In press in Coalbed Natural Gas: Energy and Environment, Nova Publishers

INNOVATIVE APPROACHES FOR TRACING WATER CO-PRODUCED WITH COALBED NATURAL GAS: APPLICATIONS OF STRONTIUM AND CARBON ISOTOPES OF PRODUCED WATER IN THE POWDER RIVER BASIN, WYOMING AND MONTANA

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ABSTRACT

Coalbed natural gas (CBNG) is an important source of natural gas in the United States, with an estimated 700 trillion cubic feet of gas in place. Of this, 100 trillion cubic feet is economically recoverable, which represents a 5-year supply of natural gas at present rates of U.S. consumption. Coalbed natural gas provides clean energy but raises environmental concerns. Primary among these is the disposal of water that is produced with the gas during depressurization of the coal seam. It is important to develop strategies to minimize water production as well as to maximize beneficial use of produced water. This chapter presents two potentially powerful tracers of CBNG produced water that can be used to help achieve this goal. We describe how strontium and carbon isotopic approaches may be used to identify: a) the degree of isolation of aquifers from which CBNG is produced, b) the fate of produced water in the surface water system, c) the infiltration of this water into the shallow ground water system, and d) beneficial use of CBNG co-produced water in agriculture. These approaches are illustrated with case examples from the Powder River Basin in northeastern Wyoming and southeastern Montana, an area that produces nearly 40% of the nation's coalbed natural gas.

INTRODUCTION

Coalbed natural gas (CBNG), also called coalbed methane, forms within coalbeds through microbial processes and by thermal processes as organic matter is buried and heated. Coalbed natural gas is an important energy resource, supplying approximately 7.5% of the natural gas consumed annually within the U.S. (USGS, 2000). Production of coalbed natural gas involves reducing the hydrostatic pressure that holds the gas in the coal seam cleats and pores by removing the coal aquifer water. The lower pressure allows the methane to desorb from the coal and to be collected and used as an energy source (DeBruin et al., 2004). The proper management of water co-produced with CBNG is an important issue both because the volume of produced water can be large and because its chemical composition may not be appropriate for all uses. In some areas the co-produced water is re-injected into aquifers, but this is not a common management technique in the Powder River Basin of Wyoming and Montana. Most disposal methods in the Powder River Basin involve discharging produced water to the surface by various means including discharge into surface drainages, discharge into on- or off-channel impoundments, dispersal into the air by sprayers, or using the produced water for surface and subsurface irrigation (Wheaton and Donato, 2004).

Responsible development of the CBNG resource requires minimization of water production during gas recovery and responsible management of produced water discharged to the land surface. A variety of approaches are being used to help ensure the most efficient recovery of the gas resource, particularly with respect to water management. This chapter describes how the naturally-occurring isotopic ratios of strontium (Sr) and carbon (C) present in CBNG produced water can be used to determine best management practices of coalbed natural gas production. These tracers can successfully address the following questions:

- Is the targeted coal seam hydraulically isolated? Are individual producing wells properly completed such that water is produced only from the target coal seam?
- When produced water is discharged at the surface, how much of the water reaches major river systems, potentially altering the volume, seasonality, and chemistry of natural flow?
- When produced water is discharged at the surface, can it be tracked as it infiltrates into the shallow ground water system?
- When used for irrigation, does the produced water impact the soil structure and fertility and can the effectiveness of amendments be evaluated?

This chapter describes the theoretical basis for strontium and carbon isotopic tracers and the analytical methods involved in sampling and measuring the isotopic composition of these elements. The development of coalbed natural gas production in the Powder River Basin is described in detail, including examples of several studies that illustrate the application of these environmental tracers to aspects of responsible coalbed natural gas production.

CARBON AND STRONTIUM ISOTOPIC TRACERS IN NATURAL WATERS

C isotopic composition of dissolved inorganic carbon in natural waters. Measurements of $\delta^{13}C$ (normalized ratio of ^{13}C to ^{12}C) of dissolved inorganic carbon (DIC) in ground water can provide a diagnostic tool to fingerprint water sources and to identify ground water interactions if there are large differences in $\delta^{13}C$ values among different carbon reservoirs in a particular region. The $\delta^{13}C$ in natural waters is controlled by the isotopic composition of the carbon sources. Subsurface waters draining temperate, moderately-vegetated areas typically have intermediate $\delta^{13}C$ values of DIC ranging from -10 to -14‰ (Mook and Tan, 1999). In surface waters, the highest reported $\delta^{13}C$ values are usually from shallow lakes, which can contain $\delta^{13}C_{DIC}$ ranging from +1 to +2‰. Higher $\delta^{13}C_{DIC}$ can only be recorded in organic-rich systems due to microbial methanogenesis preferentially removing ^{12}C from the system (Simpkins and Parkin, 1993; Taylor, 1997). Metabolic production of methane by carbon dioxide (CO_2) reduction preferentially utilizes lighter carbon; thus, in a closed system, the CO_2 gas in the CBNG reservoir will become increasingly isotopically enriched in ^{13}C. The enriched carbon isotope composition of the CO_2 will also be recorded by the $\delta^{13}C_{DIC}$, as the inorganic carbon in water precipitates in equilibrium with this CO_2. Thus, $\delta^{13}C_{DIC}$ can potentially be a diagnostic tool for distinguishing water originating from coal aquifers where biogenic methanogenesis is the primary mechanism of methane generation (Rice, 1993).

Strontium isotopic composition of natural waters. Strontium isotopes also have been shown to be useful fingerprints of ground water and tracers of ground water mixing; they have been used to characterize brines and formation waters associated with oilfield reservoirs (e.g. Chauduri et al., 1987; McNutt et al., 1990; Smalley et al., 1992; Lyons et al., 1995) and fresh water hydrologic systems (e.g. Collerson et al., 1988; Banner et al., 1994; Armstrong et al., 1998; Gosselin et al., 2001; Frost and Toner, 2004). Ground water $^{87}Sr/^{86}Sr$ isotope ratios reflect natural variations of the ratio in geologic materials. In turn, the variation in geologic material derives from natural differences in Rb/Sr ratios, because the radiogenic isotope ^{87}Sr is produced by decay of ^{87}Rb (half-life 48.8 Ga). Rocks and minerals that have high Rb/Sr will develop higher (more radiogenic) ^{87}Sr/^{86}Sr ratios with time; rocks and minerals that are young or have low Rb/Sr will have lower (less radiogenic) ^{87}Sr/^{86}Sr ratios. The precision of the ^{87}Sr/^{86}Sr analysis (± 0.00001) allows for detection of small variations in ground water Sr isotope composition. Moreover, the isotope ratio is not affected by fractionation or by mineral precipitation. The Sr isotopic composition of water is dependent only upon dissolution of minerals and ion exchange reactions; as water flows through an aquifer, it progressively acquires the ^{87}Sr/^{86}Sr ratio of the rocks and minerals with which it interacts. Its sensitivity to these processes makes the Sr isotopic ratio a powerful tool for evaluating the effects of CBNG production on the hydrology of the area.

