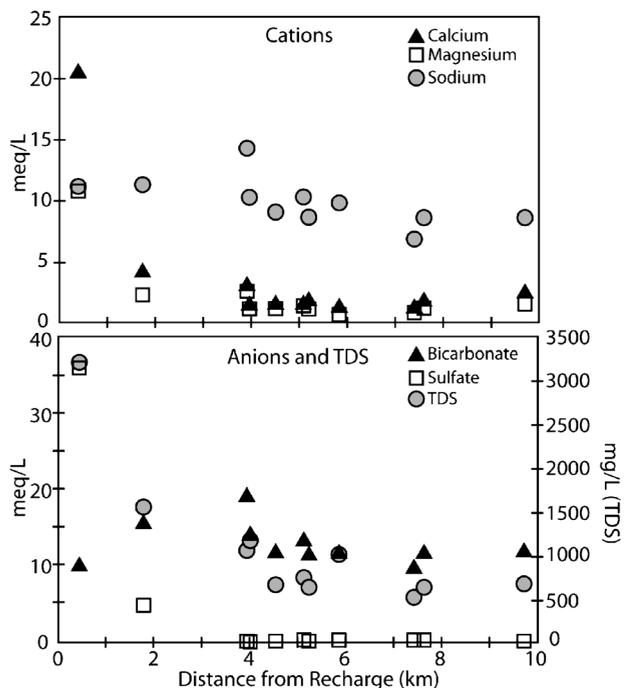


Figure 2. Summary of cation and anion data from wells in the upper Wyodak coal aquifer in the Powder River Basin from Frost et al. (2001, 2002) and Pearson (2002). All concentrations are in milliequivalents per liter and total dissolved solids are in milligrams per liter.

which is more soluble than calcite (Drever, 1997), can provide calcium ions in excess of the saturation point of calcite. These calcium ions will then precipitate with bicarbonate maintaining undersaturation with respect to gypsum. Groundwater has the ability to reach equilibrium with calcite fairly quickly as was shown by Mazor et al. (1993). Water samples from the Casper aquifer in southeast Wyoming were found to be saturated with respect to calcite within 2 km (1.2 mi) of the recharge zone.

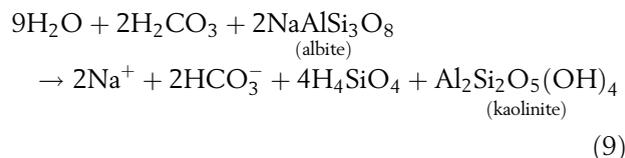
Sources of Sodium

Sodium in CBNG-produced water is commonly attributed to the weathering of and cation exchange with sodic shales and clays (such as volcanic ash), species prevalent in the Fort Union Formation (Lee, 1981; Van Voast and Reiten, 1988; Van Voast, 1991; Bartos and Ogle, 2002, and references therein; Van Voast, 2003). The evolution of groundwater from calcium and magnesium to sodium-dominated water caused by cation exchange with the surrounding aquifer material has been observed in several studies in aquifers of various lithologies (Plummer et al., 1990; Allen and Suchy, 2001;

Guo and Wang, 2004; Andre et al., 2005; Yamanaka et al., 2005; Zhu et al., 2007). In waters of the Wyodak coal aquifer, acquisition of sodium is essentially complete within the first 4 km (2.4 mi) (Figure 2). The larger data set illustrated in Figure 3 shows more scatter in sodium concentration (probably because the samples were not taken from a single coal aquifer), but again, acquisition of sodium appears to occur mostly in the first few kilometers. The predominance of sodium in the produced waters is not primarily a result of a source of sodium in the deeper part of the aquifers, where methane generation is occurring, but reflects a loss of calcium as a consequence of sulfate reduction.

Cation exchange that preferentially takes up calcium and magnesium and releases sodium would only be expected to occur in a system where the ratio of dissolved calcium (or magnesium) to sodium is relatively high. This is not the situation in coal aquifer water in this part of the Powder River Basin, even a short distance from the recharge zone (Figure 2). However, cation exchange may well be a source of sodium close to the recharge area, where the dissolution of calcite or gypsum would cause high calcium concentrations and sulfate reduction has not caused the precipitation of calcium as calcite.

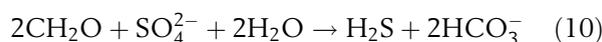
Direct enrichment of sodium can occur through alteration of feldspars or volcanic ash as well (Lee, 1981):



The low concentrations of dissolved silica in coal aquifer groundwater suggest that alteration of silicates is not an important process in the subsurface; however, alteration of silicates in the soil zone may be significant: silica released would be immobilized by evaporation (Drever and Smith, 1978).

Reduction of Sulfate

Anaerobic conditions will cause the bacterial reduction of sulfate, which decreases the concentration of sulfate and increases the concentration of bicarbonate. The organic carbon source in this situation is the subbituminous coal represented by CH_2O . For pH below 7:



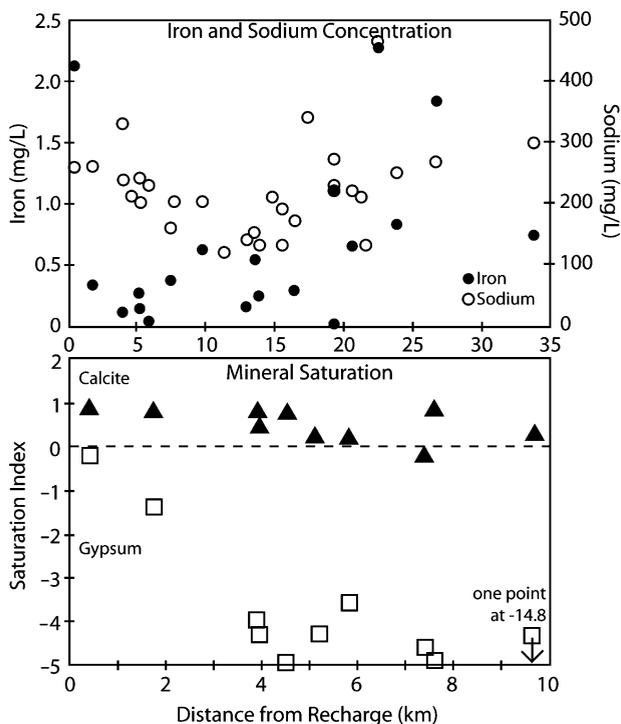
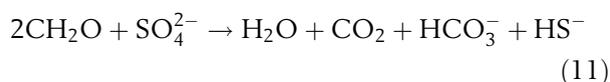
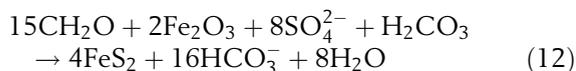


Figure 3. Summary of iron and sodium concentrations and saturation indices from wells in coal aquifers in the Powder River Basin from Frost et al. (2001, 2002) and Pearson (2002). TDS = total dissolved solid.

For pH above 7 (Lee, 1981; Van Voast and Reiten, 1988)



or in the presence of iron (Clark, 1995)



Sulfate-reducing bacteria are common in the Powder River Basin (Dockins et al., 1980; Lee, 1981). The increase in bicarbonate from the reduction of sulfate makes calcium carbonate and magnesium carbonates less soluble and will cause much of the remaining Ca and Mg to precipitate as carbonates. This further reduces the concentrations of Ca and Mg and will tend to decrease the TDS of the groundwater. Additionally, the lower sulfate concentration will allow barium and strontium to remain in solution. In the presence of sulfate, these species form very insoluble salts (Hem, 1985; Drever, 1997). Water coproduced with CBNG is commonly associated with

high levels of the trace element barium (Rice et al., 2002) perhaps because of these low sulfate concentrations.

Oxidation, Reduction, and Methanogenesis

Reduction and oxidation reactions, commonly referred to as redox reactions, are microbially mediated pairs of reactions that transfer electrons (Clark and Fritz, 1997). During oxidation, electrons are donated by a reduced form of an element forming the oxidized species plus one electron; for example, Fe^{2+} can be oxidized to Fe^{3+} , which produces one electron (Essington, 2004). Similarly, this reaction can proceed in the opposite direction in which Fe^{3+} is reduced by accepting one electron to form Fe^{2+} . Coal aquifers are reducing environments because of the readily available organic carbon (a reduced form of carbon) (Deutsch, 1997; Essington, 2004).

The anaerobic oxidation of kerogen or coal by bacteria is a complex, multistep process involving consortia of different microorganisms. The familiar anaerobic organisms that we think of, sulfate reducers or ferric iron reducers, cannot directly use the macromolecular organic matter that is coal or kerogen. They rely on other organisms to break this material down to the small molecules that they can use. A simplified version of the process (following Chapelle, 2001) is as follows. Fermentative bacteria cleave off aliphatic side chains from the solid organic matter to form low-molecular-weight organic acids, such as acetic (CH_3COOH) and lactic ($\text{CH}_3\text{CH}(\text{OH})\text{COOH}$), plus molecular hydrogen. They derive energy from this process. For a simple hydrocarbon (ethane), the stoichiometry of the reaction would be



The hydrogen and the low-molecular-weight acids are consumed by other microorganisms, which oxidize the organic acids to CO_2 and hydrogen to water, reducing a terminal electron acceptor such as sulfate or ferric iron in the process. The various oxidizing bacteria compete for the available hydrogen: the ones that succeed are the ones that derive the most energy from the oxidation reaction. They drive the hydrogen concentration down to the lowest concentration that they can use. The more energy available to an organism from oxidation of hydrogen, the lower the hydrogen concentration it can use (Figure 4). Thus, the various terminal electron acceptors are used in succession, with the ones that yield the

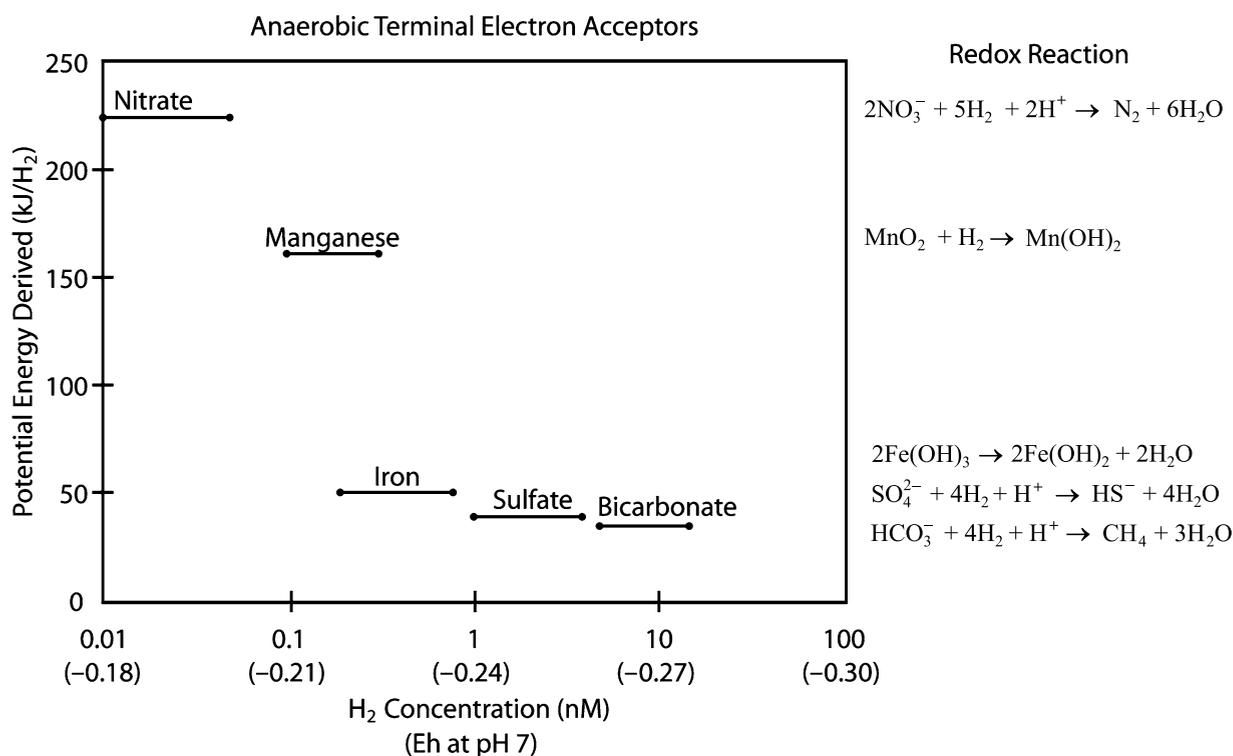
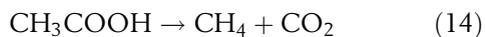


Figure 4. Measured hydrogen concentrations (and corresponding equilibrium Eh values at pH 7) for a typical succession of terminal electron acceptors in anaerobic conditions. Data are from Chapelle (2001). Parenthetical values along the x axis represent the approximate Eh at pH 7 for the given H₂ concentrations.

most energy (for metabolic processes) being used first. The reduction of nitrates and manganese oxides occurs before the reduction of iron oxides, which is followed by the reduction of sulfate and ultimately the reduction of bicarbonate. The reduction of bicarbonate is not the only pathway to methane formation; another important pathway is acetate cleavage:



The concentrations of low-molecular-weight acids in groundwaters are typically very low (they are used as fast as they are produced), but they are very important intermediaries in microbial processes.

In addition to biogenic methane, aquifers may also contain thermocatalytic methane, which is generated through the breakdown of high-mass hydrocarbons at the higher temperatures in deep aquifers (Clark and Fritz, 1997). Both biogenic and thermogenic methane have been isotopically identified in Wyoming coal beds; however, only biogenic methane is found in the Fort Union Formation coals (Gorody, 1999; Bartos and Ogle, 2002; DeBruin et al., 2004).

Time and Length Scales of Groundwater Evolution: Evidence from Powder River Basin Data

Water quality results presented by Frost et al. (2001) indicate that the coal aquifer water in the Powder River Basin reaches a sodium-bicarbonate-dominated character within 4 km (2.4 mi) of the recharge zone. This agrees well with the observations of Van Voast and Reiten (1988) and Bartos and Ogle (2002). Van Voast and Reiten (1988) found that areas of high ion exchange and reduction activity such as the Decker, Montana, area, reached a sodium-bicarbonate nature within a few kilometers down gradient from the recharge zones. Bartos and Ogle (2002) analyzed several coal wells and found all to be of sodium-bicarbonate type, two of which were 6 and 8 km (3.7 and 4.9 mi) from the recharge zone.

Several groundwater samples from the Jacobs Ranch Mine, a coal mine on the eastern edge of the Powder River Basin, were interpreted by Frost et al. (2001) to represent water recharging the coal seams, which are used for CBNG production further into the basin. Most of the recharge to the coal aquifers in the Powder River Basin has been attributed to the clinker outcrops in the Rochelle Hills escarpment (Rice et al., 2002). Additionally,

Pearson (2002) compiled water quality data from wells throughout the basin, some of which were interpreted by Frost et al. (2002) in terms of distance from the recharge zone in the clinker outcrop. Figure 2 is a summary of the water quality from only those wells that were completed in the upper Wyodak coal zone (a part of the Fort Union Formation). Of the water samples summarized in Figure 2, four are from the Jacobs Ranch Mine (Frost et al., 2001) and 27 samples are compiled from Pearson (2002) and Frost et al. (2002).