ANALYTICAL METHODS

Dissolved inorganic carbon isotopic analyses. Samples collected for dissolved inorganic carbon (DIC) analyses are passed through 0.45 μm filter to remove particulates. The water sample is then transferred to 30 ml Wheaton glass serum vials with teflon septa and sealed with Al caps using a crimper. A few drops (2-3) of benzalkonium chloride are added to each vial before filling it with water to halt any metabolic activity. Samples are analyzed for $\delta^{13}C_{DIC}$ by mass spectrometry; in the following examples this was done on a GasBench-II device coupled to a Finnigan DELTA plus mass spectrometer at the University of Wyoming Stable Isotope Facility. The reproducibility and accuracy is monitored by replicate analysis of samples and internal lab standards and at the University of Wyoming is better than ± 0.1‰. The $\delta^{13}C_{DIC}$ values are reported in per mil relative to the V-PDB standard. The DIC concentrations of the samples may be quantified from the mass spectrometry data. At the University of Wyoming, three $NaHCO_3$ stock solutions of different DIC concentrations have been prepared for this purpose. DIC concentrations are quantified based on the peak areas of the mass 44-ion trace of these standards. Plotting peak area of CO_2 vs. concentration of DIC in these standards gives an excellent correlation (r^2=0.995). The relative standard uncertainty of the DIC concentration measurement in this study was ± 3%.

Strontium isotopic analysis. Strontium isotopic ratios are obtained from water samples collected in accordance with standard water quality sampling protocols including filtering through a 0.45 µm filter to remove particulate matter and keeping the sample cool and dark until analysis. Strontium is isolated from a 3 ml aliquot of the sample using cation specific resin; in the following examples this was done in Teflon columns filled with Eichrom® Sr-Spec resin at the University of Wyoming. The most precise measurements of strontium isotope composition are obtained by thermal ionization mass spectrometry with typical internal precisions of ± 0.00001 for $^{87}Sr/^{86}Sr$ isotope ratio measurements. External reproducibility is determined by repeated measurement of a standard; at the University of Wyoming Radiogenic Isotope Laboratory external reproducibility is determined from repeated analysis of the NBS 987 strontium standard, which gives an average value of $^{87}Sr/^{86}Sr = 0.71026 \pm 0.00002$ (2 standard deviations, n = 76). Analyses are normalized to an $^{86}Sr/^{88}Sr$ ratio value of 0.1194. Analytical blanks are typically less than 0.2 ng, negligible compared to sample sizes of at least 0.1 microgram strontium. Strontium concentrations may be determined by a variety of methods, including isotope dilution, which involves spiking an additional 1-ml aliquot with an ^{84}Sr-enriched tracer followed by mass spectrometric analysis of the resulting isotopic ratio, and inductively coupled plasma mass spectrometry. Both methods were used in the following examples. Strontium concentration measurements are typically reproducible at the 1% level.

Sr AND C ISOTOPIC TRACING OF COALBED NATURAL GAS PRODUCED WATER: CASE STUDIES FROM THE POWDER RIVER BASIN, WYOMING AND MONTANA

Coalbed Natural Gas Production in the Powder River Basin. The Powder River Basin of northeastern Wyoming and southeastern Montana is one of the most significant energy-producing regions of the United States. Powder River Basin coal provides approximately 40% of all the coal consumed in the nation annually (467.4 million tons in 2008) (U.S. Energy Information Administration, 2009). These Tertiary-age, non-marine, subbituminous coals are valued for their low sulfur (~0.5% S) and ash (6-7%) content (Ellis, 1999; Lyman and Hallberg, 2000). Powder River Basin coals also host an important natural gas resource. Economically recoverable reserves in the Wyoming portion of the Powder River Basin are estimated at 25.2 trillion cubic feet (Bank and Kuuskraa, 2006). Production of this resource requires drilling a well to the target coal seam, typically less than 2000 feet, and removing water from the coal seam to reduce hydrostatic pressure, allowing the methane to desorb and rise up the annular space of the cased well (DeBruin and Lyman, 1999). After an initial period of water production, a typical well produces 175,000 cubic feet (175 Mcf, 4,955 cubic meters) of methane per day and 3,500 gallons (13,250 liters) of water per day (based on January 2009 data from the Wyoming Oil and Gas Conservation Commission, 2009). Most production in the Powder River Basin comes from the Wyoming portion of the basin. As of January 2009 Wyoming is producing approximately 1,444,000 Mcf (40,889,500 cubic meters) of methane per day (compared to 2,900 Mcf/day in Montana) and 57.8 million gallons (219 million liters) of water per day (Wyoming Oil and Gas Conservation Commission, 2009; Montana Board of Oil and Gas, 2009).

The natural gas resource was developed rapidly: in Wyoming, the number of CBNG wells has increased from 152 wells in 1995 to more than 22,000 wells in 2008 (Figure 1) (Surdam et al., 2007; Wyoming Oil and Gas Conservation Commission, 2009). More recently, however, the pace of development has slowed due to a number of concerns including beneficial use and proper disposal of co-produced water (Bank and Kuustraa, 2006), decrease in the price of natural gas, and limitations on drilling instituted to minimize disturbance of sage grouse habitat. Discharging CBNG produced water to the surface in the Powder River Basin introduces approximately 20°C, sodium-bicarbonate dominated water, with total dissolved-solids (TDS) concentrations ranging from 300 to 4,500 mg/L (Campbell et al., 2008) to this semi-arid watershed. In addition to the potential biological and geochemical changes one would expect with the addition of CBNG produced water to semi-arid drainage basins, other topics of concern include rate and location of recharge to aquifers and the impacts of discharged produced water upon drainages and soils (Rice et al., 2002). Additional considerations include Wyoming's Department of Environmental Quality regulations that require the class of use of ground water be protected in all situations (Wyoming Department of Environmental Quality, 2001) and produced water be put to beneficial use (Wyoming Statute 41-3-101). In 2003 (and amended in 2006), the State of Montana issued standards for water quality in the Powder, Little Powder, Tongue River and Rosebud Creek watersheds (Administrative Rule of Montana 17.30.1670, 2007) that require water entering Montana to be below particular thresholds for electrical conductivity (EC) and sodium absorption ratio (SAR).[1]