The data illustrate how coal aquifer water in this part of the Powder River Basin is depleted in Ca, Mg, and SO₄ within 4 km (2.4 mi) of the recharge zone (Figure 2). Sulfate concentrations drop precipitously within the first 2 km (1.2 mi). However, sulfate-reducing bacteria cannot directly oxidize kerogen or coal. Sulfate reduction in groundwater is therefore typically a slow process (Drever, 1997). A rough estimate of the rate of groundwater flow is provided by tritium data because groundwaters older than approximately 50 yr will not contain elevated tritium contents associated with aboveground nuclear detonations. In the eastern Powder River Basin, no tritium was measured in wells more than 3 km (1.8 mi) from recharge (Swanson et al., 2000). This suggests that approximately 50 yr or less is sufficient to reduce nearly all the available sulfate along the first 4 km (2.4 mi) of flow. A general relationship between a reduction in sulfate concentration and increase in bicarbonate concentration in the first 4 km (2.4 mi) of recharge is observed (Figure 2). After 4 km (2.4 mi), sulfate is nearly absent from the aquifer water and therefore bicarbonate has no additional input after that point (equations 10–12). Similar trends in decreasing calcium and magnesium concentrations from the edge of the basins to the center and an almost depleted sulfate concentration in produced water have been identified in most of the major CBNG-producing basins in the United States (Van Voast, 2003).

The TDS of the coal aquifer water drops sharply within the first 4 km (2.4 mi) before leveling off (Figure 2). The initial elevated TDS is most likely caused by the dissolution of salts in the recharge zone; the following decrease in TDS correlates with decreasing sulfate reflecting sulfate reduction and decreasing calcium reflecting calcite precipitation as predicted by the oversaturation of calcite (Figure 3).

Unlike other water quality indicators, iron concentration tends to increase with increasing distance from the recharge zone (Figure 3). This is presumably caused by a reduction of ferric-iron-containing minerals in the aquifer. In the absence of dissolved sulfur species (after

sulfate reduction is complete), dissolved ferrous iron concentrations will increase until siderite precipitates. Darling and Gooddy (2006) in their study of English groundwaters noted a correlation between increasing methane concentration and iron concentration. Additionally, they saw trends in some methane-bearing waters having high bicarbonate and low sulfate concentrations. The saturation indices for calcite indicate that it is oversaturated or near saturation from the first water sample taken 0.4 km (0.2 mi) from the recharge zone (Figure 3). Gypsum is undersaturated throughout the first 10 km (6.2 mi) of the flow path. One reason may be that gypsum is not present in the aquifer; alternatively, gypsum may be dissolving, but because of the oversaturation of calcite, the calcium ions introduced from the dissolution of gypsum quickly precipitate as calcite maintaining undersaturated conditions for gypsum. In this part of the Powder River Basin, the coal aquifers reach equilibrium with calcite by the first monitoring well, less than 1 km from the recharge zone. A similar situation was found in the Casper aquifer in southeast Wyoming, which reached saturation with calcite within 2 km (1.2 mi) of the recharge zone (Mazor et al., 1993).

INTRODUCTION TO ATMOSPHERE AND PONDS

Water coproduced with CBNG is dominated by sodium and bicarbonate. This is true not only in the Powder River Basin (Rice et al., 2000) but also in the five other major CBNG-producing basins in the United States, including the Black Warrior Basin in Alabama and the San Juan Basin in Colorado and New Mexico (Van Voast, 2003). The nonmarine origin of the Powder River Basin results in CBNG-produced water with bicarbonate as its only major anion. Other CBNG-producing coal basins have marine influences in their depositional history, and therefore have both chloride and bicarbonate as major anions in produced water (Van Voast, 2003).

Comparison of CBNG-Produced Water and Powder River Basin Surface Water

The chemical composition of produced water is important when considering how it will interact with the environment to which it is discharged. The chemical interactions of CBNG-produced water with surface water and soil chemistry are an important environmental

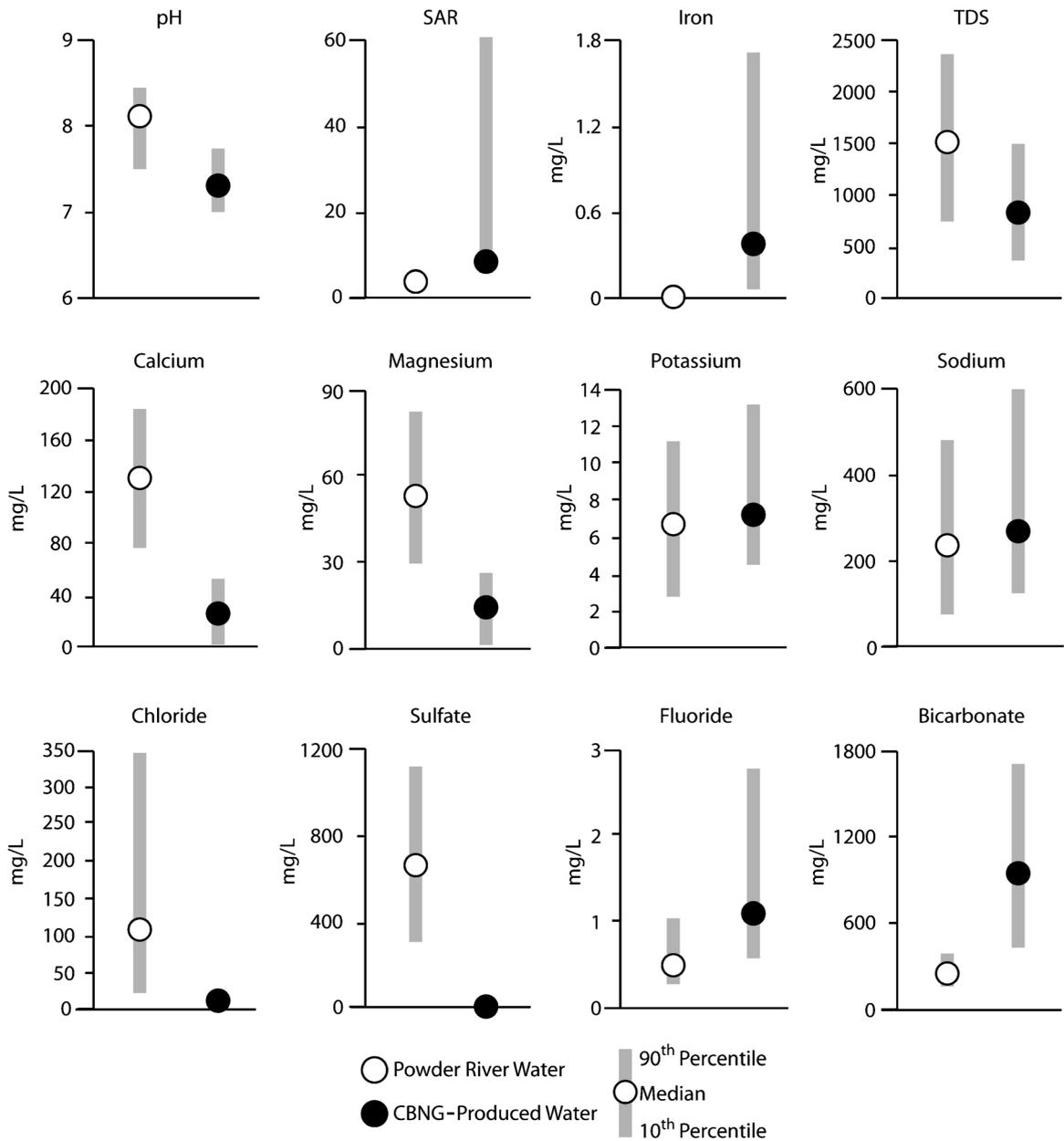
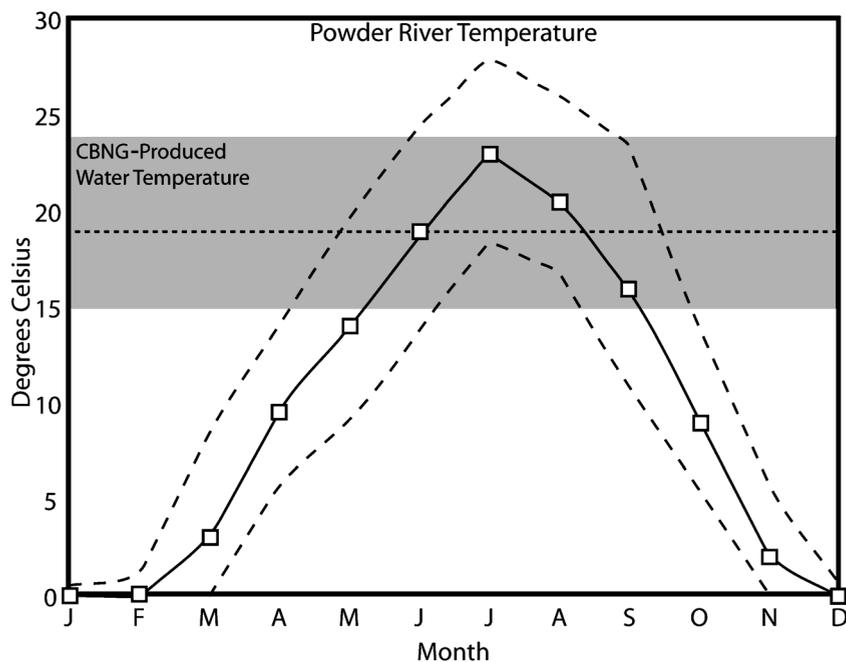


Figure 5. Major ion chemistry for the Powder River (open circles) and coalbed natural gas (CBNG)-produced water (closed circles). Circles represent the median value; gray rectangles represent the range between the 10th and 90th percentiles. Powder River data are from the U.S. Geological Survey and CBNG data are from Rice et al. (2002). TDS = total dissolved solid; SAR = sodium adsorption ratio.

concern. The Powder River runs roughly through the center of the Powder River Basin and is the main hydrologic channel for the basin. Clark et al. (2001) compared the major ion chemistry of the Powder River water sampled at Arvada, Wyoming, to water produced at one CBNG well. Here, we present a more extensive compilation of water quality measurements of samples taken from the Powder River Basin between 1946 and 2005 (Figure 5). The sampling locations are located on the Powder River near Kaycee, Sussex, Buffalo, and

Arvada, Wyoming, and Moorhead, Broadus, Powderville, Mizpah, and Locate, Montana. These data are available online at the U.S. Geological Survey's National Water Information System (U.S. Geological Survey). We compare the geochemical characteristics of the Powder River to the characteristics of CBNG-produced water from Fort Union coal in the Powder River Basin as presented by Rice et al. (2002). The number of samples used to produce the median and 90th and 10th percentiles presented for pH, sodium adsorption ratio (SAR), iron,

Figure 6. The median temperature for the Powder River is plotted as a solid line; the 90th and 10th percentiles are represented by dashed lines. The dotted line is the median value for coalbed natural gas (CBNG)-produced water and the shaded area represents the range from the 90th to the 10th percentile. Powder River data are from the U.S. Geological Survey and CBNG data are from Rice et al. (2002).



TDS, calcium, magnesium, potassium, sodium, chloride, sulfate, fluoride, and bicarbonate is between 693 and 2096 for the Powder River (U.S. Geological Survey) and 70 and 83 for CBNG-produced water (Rice et al., 2002). The range in the number of samples used for comparison is because of the variation in the completeness of the published analyses.

The Powder River has more calcium, magnesium, chloride, and sulfate than CBNG-produced water. Additionally, the Powder River has less bicarbonate, a higher pH, and a lower average SAR than CBNG-produced water (Figure 5). The CBNG-produced water has relatively high concentrations of the reduced species Fe^{2+} and Mn^{2+} compared to surface waters because the coal aquifer is in general a reducing environment (Rice et al., 2000). Total dissolved solids were measured in Powder River water as the residue from filtered water on evaporation at 180°C (in mg/L). The TDS was calculated as the sum of constituent parts in CBNG-produced water using approximately half the bicarbonate (0.4917) (Hem, 1985) to ensure numerical values comparable to evaporative TDS values (Rice et al., 2000). The two water types have similar TDS; however, the TDS of CBNG-produced water varies by basin location. The TDS generally increases from the southeast part of the basin to the northwest and is associated with increases in sodium and bicarbonate concentrations (Rice et al., 2000, 2002).

The temperature of the CBNG water does not vary seasonally and is commonly around 20°C (Figure 6)

(Rice et al., 2002). The shaded region in Figure 6 represents the range of temperatures between the 10th and 90th percentiles of the 83 measured samples from Rice et al. (2002). Seasonal variation in the temperature of the Powder River, using the same data set stipulated previously (U.S. Geological Survey), implies that surface water in this area falls within the normal range of CBNG-produced water temperatures from approximately May to October (Figure 6).

Geochemical Evolution of Pond Water

When natural gas production first started in the Powder River Basin, CBNG-produced water was primarily discharged into constructed reservoirs or into existing surface drainages (Clark et al., 2001). Currently, several methods are employed in the disposal of CBNG-produced water, including impoundments (ponds) excavated within existing channels, impoundments off existing channels, surface and subsurface irrigation, reinjection, sprayers (atomizers), and treatment (Wheaton and Donato, 2004). In all CBNG-produced water disposal situations, save for reinjecting produced water into subsurface aquifers, the produced water will be interacting with the atmosphere and soil. Several studies have described the geochemical evolution of CBNG-produced water discharged to ponds (Figure 7) and streams (McBeth et al., 2003; Patz et al., 2006; Brinck and Frost, 2007a; Jackson and Reddy, 2007a, b; Milligan and Reddy, 2007).