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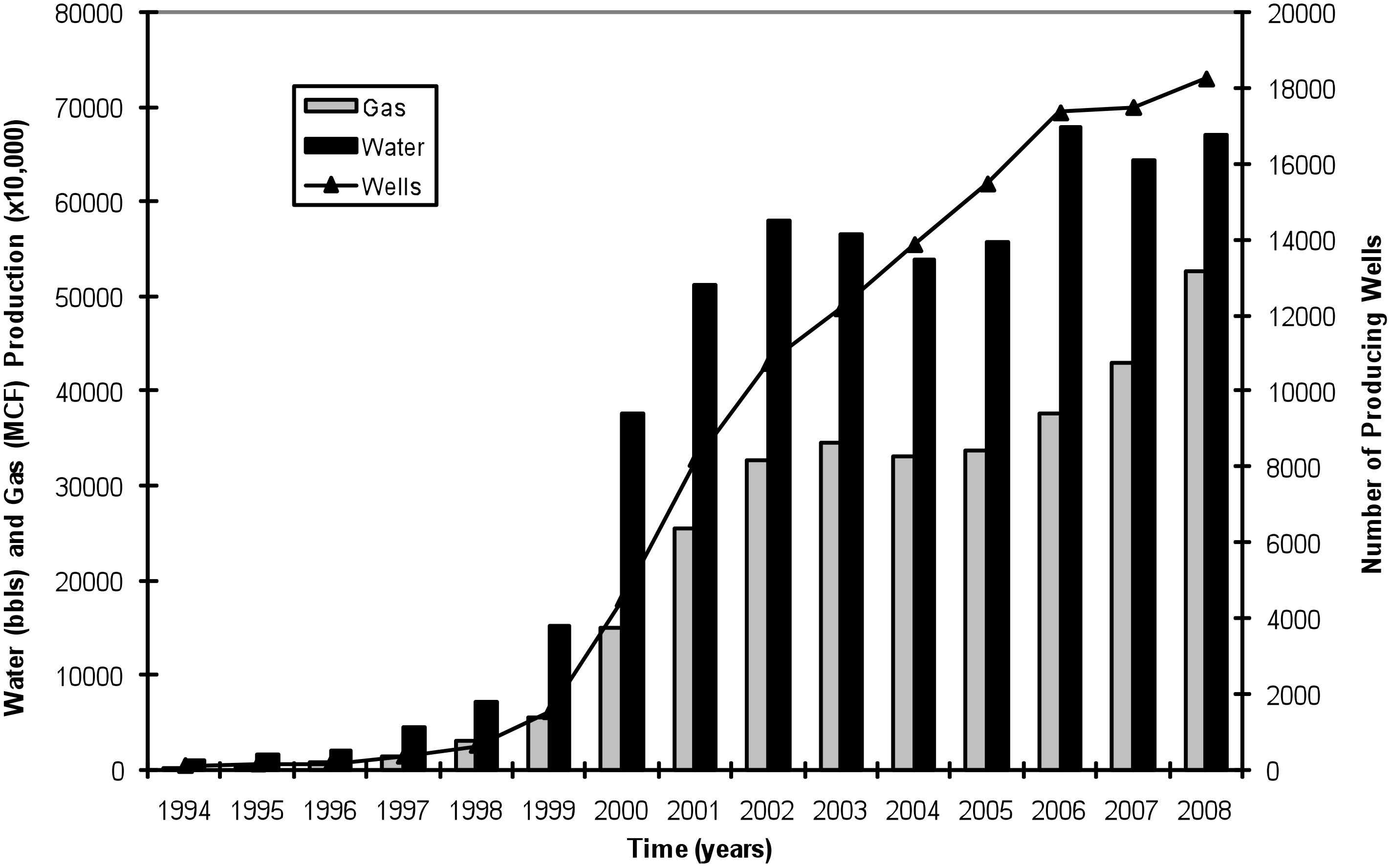
[1] The sodium adsorption ratio, or SAR, provides an indication of the suitability of water to be used for irrigation, and is defined as the ratio of sodium to magnesium and calcium (units: $\mathrm{mmol}^{1/2}\ \mathrm{L}^{-1/2}$). The specific SAR value that precludes water from use as a source of irrigation depends upon a number of factors including the electrical conductivity (EC) of the water and clay composition of the soil. In general, SAR of irrigation water higher than around 6 to 12 $\mathrm{mmol}^{1/2}\ \mathrm{L}^{-1/2}$, indicates that the sodium in the irrigation water can displace calcium from the exchange sites on soil clays and organic matter (Essington, 2004).

Figure 1. Water and gas production in the Powder River Basin, 1994-2008. Since 2006 gas production has increased without a corresponding increase in water production. Data from the Wyoming Oil and Gas Conservation Commission.



Geochemical Evolution of Coalbed Natural Gas Produced Water in the Powder River Basin. Several previous studies have summarized the geochemical evolution of CBNG produced water in the Powder River Basin throughout the cycle of infiltration, ground water-rock interaction, reactions with atmosphere upon withdrawal and discharge at the surface, and interaction with soil, shallow bedrock and vegetation (Lee, 1981; Van Voast and Reiten, 1988; Clark, 1995; Van Voast, 2003; Wheaton and Donato, 2004; Brinck et al., 2008). Water produced with coalbed natural gas 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 (Brinck et al., 2008). After produced water is discharged to the surface, interaction with the atmosphere will initiate precipitation of calcite, iron hydroxide and barite among other minerals. In semi-arid regions, the interaction of CBNG produced waters can mobilize accumulated salts that, through infiltration, can then reach the water table – potentially affecting the quality of the ground water. The high SAR of some produced water requires careful management when used as an irrigation source to prevent sodification of irrigated soils. In many instances, irrigation with produced water requires the addition of soil amendments such as gypsum and sulfur to maintain the fertility and physical qualities of the soil.

Currently, most regulation is based upon the initial chemical composition of the CBNG produced water (Buccino and Jones, 2004). Brinck et al. (2008) caution, however, that in most situations the subsequent changes to the water caused by its interaction with the atmosphere and local soils ultimately will determine its impact upon the environment.

The first steps to address produced water concerns are to: 1. minimize produced water by using hydraulically isolated coalbeds, 2. quantify produced water in surface flows, 3. identify the specific aquifers with which the discharged water is interacting and 4. ensure produced water does not negatively impact the soils with which it interacts (Brinck and Frost, 2007). This can be accomplished by fingerprinting and tracking the produced water as it is pumped from coal aquifers, discharged into surface drainages and ponds, infiltrates into the shallow ground water system, and interacts with soils. However, geochemical concentration measurements, even in addition to stable isotopic ratios of oxygen and hydrogen, are insufficient to distinguish ground water in coal aquifers from other surface- and ground water in the Powder River Basin (Frost et al., 2002). The following examples illustrate how stable isotopes of C and Sr can be used to accomplish these goals.

<u>Case study 1: Identification of hydraulically isolated coal seams in the eastern Powder River Basin, Wyoming.</u> Coal aquifer water samples were collected from individual producing CBNG wells throughout the Powder River Basin and include ground water from the Eocene, Wasatch-Formation Lake DeSmet and Felix coal zones, and from the Upper-Paleocene, Fort Union-Formation Wyodak Rider, Upper Wyodak, Lower Wyodak and Knobloch coal zones (Table 1). Geochemical and isotope data were obtained from more than 150 samples of ground water from the Powder River Basin, including samples from these coal zones and from sandstone aquifers (Frost et al., 2001, 2002; Frost and Brinck, 2005; Brinck and Frost, 2007; Campbell et al., 2008; Sharma and Frost, 2008). The majority of samples were collected from wells on the eastern side of the basin axis in Wyoming, where the CBNG development began. The recharge area for these samples is along the eastern margin of the basin. Ground water recharged on the eastern side of the basin is driven westward by the topographic gradient towards the Powder River and the basin axis. The distance of the well from the eastern clinker outcrops is a proxy for relative ground water residence time, such that wells closer to the clinker outcrop yield water with shorter residence time than wells located farther west.

Table 1. Coal zones of the Powder River Basin, Wyoming and Montana. Coal-zone nomenclature is from the Wyoming State Geological Survey Coal Section (2007).

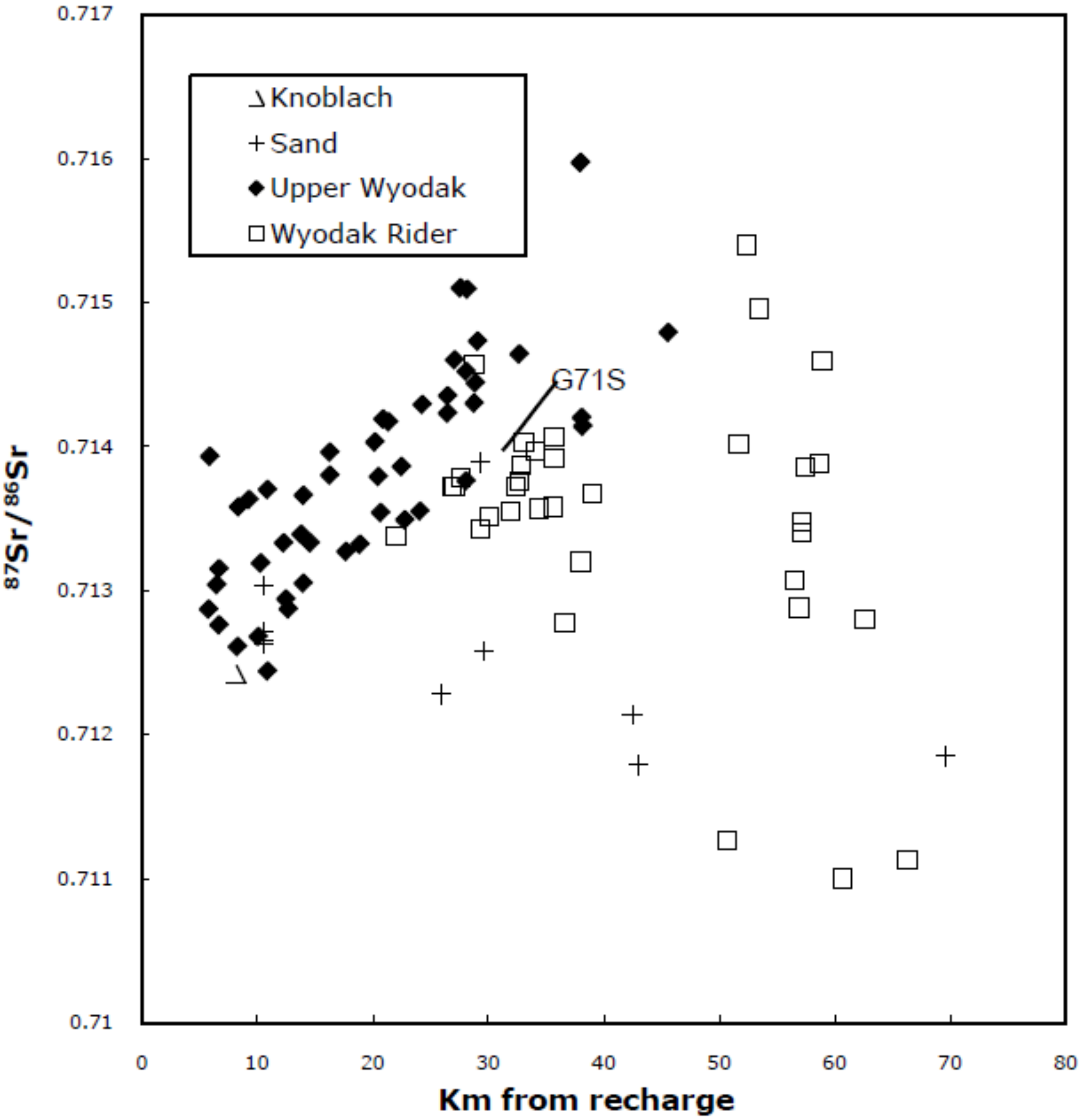
Formation	Coal Zone
Wasatch	Lake De Smet
	Felix
Fort Union (Tongue River Member)	Wyodak Rider
	Upper Wyodak
	Lower Wyodak
	Knobloch
	Sawyer
	Basal Tongue River

Campbell et al. (2008) determined the specific coal zone from which each CBNG produced water sample was collected by analyzing gamma logs for each well, which are available from the Wyoming Oil and Gas Conservation Commission and Montana Board of Oil and Gas websites. The lithologic interpretations of these logs were combined with the database used by the Wyoming State Geological Survey to construct cross sections and identify the coal zone from which the water was withdrawn. Geochemical and Sr isotopic data were measured on all samples, and a subset was analyzed for C isotopes.