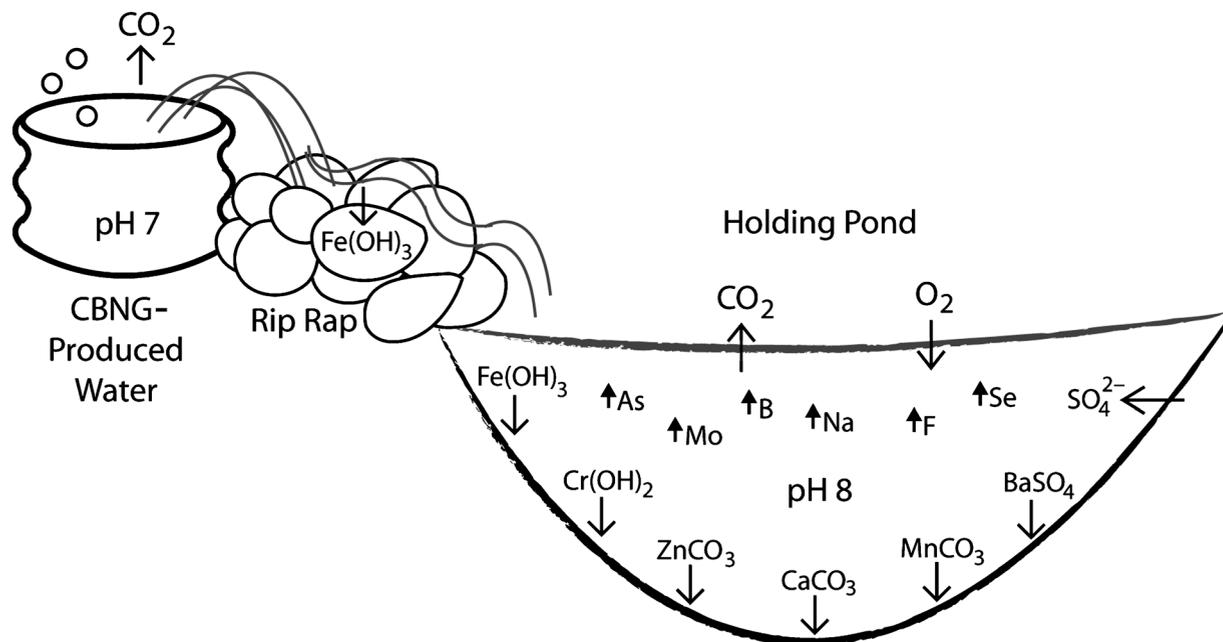


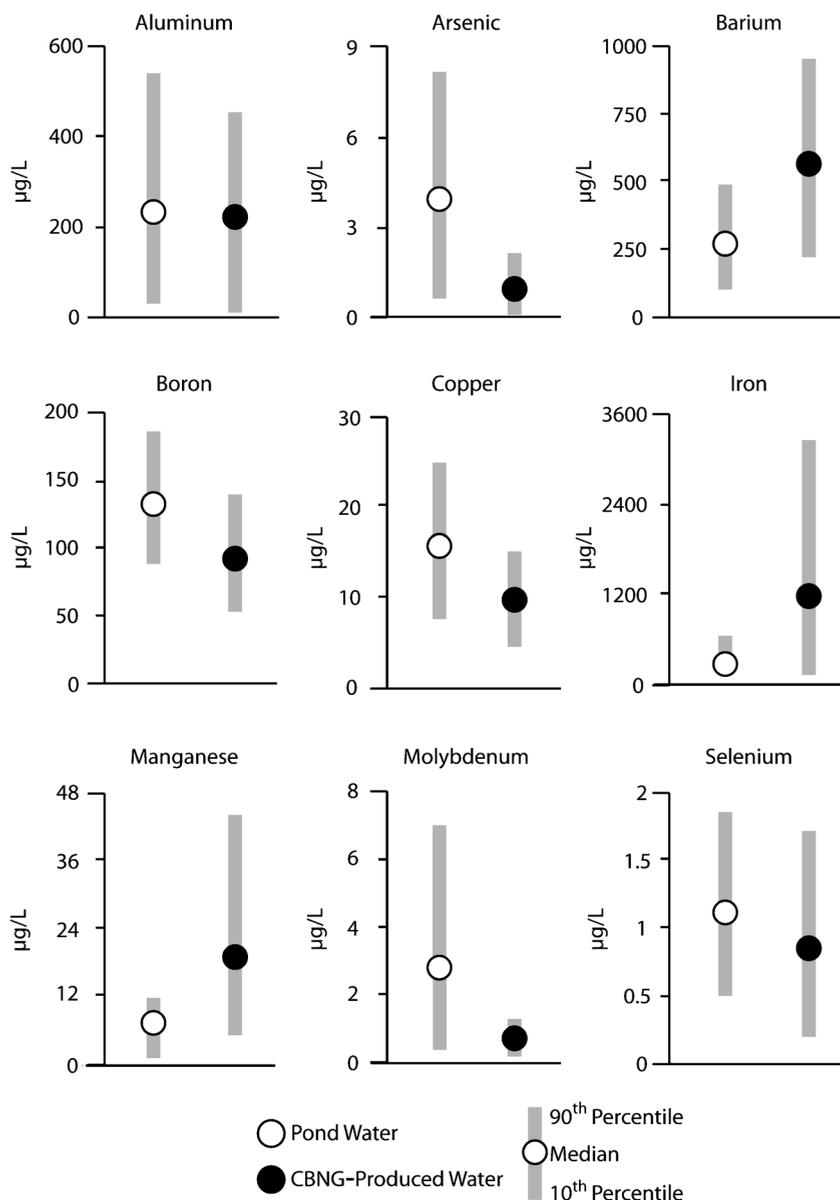
Figure 7. Summary of geochemical changes that occur when coalbed natural gas (CBNG)-produced water is held in an impoundment. Arrows directed to the floor of the pond and rip rap indicate the precipitation of minerals out of CBNG-produced water and pond water. Upward arrows indicate the loss to atmosphere of gas. Downward arrows across the surface of the pond indicate the incorporation of atmospheric gases into pond water. Arrows crossing the floor of the pond indicate incorporation of soil minerals into pond water. Solid upward arrows represent increasing concentrations of the species in the pond water.

All studies (McBeth et al., 2003; Patz et al., 2006; Brinck and Frost, 2007a; Jackson and Reddy, 2007a, b; Milligan and Reddy, 2007) found that the discharged CBNG water increases in pH from around 7 to around 8 in impoundments. This increase in pH is uniformly attributed to the degassing of CO_2 as the CBNG-produced water interacts with the atmosphere (equations 1–3 in reverse). The amount of increase in pH (highest reported pH values in pond water were above 9) varies by study and by watershed. McBeth et al. (2003) attributed the variability in the final pH of the pond to the alkalinity of the soils in which the pond is constructed. The highest pH values are found in ponds constructed in the more alkaline, calcareous soils. Pond water pH may also be controlled by calcite precipitation, activity of wetland plants, and evaporation (McBeth et al., 2003). Additionally, the dissolved oxygen content of the CBNG-produced water increases from CBNG-produced water to pond water in all studies in which it was measured (Patz et al., 2006; Milligan and Reddy, 2007). As a result, the redox potential for the water increases from CBNG-produced water to ponds (Jackson and Reddy, 2007a; Milligan and Reddy, 2007). The CBNG-produced waters, in general, have negative redox potentials (reducing), and pond waters, in general, have positive redox potentials (oxidizing) (Milligan and Reddy, 2007).

The increase in pH that occurs during the CBNG-produced waters' internment in the constructed impoundments results in several subsequent changes in pond water geochemistry. Two studies found that CBNG-produced water was near- or oversaturated with respect to calcite (Brinck and Frost, 2007a; Jackson and Reddy, 2007a), and it was noted that the saturation indices increased for calcite from CBNG-produced water to pond water (Brinck and Frost, 2007a). The initial oversaturation in conjunction with an increase in pH, which would drive the saturation index up, causes the precipitation of calcium in the form of calcite. Decreases in calcium concentration from CBNG-produced water to pond water are attributed to the precipitation of calcite by Brinck and Frost (2007a) and Jackson and Reddy (2007a).

Some trace element concentrations vary between the produced water outfall and the containment ponds. Trace element data compiled from McBeth et al. (2003), Patz et al. (2006), Brinck and Frost (2007a), Jackson and Reddy (2007b), and Milligan and Reddy (2007) are plotted on Figure 8. The concentrations presented here are approximate because all the studies were conducted slightly differently. Patz et al. (2006) measured CBNG-produced water in streambeds and downstream from holding ponds, whereas the other studies collected the pond water from the actual holding ponds. Some studies

Figure 8. Trace element concentrations in coalbed natural gas (CBNG)-produced water and pond water. Data are compiled from McBeth et al. (2003), Patz et al. (2006), Brinck and Frost (2007a), Jackson and Reddy (2007b), and Milligan and Reddy (2007).



only presented average concentrations, which represented up to eight samples but were included in this compilation as one measurement. The number of samples used to calculate the mean 10th and 90th percentiles ranged from 15 (molybdenum) to 30 (boron and manganese).