The CBNG wellhead samples collected from different coal zones and different parts of the basin show positive $d^{13}C_{DIC}$ values of +12 to +22‰ and high DIC concentrations of above 100 mg C/L (Sharma and Frost, 2008). The DIC concentrations are similar in the coproduced water from both coal zones. However, the CBNG produced water from the Upper Wyodak coal zone, which varies in $\delta^{13}C_{DIC}$ from +18.4 to +22.1‰, is 7-8‰ more enriched in $\delta^{13}C_{DIC}$ than water being produced from the Lower Wyodak coal zone, which yielded $\delta^{13}C_{DIC}$ of +12.2 to +14.3‰ (Sharma and Frost, 2008). This difference in the $\delta^{13}C_{DIC}$ values could reflect differing microbial conditions or degree of methanogenesis. Additionally, the Lower Wyodak water might be affected by leakage of ground water from other aquifers with lower $\delta^{13}C_{DIC}$ values. These results indicate that carbon isotopic compositions can be used to fingerprint water withdrawn from different coal zones.

Whereas the carbon isotopic composition of produced water indicates the presence of methanogenic bacteria, and potentially also identifies the coal zone from which the water was withdrawn, Sr isotopic composition provides information about the degree of isolation of the coal zone aquifers. The $^{87}Sr/^{86}Sr$ ratios of Upper Wyodak coal zone waters in the Gillette area show an increasing ratio with increasing distance from the recharge zone, as described by Frost et al. (2002) and Campbell et al. (2008) (Figure 2). However, the Wyodak Rider coal zone waters fall below this trend, and extend to very low ratios. The sandstone aquifer waters have similarly low $^{87}Sr/^{86}Sr$ ratios (Campbell et al., 2008). These results prompted Campbell et al. (2008) to conclude that the Wyodak Rider coals were not hydraulically isolated from the nearby sandstones.

Figure 2. $^{87}Sr/^{86}Sr$ ratios as a function of distance from the recharge area for water samples in the Gillette and Schoonover areas. Note the regular increase in Sr isotope ratio for samples from the Upper Wyodak coal zone; this is suggested to reflect water-rock interaction along the flow path in a well-confined aquifer. The Wyodak Rider samples depart from this trend, particularly in the Schoonover area, and may reflect incomplete isolation of this coal aquifer from deep sandstone aquifers containing less radiogenic (lower) $^{87}Sr/^{86}Sr$ ratios. Data from Campbell et al. (2008).



The correlation of $^{87}Sr/^{86}Sr$ ratios of the Upper Wyodak coal zone waters with distance into the basin from the recharge zone suggests that the $^{87}Sr/^{86}Sr$ ratio increases with increased water-rock interaction along the flow path. This hypothesis is corroborated by a trend of increasing TDS with distance westward into the basin and concomitant increased residence time (Campbell et al., 2008).

Water from shallow sandstone aquifers in the Gillette and Schoonover areas has relatively low $^{87}Sr/^{86}Sr$ isotopic ratios irrespective of distance from the recharge area (Frost et al., 2002; Brinck and Frost, 2007). As a result, the distinction between Upper Wyodak coal zone waters and water from shallow sandstone aquifers becomes pronounced for wells located more than 5 km into the basin, and suggests that the Upper Wyodak aquifer system is isolated from shallower sandstone aquifers.

In contrast, one ground water sample collected from a deep sandstone (G71S, 1,450 ft depth, see Figure 2), has a Sr isotopic ratio indistinguishable from neighboring Upper Wyodak wells. Moreover, where Upper Wyodak coals are in direct contact with overlying sandstones, as determined from gamma log analysis, the water samples do not have higher TDS and lower $^{87}Sr/^{86}Sr$ that might be expected if these wells produced ground water from both coal and a chemically and isotopically distinctive sandstone aquifer. These results suggest that the Upper Wyodak aquifer is a composite aquifer composed of interbedded coal and sandstone lithologies.

The chemical and isotopic characteristics of the ground water samples from the Wyodak Rider coal zone contrast with those from the Upper Wyodak coal zone (Figure 2). A large range in TDS and $^{87}Sr/^{86}Sr$ ratios is observed in the Wyodak Rider coal zone waters, particularly at 50 to 70 km into the basin from the eastern recharge zone. In some cases this may reflect well completion: two of the wells are perforated to draw water from the coal and overlying sands, hence elevated TDS and lower $^{87}Sr/^{86}Sr$ ratios compared to typical Wyodak Rider aquifer water reflect the introduction of water from both aquifers into these wells. For wells that are open only to coal, the variability may indicate incomplete aquifer isolation and resulting interaction of ground waters between coal and sandstone aquifers.

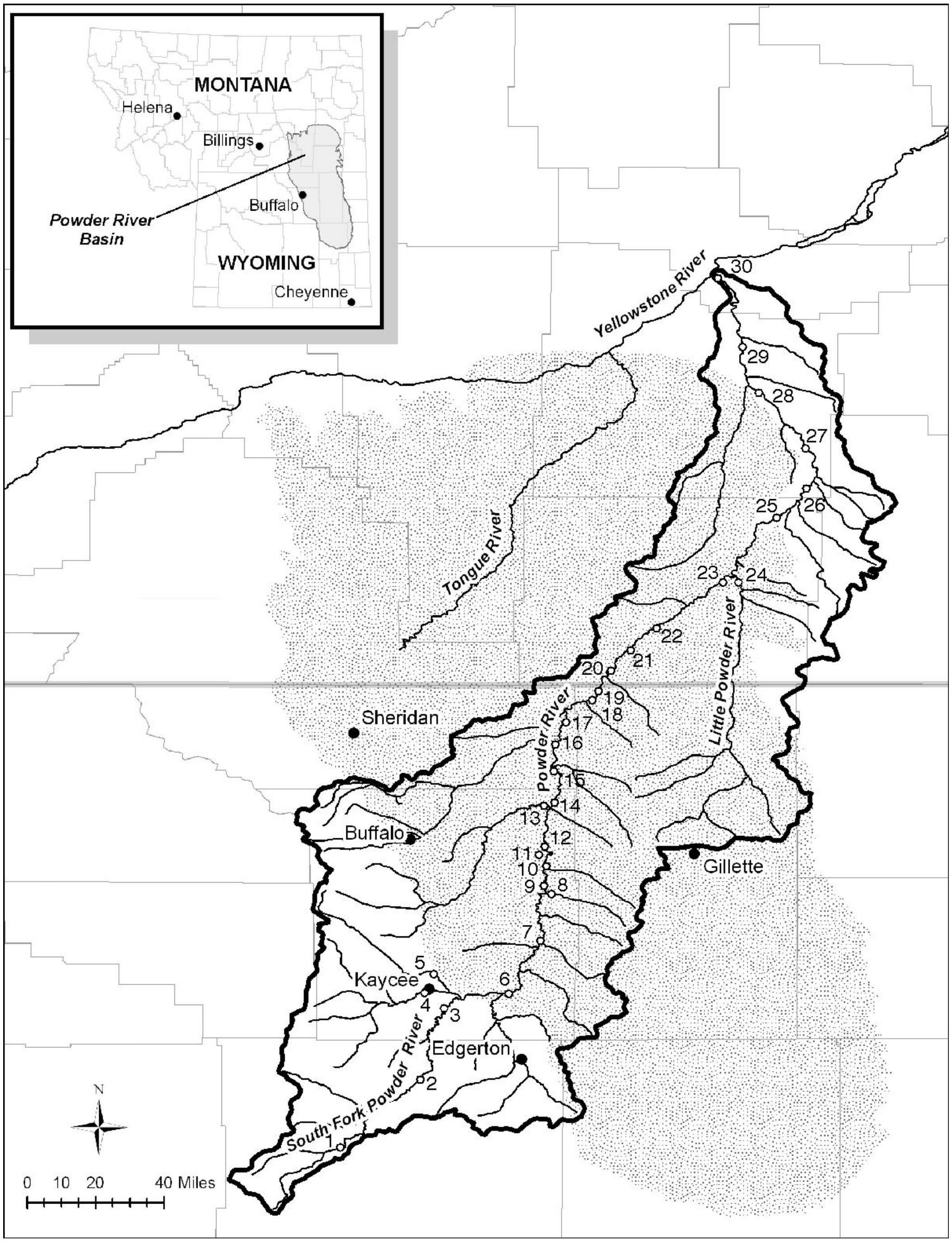
Many Wyodak Rider wells produce higher water-to-gas ratios than average for the Powder River Basin. For over 19,000 coalbed natural gas wells that have produced for more than two years, the average water/gas ratio is 1.8 bbls/Mcf (Surdam et al., 2007). Although 30% of the wells included in Campbell et al. (2008) that are completed in the Wyodak Rider coal zone have average or below average water/gas ratios, an equal number have water/gas ratios greater than 20, and 15% exceed 100 (Wyoming Oil and Gas Conservation Commission, 2007). By contrast, water/gas ratios for other coal seams include few to no ratios exceeding 20 (Wyoming Oil and Gas Conservation Commission, 2007). The intermediate Sr isotope ratios and elevated TDS compared to other coal aquifer waters, coupled with evidence of faults in the subsurface, long dewatering periods and minimal gas production, all suggest that the Wyodak Rider coal zone is not well isolated from adjacent aquifers.