Relatively high barium concentrations are generally associated with CBNG-produced water (Rice et al., 2002). The concentration of barium in CBNG-produced water decreases as it interacts with the atmosphere and surface environment (Figure 8). Barium, in the form of Ba^{2+} (Jackson and Reddy, 2007b), remains in aqueous form in coal aquifers because sulfate reduction has removed sulfate ions that would cause barium to precipitate as the very insoluble species barite ($BaSO_4$).

Geochemical modeling suggests that CBNG-produced water is near saturation with barite (McBeth et al., 2003; Jackson and Reddy, 2007b). By bringing the coal aquifer water to the surface in the form of CBNG-produced water, the water can interact with soil that provides a source of sulfate allowing barium to precipitate as barite. Lower barium concentrations in pond water as opposed to the CBNG-produced water are observed throughout the Powder River Basin (McBeth et al., 2003; Brinck and Frost, 2007a; Jackson and Reddy, 2007b; Milligan and Reddy, 2007).

Increasing pH will cause other elements to precipitate as well. The CBNG-produced water is near saturation for $MnCO_3$, $Cr(OH)_3$, and $ZnCO_3$ (McBeth et al., 2003). This causes the concentrations of Mn

(Figure 8), Cr, and Zn in CBNG-produced water to decrease from discharge point to the pond. Decreasing concentrations of Mn, Cr, or Zn from CBNG-produced water discharge point to the pond is also observed throughout the basin (McBeth et al., 2003; Patz et al., 2006; Brinck and Frost, 2007a).

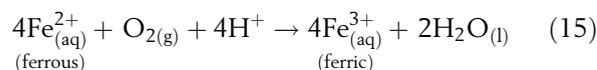
Not all trace elements, however, decrease on interaction with the atmosphere. The more alkaline pH that is found in pond water as opposed to CBNG-produced water results in more mobility in the anionic trace elements such as arsenic, molybdenum, boron, selenium (Figure 8), and fluoride (McBeth et al., 2003; Patz et al., 2006; Jackson and Reddy, 2007b). The concentrations of these anionic species are primarily controlled by adsorption and desorption reactions (Jackson and Reddy, 2007b). These species are more mobile in alkaline natural waters because common adsorption media, mineral oxides and hydroxides, take on a negative charge in alkaline environments, which decreases the adsorption of anionic species. Additionally, within some ponds, a general trend of increasing concentrations of arsenic, barium, and boron with time is observed (Jackson and Reddy, 2007b; Milligan and Reddy, 2007). However, this trend appears to be watershed dependent because it was not seen in all ponds. Further work should be done to determine the original source of these trace elements, whether the arsenic, molybdenum, boron, selenium, and fluoride enter the pond through the CBNG-produced water or are mobilized from the pond floor. If the original source is the soil with which the water is interacting, it may be possible to construct CBNG-produced water impoundments in locations that minimize the accumulation of the trace elements of concern such as arsenic and selenium.

Trends in concentration changes in aluminum as the CBNG-produced water entered the pond system are varied (Figure 8). Some studies found that concentrations of aluminum were generally greater in pond water than in the CBNG-produced water (McBeth et al., 2003; Brinck and Frost, 2007a; Jackson and Reddy, 2007b); however, some ponds were found to have lower concentrations of aluminum than the CBNG-produced water discharged to them (Jackson and Reddy, 2007b). Geochemical modeling indicates that most aqueous aluminum is in the form $\text{Al}(\text{OH})_4^-$ (Stumm and Morgan, 1996; McBeth et al., 2003; Jackson and Reddy, 2007b). Jackson and Reddy (2007b) identified aluminum as an element whose concentration is primarily controlled by dissolution and precipitation, although in one situation wherein substantially more aluminum in the pond water was observed compared to the CBNG-produced water,

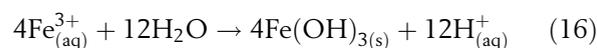
it was speculated that sulfuric acid added to the water prior to disposal resulted in higher aluminum mobility and therefore higher aqueous aluminum concentrations.

Rice et al. (2002) predicted the precipitation of Fe^{2+} and Mn^{2+} on CBNG-produced waters' interaction with oxygen. Many studies found that the concentration of iron decreased from CBNG-produced water to pond water (Patz et al., 2006; Brinck and Frost, 2007a); however, McBeth et al. (2003) found higher concentrations of iron in pond water as compared to the CBNG water produced in the area. Data compilation, however, suggests an overall decrease in iron concentration from CBNG-produced water to pond water (Figure 8). A common water collection practice includes filtration in the field using 0.45- μm filters (McBeth et al., 2003; Patz et al., 2006; Brinck and Frost, 2007a, in press; Jackson and Reddy, 2007a, b; Milligan and Reddy, 2007); however, Rice et al. (2000), affiliated with the U.S. Geological Survey, used 0.1- μm filters. Colloids range in size from 0.001 to 100 μm , therefore a 0.45- μm filtration can allow colloidal $\text{Al}(\text{OH})_3$ and FeOOH into the collected water sample (Stumm and Morgan, 1996). Subsequent acidification prior to measurement on an inductively coupled plasma mass spectrometer (ICP-MS) can cause aluminum and iron to desorb resulting in higher measured concentrations than were actually in aqueous form in the aquifer. Filtration effects on aluminum and iron concentrations (the filtration artifacts) are discussed in depth by Horowitz et al. (1996). Filtration artifacts may be one of the reasons mixed trends have been found in the geochemical evolution of aluminum and iron in pond water. To prevent this problem and more accurately represent aluminum and iron concentrations, field collection techniques should incorporate the use of large surface area membrane filters (Horowitz et al., 1996) or 0.1- μm filters, which would exclude more of the colloidal forms of aluminum and iron.

Decreases in iron concentration are attributed to the precipitation of iron hydroxide; visible red staining is found in the vicinity of many CBNG-produced water discharge points. Introducing CBNG-produced water to the atmosphere allows the reduced ferrous iron to be oxidized to ferric iron:



Ferric iron then precipitates as solid:



The aluminum and iron concentrations in ponds monitored by McBeth et al. (2003) were found to exceed the aquatic life and drinking water limits, respectively.

Jackson and Reddy (2007a) sampled several ponds throughout the Powder River Basin from 2003 to 2005. They found increasing concentrations of sodium and bicarbonate in the pond water, which they attributed to evaporative concentration. Indeed, they attributed the corresponding increase in electrical conductivity primarily to increases in sodium and bicarbonate concentrations. Increasing concentrations of sodium coupled with decreasing concentrations of calcium caused by the precipitation of calcite will cause the SAR to increase, which has negative implications for the irrigation potential of pond water (discussed in the following section). In those ponds that experienced a significant evaporative concentration of sodium, increasing values of SAR were also found (Jackson and Reddy, 2007a).

INTERACTION WITH SOIL

Water coproduced with CBNG interacts with Powder River Basin soil when it is discharged to unlined ponds, flows through stream channels, or is used as an irrigation source. Wyoming groundwater protection laws do not allow groundwater to be degraded below its original use classification (Wyoming Department of Environmental Quality). This is a concern when CBNG-produced water is allowed to infiltrate in on-channel or off-channel ponds and in stream channels. Additionally, Wyoming state regulations require the beneficial use of produced water, which includes agricultural uses such as irrigation (Wyoming statute 41-3-101; Wyoming Legislative Service Office). In irrigation situations, the CBNG-produced water has the potential to impact the chemical and physical properties of the soil of the irrigated field.

Potential Effects on Groundwater

Infiltration of CBNG-produced water through soil and geologic material to near-surface aquifers has been shown to mobilize accumulated available salts and carry them to the water table (Wheaton and Brown, 2005; Brinck and Frost, 2007a), potentially raising the salinity (as measured by the TDS) of the groundwater. However, distinct differences in the magnitude of salinity increases were found in monitoring wells screened in

near-surface aquifers below ephemeral channels, flood plains, and below off-channel ponds in the Powder River Basin (Frost and Brinck, 2005; Wheaton and Brown, 2005; Brinck and Frost, 2007a).

In a study of CBNG-produced water discharged at the headwaters of Beaver Creek, little to no increase in TDS was found directly below this once ephemeral drainage now carrying CBNG-produced water (Brinck and Frost, 2007a). However, an increase of approximately 5000 mg/L was found in wells monitoring the groundwater below the flood plain associated with the same stream channel (Brinck and Frost, 2007a). A greater increase of 10,000 mg/L was measured in wells monitoring groundwater below a holding pond that was excavated off any existing channels in the hills above Coal Creek (Frost and Brinck, 2005; Wheaton and Brown, 2005).

These differences in the salinity of the groundwater impacted by CBNG-produced water discharge can be attributed to the hydrologic history of the soils interacting with the CBNG-produced water and not the salinity and chemistry of the water itself. In the Beaver Creek location, the TDS of the CBNG-produced water ranged from 1267 to 1390 mg/L; at the off-channel, Coal Creek pond site, the TDS of the CBNG-produced water was 995 mg/L in December 2003 (Wheaton and Brown, 2005). The increase in TDS measured in the impacted groundwater of the alluvial and Eocene Wasatch Formation aquifers was much higher than that of the associated CBNG-produced water infiltrating to the aquifer (5000 vs. 1300 mg/L at Beaver Creek and 10,000 vs. 1000 mg/L at Coal Creek). The increased salinity of the shallow aquifers is attributed to the mobilization of soil salts upon introduction of CBNG-produced water. In the case of the ephemeral stream, the soils directly below and near the channel experienced saturated conditions during spring runoff, thus experienced periodic flushing of salts prior to CBNG-produced water discharge. In contrast, the flood plain experienced saturated conditions and salt mobilization only during rare flooding events. Additionally, the soil and geologic material below the off-channel pond had never experienced saturated conditions prior to the introduction of CBNG-produced water. Progressively more salt had built up in each of these situations; the salt was then mobilized with the introduction of CBNG-produced water, impacting the groundwater salinity in proportion to the salt buildup in the soil.

Increases in TDS in the aquifer below the flood plain are caused primarily by increases in sodium, magnesium, calcium, alkalinity, chloride, and sulfate with

the greatest increases occurring in sodium and sulfate (Wheaton and Brown, 2005; Brinck and Frost, 2007a). The increases in TDS at the off-channel pond site are primarily driven by increases in magnesium, sodium, and sulfate; however, increases in all cations are observed. The result in both these situations is that groundwater is dominated by sodium and sulfate. This indicates that the ultimate composition of the shallow aquifer water is primarily controlled by the constituents dissolved from the soil and geologic material and not the original CBNG-produced water composition; CBNG-produced water is almost completely depleted of sulfate (Wheaton and Brown, 2005).

These studies indicate that CBNG-produced water discharge regulations and groundwater quality protection efforts cannot be concerned simply with the original composition of the CBNG-produced water. The geochemistry of the soil and geologic material with which the water will be interacting will be a major factor in the final composition and quality of the groundwater.

Potential Effects on Soil and Vegetation

In addition to groundwater quality issues associated with the discharge of CBNG-produced water, soil chemistry and vegetation changes have been identified because of prolonged exposure to CBNG-produced water. Several studies indicate that soils in contact with CBNG-produced water can display the effects of both salinization and sodification (Ganjegunte et al., 2005; Stearns et al., 2005; Micale and Marrs, 2006). Micale and Marrs (2006) found that water along stream banks carrying CBNG-produced water has higher pH (8.7 vs. 7.3), electrical conductivity (821 vs. 499 $\mu\text{mho}/\text{cm}$), and SAR (19 vs. 0.25) than soil along stream banks not carrying CBNG-produced water. Additionally, increased biomass and increased number of introduced vegetation species are associated with CBNG-produced water discharge (Stearns et al., 2005; Micale and Marrs, 2006; Bergquist et al., 2007). The dense biomass adjacent to CBNG-produced water ponds has been identified as potential larval habitats of *Culex tarsalis*, the mosquito implicated as the primary vector of the West Nile virus (Zou et al., 2006). Additional changes in vegetation are found on disturbed soils associated with CBNG development such as drill pads, dams, roads, and pipelines. Disturbed areas have greater nonnative species richness and less native species cover than control sites (Bergquist et al., 2007).

The shift from native vegetation species to more salt-tolerant introduced species in the riparian zones

of CBNG-produced water impoundments and stream channels could have long-term implications for the re-establishment of the native ecology. Fewer native species and more salt-tolerant introduced species are found in gullies carrying CBNG-produced water than in control gullies (Stearns et al., 2005). Salt- and sodium-tolerant species will fare better in the saline and sodic environments created by CBNG-produced water discharge sites. Additionally, there may be long-term surface water quality effects resulting from the changes to the stream-channel soils. The sodium-rich soils in channels carrying CBNG-produced water may potentially release sodium to surface water after the cessation of CBNG-produced water discharge (Stearns et al., 2005). The higher salinity and sodicity in soils in conjunction with the reduced native species richness along CBNG-produced water stream channels may act to delay the recovery to baseline vegetation and ecological conditions.

Implications for Irrigation

The desire to put CBNG-produced water to beneficial use has spurred the development of CBNG-produced water irrigation systems. One measure of water's suitability for use as an irrigation source is the ratio of sodium to calcium and magnesium, the SAR (units $\text{mmol}^{1/2} \text{L}^{-1/2}$). When units of concentration are in millimoles per liter, SAR is defined (Essington, 2004)

$$\text{SAR} = \frac{[\text{Na}^+]}{\left([\text{Ca}^{2+}] + [\text{Mg}^{2+}]\right)^{1/2}} \quad (17)$$

However, when units are in milliequivalents per liter, the equation for SAR is (Stumm and Morgan, 1996)

$$\text{SAR} = \frac{[\text{Na}^+]}{\left(\frac{[\text{Ca}^{2+}] + [\text{Mg}^{2+}]}{2}\right)^{1/2}}$$

Excess sodium is one of the greatest concerns when applying irrigation water to a field. When the concentration of sodium in irrigation water is in excess of the calcium and magnesium concentrations (a high SAR value), sodium has the potential to displace calcium and magnesium from the soil's cation exchange sites. The large hydrated radius of the sodium ion can cause the soil structure to be degraded through swelling and dispersion of clays and organic matter. These structural

changes can reduce the soil's infiltration capacity and limit root penetration (So and Aylmore, 1993; Bagarello et al., 2006). The amount of sodium required to affect these changes is dependent in part on the soil's texture, mineralogy, and organic matter content. In general, a soil is considered sodic when the number of exchange sites occupied by sodium exceeds 15% (U.S. Salinity Laboratory Staff, 1954; Sumner, 1993; Essington, 2004).