The results of these Sr isotopic studies of coalbed natural gas produced water indicate that the Upper Wyodak coal zone appears to be isolated, and thus CBNG development likely removes water only from a composite Upper Wyodak coal/sandstone aquifer system. On the other hand, the TDS and Sr isotopic characteristics of some of the waters from Wyodak Rider wells suggest that there may be leakage from adjacent aquifers when these wells are depressurized, particularly in the center of the basin. Strontiom isotopic data thus can be used to guide operators to identify those wells where gas/water production ratios will be maximized and water production minimized.

Case study 2: Identification of coalbed natural gas produced water reaching the Powder River in Wyoming. Strontium and carbon isotopic analysis also can be useful in determining the fate of produced water discharged into ephemeral or perennial stream channels. Evapotranspiration, infiltration, and irregular production rates all make it difficult to determine the volume of water that reaches major tributaries and river channels, yet this knowledge is prerequisite to drafting appropriate environmental regulations. In this case study, surface water samples from the Powder River and several tributaries were analyzed to evaluate whether CBNG produced water discharged to surface drainages can be traced geochemically and isotopically into a major river system (Sharma and Frost, 2008; Carter, 2008; Mailloux et al., submitted). Samples were collected along the Powder River from its headwaters west of Casper, Wyoming to its confluence with the Yellowstone River in Montana (Figure 3). Sampling was undertaken during both high- and low-flow conditions from 5 sample locations in headwater tributaries, 22 locations along the main stem of the Powder River, and 3 tributaries in Wyoming and Montana.

Large volumes of produced water are discharged into two of the sampled tributaries: Beaver Creek (PR8) and Flying E Creek (PR11).

Figure 3. Location map of samples collected along the Powder River, Wyoming and Montana. Inset shows the location of the Powder River Basin in Montana and Wyoming. The Powder River drainage is outlined in black; the Powder River Basin is stippled. PR sample stations along the river are numbered.



Brinck et al. (2008) compared the major ion chemistry for the Powder River and coalbed natural gas produced water (Figure 4). Their compilation shows that Powder River water and produced water have similar TDS and sodium contents, but that the Powder River has lower SAR values because it has higher calcium and magnesium concentrations. Because the natural salinity of the river is similar or higher than the salinity measured in the produced water, TDS is not an effective tracer of produced water contributions to the Powder River. On the other hand, input of produced water to the Powder River may be responsible for the increase in SAR in the portion of the river at Sussex, Wyoming (PR6) (Figure 5).

Figure 4. Major ion chemistry for the Powder River (open circles) and coalbed methane 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 USGS and coalbed methane produced water data are from Rice et al. (2002).