As discussed previously, CBNG-produced water generally has high concentrations of sodium and low concentrations of calcium and magnesium and therefore high SAR values. The CBNG-produced water from the Fort Union coal formation has a median SAR of $8.8 \text{ mmol}^{1/2} \text{ L}^{-1/2}$ and 10th and 90th percentiles of 6.1 and $59.9 \text{ mmol}^{1/2} \text{ L}^{-1/2}$, respectively (Rice et al., 2002). The specific SAR value that is considered too high for water to be put to use as an irrigation source depends in part on the electrical conductivity of the irrigation water and the clay content of the irrigated field. As a general rule, SAR values of 6 to $12 \text{ mmol}^{1/2} \text{ L}^{-1/2}$ are considered too high (Essington, 2004). Therefore, in many CBNG-produced water irrigation systems, precautions must be taken to prevent the salinization and sodification of the soil.

The CBNG-produced water is flowing nearly constantly while the CBNG wells are operating; however, irrigation water is only applied intermittently. Because of this disconnect in timing, the CBNG-produced water that will be used for irrigation is commonly put into impoundments until needed. Evaporative concentration of sodium and calcite precipitation in ponds can cause the SAR of the CBNG-produced water to increase while in the pond (Jackson and Reddy, 2007a). However, the length of time that the water is in the pond may not be long enough for the evaporative concentration of sodium to impact the SAR significantly. The precipitation of calcite in the pond, however, can increase the SAR values irrespective of increases in sodium concentration. For this reason, some irrigation management techniques include the acidification of the CBNG-produced water, which serves to convert some of the bicarbonate to carbon dioxide thus reducing the saturation index, and therefore the rate of precipitation, of calcite. Similarly, elemental sulfur (which oxidizes slowly to sulfuric acid) can be applied to the surface of the irrigated soil, which will lower the pH of the irrigation water lessening the precipitation of calcite from the water. The surface-applied sulfur may also lower the pH of the soil, which may potentially bring naturally occurring calcite in the soil into solution providing a source of calcium ions (Essington, 2004; Qadir

et al., 2006). Additional methods used to lower SAR values of CBNG-produced water include adding gypsum to the surface of the soil that will be irrigated. As the gypsum dissolves, it provides an additional source of calcium ions.

Several studies have measured soil chemical and physical changes caused by CBNG-produced water irrigation (Ganjugunte et al., 2005; Brinck and Frost, 2007b, in press; Johnson et al., 2007; Ganjugunte et al., 2008; Vance et al., 2008). All found an initial degradation in the irrigated soil's physical and chemical properties in the form of decreased infiltration rates and increased salinity (as measured by electrical conductivity [EC]) and sodicity (as measured by SAR). Baseline Powder River Basin soil salinity and sodicity varied from around EC values of 1–4 dS/m and SAR values of 0.5–2 $\text{mmol}^{1/2} \text{ L}^{-1/2}$ (Brinck and Frost, in press; Ganjugunte et al., 2008; Vance et al., 2008). The CBNG-produced water irrigated soil salinity and sodicity values varied from EC values around 3–10 dS/m and SAR values around 8–20 $\text{mmol}^{1/2} \text{ L}^{-1/2}$ (Brinck and Frost, in press; Ganjugunte et al., 2008; Vance et al., 2008). The ultimate salinity and sodicity levels depended on several factors, including the number of irrigation seasons the field had undergone and the water and soil treatments applied. In general, for increasing sodicity levels, the soil structure will remain intact if a corresponding increase in salinity occurs. Higher salinity will allow the clay molecules to remain closer together (flocculated) because of the compressed double layer (Essington, 2004). Longer term studies, such as Brinck and Frost (in press), found that after the initial increases in salinity and sodicity during the first 2 yr, no further increases were found on one CBNG-produced water irrigated field within the central Powder River Basin in the following 2 yr.

Ganjugunte et al. (2008) found mixed trends in pH changes on several fields. Although some fields showed no significant changes in pH, some irrigated fields showed significant decreases in pH as compared to the associated control fields. This acidification of irrigated soils is attributed to the application of sulfur burners on those fields. Sulfur burners acidify the irrigation water prior to the application to the field by converting elemental sulfur to sulfurous or sulfuric acids (Ganjugunte et al., 2008; Vance et al., 2008). The lower pH of the irrigation water reduces bicarbonate concentrations limiting the precipitation of calcite and increases the solubility of naturally occurring calcite in the soil. Both of these effects should help protect the soil from sodification. The application of gypsum increased calcium in the soil to a

similar extent as the sulfur-burning treatment without the corresponding decrease in soil pH. Oxidation of sulfur has the potential to create low pH values, which will consume the buffering capacity of the soil. If low pH conditions persist in irrigated fields, it can become detrimental to plant growth and potentially increase mobility and uptake of heavy metals (Ganjugunte et al., 2008; Vance et al., 2008).

The potential for further reduction in infiltration rate and increases in SAR once irrigation with CBNG-produced water and surface amendments has ceased has been addressed by Johnson et al. (2007), Ganjugunte et al. (2008), Vance et al. (2008), and Brinck and Frost (in press). Low-salinity precipitation preferentially leaches the calcium and magnesium from the surface soil increasing the SAR of the soil water potentially causing the swelling of clay minerals (Ganjugunte et al., 2008; Vance et al., 2008). Additionally, atmospheric precipitation may lower the salinity of the soil water causing the diffuse double layer, the halo of ions surrounding clay and organic matter surfaces, to increase and disperse the clay minerals (Drever, 1997; Brinck and Frost, in press). Care must therefore be taken to ensure that the salinity and sodicity levels are low enough prior to the cessation of CBNG-produced water irrigation and that the subsequent addition of low-salinity, low-sodic rain water does not cause further reductions in soil quality.

CONCLUSIONS

The natural processes of salt dissolution, pyrite oxidation, sulfate reduction, and methanogenesis that occur in deep coal aquifers result in groundwater dominated by sodium and bicarbonate. Sodium in the coal aquifer water originates in the soluble salts in the soil, weathering of shale and clay, and through cation exchange early in the water's evolution. The process of bringing coal aquifer water to the surface during CBNG production initiates a series of further geochemical changes, including the precipitation of calcite and iron hydroxide. Some trace elements tend to concentrate in impoundments; however, their origin is unclear. If the source of trace elements of concern such as arsenic and selenium is the local soil, it may be possible to locate CBNG-produced water impoundments in areas that would minimize the mobilization of these species. When CBNG-produced water is discharged to the surface, it will interact with the local soil and near-surface aquifers. In semiarid basins such as the Powder River

Basin, soluble salts naturally accumulate in the soil. The addition of CBNG-produced water can mobilize these salts, potentially increasing the salinity of shallow groundwater. Additionally, the riparian areas in contact with CBNG-produced water have shown increased numbers of introduced and salt-tolerant species and increased soil salinity and sodicity. Irrigation with CBNG-produced water also has the potential to increase the salinity and sodicity of the fields to which it is applied, not only through application of CBNG-produced water but also through soil amendments. Careful management of CBNG-produced water irrigation sites is necessary to maintain the quality of the soil's physical and chemical characteristics.

Understanding the geochemical evolution of CBNG-produced water is important for predicting potential environmental impacts. Regulating the produced water based on its initial chemical composition at the wellhead is not enough. As the water sits in holding ponds, flows through stream channels, and infiltrates to near-surface aquifers, the resultant chemical composition of the CBNG-produced water can be quite different from the original composition. Additionally, further work is needed to understand the potential impact the cessation of CBNG-produced water irrigation may have on the fields to which it is being applied, to avoid the degradation of soil quality. Understanding and mitigating potential environmental changes caused by the discharge of CBNG-produced water may determine the future of CBNG production in Wyoming and Montana.

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