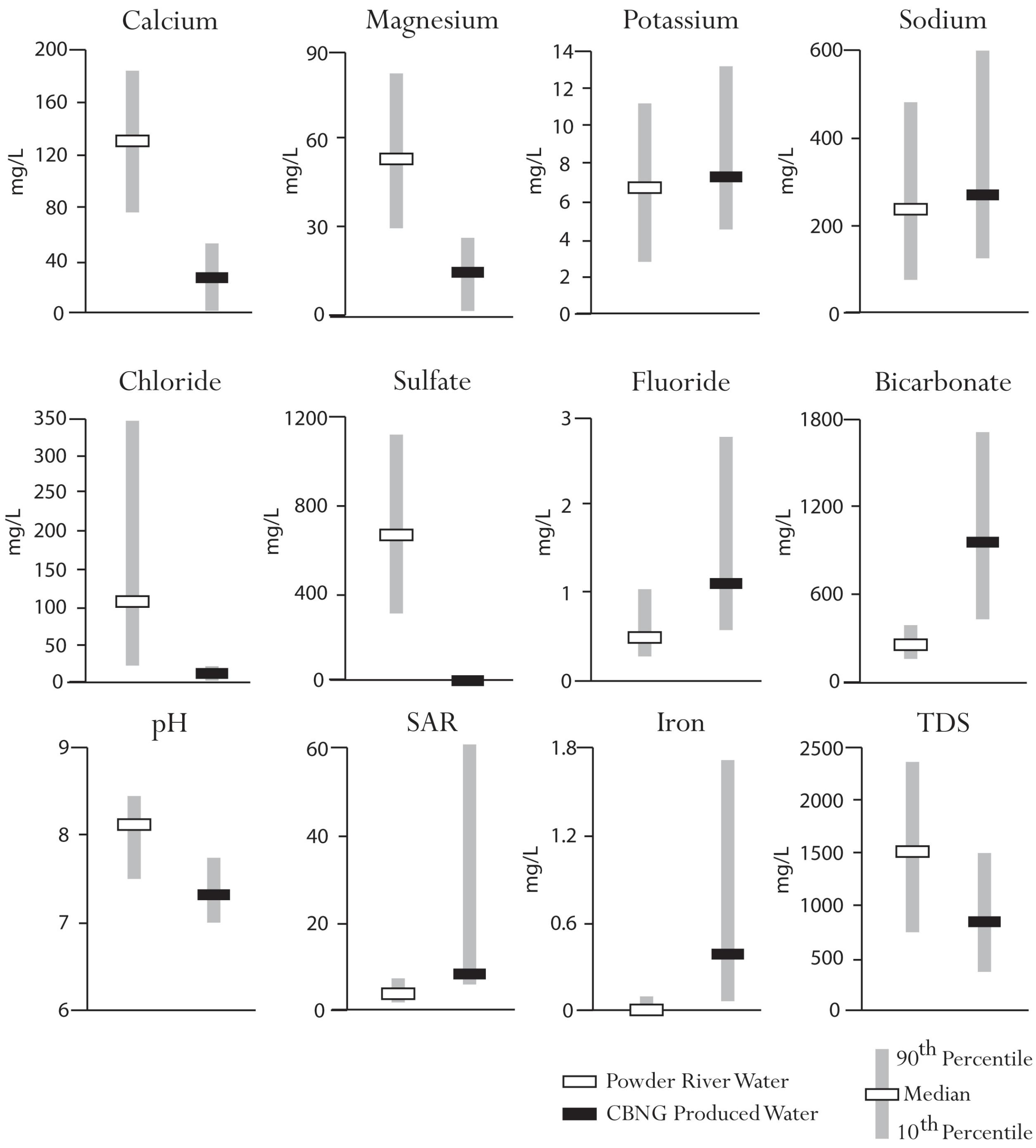
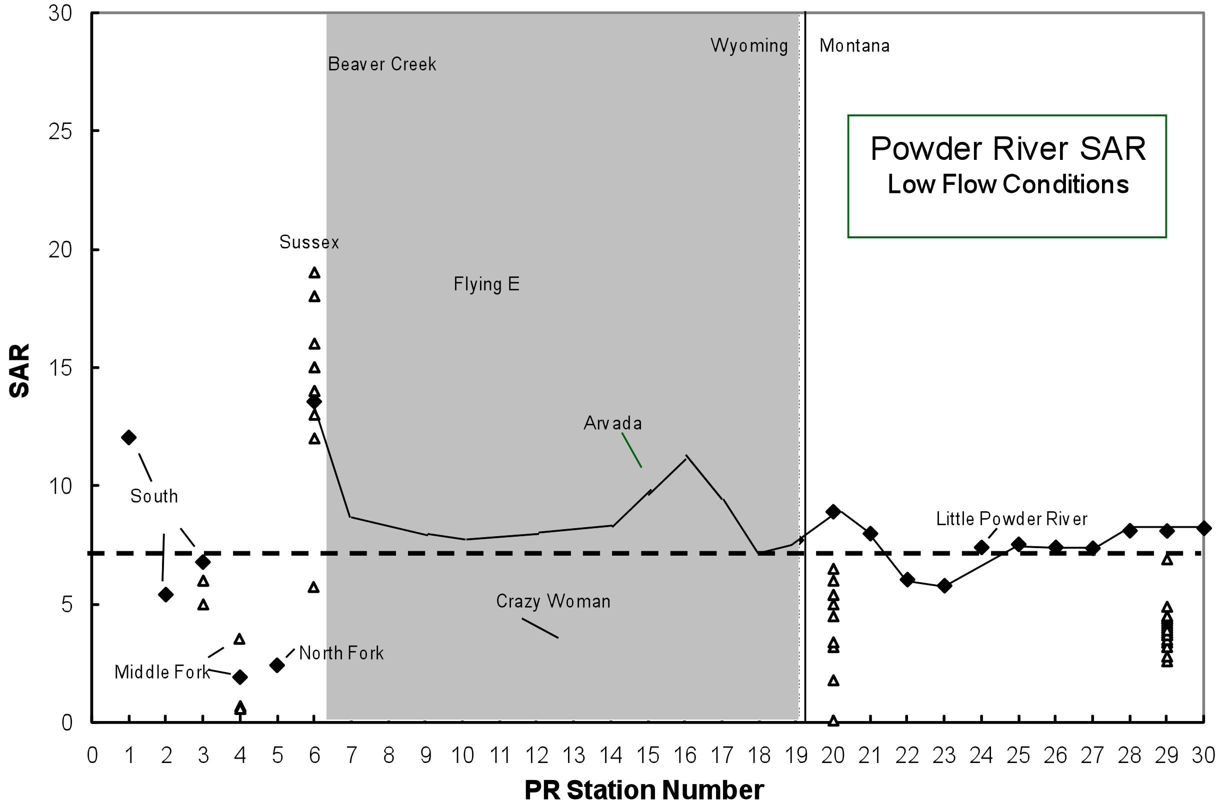


Figure 5. Sodium adsorption ratio at low flow in 2007 (solid diamonds) compared to historic data (open triangles) with position on the river. Shaded area indicates area of most intense CBNG development. Dashed line represents Montana's limit at the time of sampling (7.5 instantaneous). Data from Hembree et al. (1952) and USGS (2008) from the beginning of record (~1940s) through 1989. Data from Carter (2008).



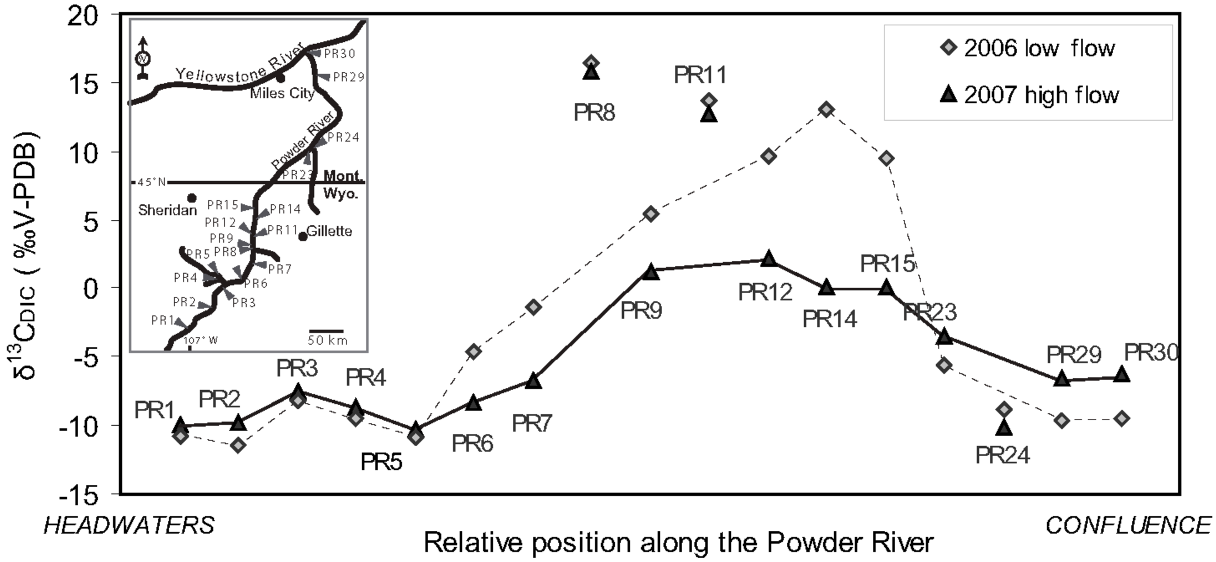
Montana's numeric standards for EC and SAR of surface water crossing the Wyoming-Montana border are problematic. Carter (2008) showed that historically (prior to CBNG development) Powder River water in Montana exceeded Montana's EC standard. At low flow, SAR exceeds Montana's standards both in Wyoming and Montana. The rise in SAR in Montana downstream of the confluence with the Little Powder River is unlikely to be related to CBNG activity because little CBNG production occurs in this part of the watershed.

<u>Calculation of proportion of produced water in the Powder River using Sr isotopic data.</u>

Mailloux et al. (submitted) undertook a Baysian statistical analysis of the Sr isotopic data from the dissolved load samples of the Powder River in order to quantify the amount of CBNG produced water in the Powder River. Using the $^{87}Sr/^{86}Sr$ ratio and Sr concentration of water collected from the Powder River at 30 locations, they implemented a four end-member mixing model that accounts for the $^{87}Sr/^{86}Sr$ ratio and strontium concentration of the different lithologies encountered in the PRB, as well as CBNG produced water. The strontium data and mixing model were coupled in a Bayesian statistical framework that estimates the relative contribution of these different end-members to the river water, while explicitly incorporating uncertainty associated with the strontium measurements and process errors. Model results confirm that one of the tributaries associated with high CBNG activity, Beaver Creek, is almost entirely composed of CBNG produced water. Importantly, the results also indicate that less than 1% of surface flow in the Powder River is composed of CBNG produced water at the Powder River-Beaver Creek confluence and the CBNG contribution decreases with distance downstream from Beaver Creek. Thus, the CBNG produced water is volumetrically an insignificant fraction of water carried by the Powder River. However, this work, combined with the results of Carter (2008), shows that it is possible for even a small amount of CBNG produced water to affect water quality parameters such as the sodium adsorption ratio (SAR; Figure 5), which affect the irrigation quality of water.

Carbon isotopic identification of a produced water component in the Powder River. Carbon isotope values of the Powder River clearly identify the area of greatest CBNG activity, between sites PR7, north of Sussex, Wyoming, and the Wyoming-Montana state line (Sharma and Frost, 2008; Figure 6). Samples collected during high- and low-flow show similar trends, although the $\delta^{13}C_{DIC}$ of the Powder River samples at high-flow are not as distinctive as during low-flow, reflecting a greater proportion of water from snowmelt during the spring runoff. Of note are the Beaver Creek and Flying E drainages, which receive significant produced water discharge. The $\delta^{13}C_{DIC}$ of water from Beaver Creek (PR8) is +16.4‰ and Flying E (PR11) is 13.7‰, which is similar to the range of $\delta^{13}C_{DIC}$ values measured for CBNG produced water. These carbon isotope ratios indicate that the water in these tributaries contains a significant contribution of CBNG coproduced water.

Figure 6. Carbon isotopic compositions of dissolved inorganic carbon in surface water samples collected from the Powder River and its tributaries. The high values correspond to the region where CBNG production is concentrated. Modified from Sharma and Frost (2008).

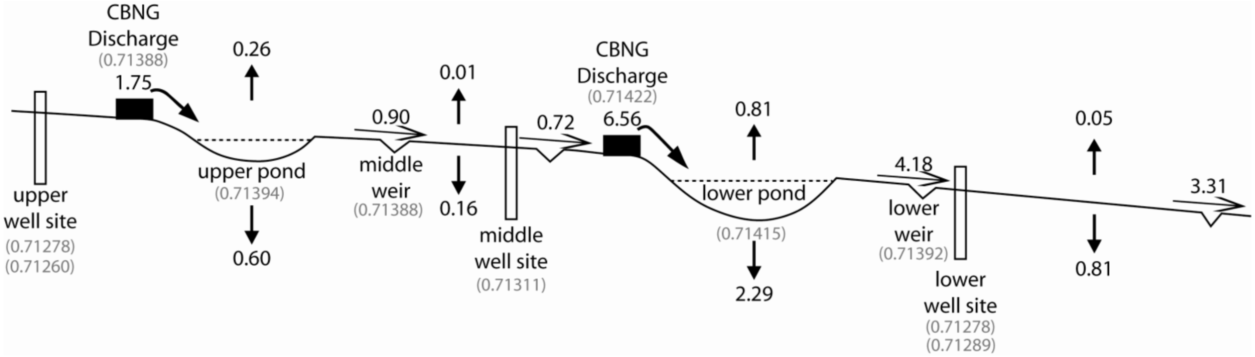


The highly positive $\delta^{13}C_{DIC}$ of Powder River samples in Wyoming downstream from Beaver Creek (PR 9-15) suggests the presence of CBNG produced water in the river related to local CBNG production. The Powder River samples collected in Montana all have negative $\delta^{13}C_{DIC}$. Only sample PR23, from the Powder River at Broadus, Montana, has $\delta^{13}C_{DIC}$ (-5.58‰) above the ambient value of approximately -10‰. These data, along with the Sr isotopic evidence, suggests that isotopic values of the Powder River in Montana are minimally affected by CBNG production during low flow conditions. A comparison of figures 5 and 6 shows that SAR does not correlate with $\delta^{13}C_{DIC}$ values, which indicates that other sources in addition to CBNG produced water must contribute to elevated SAR.

Case study 3: Isotopic identification of produced water infiltration into shallow aquifers.

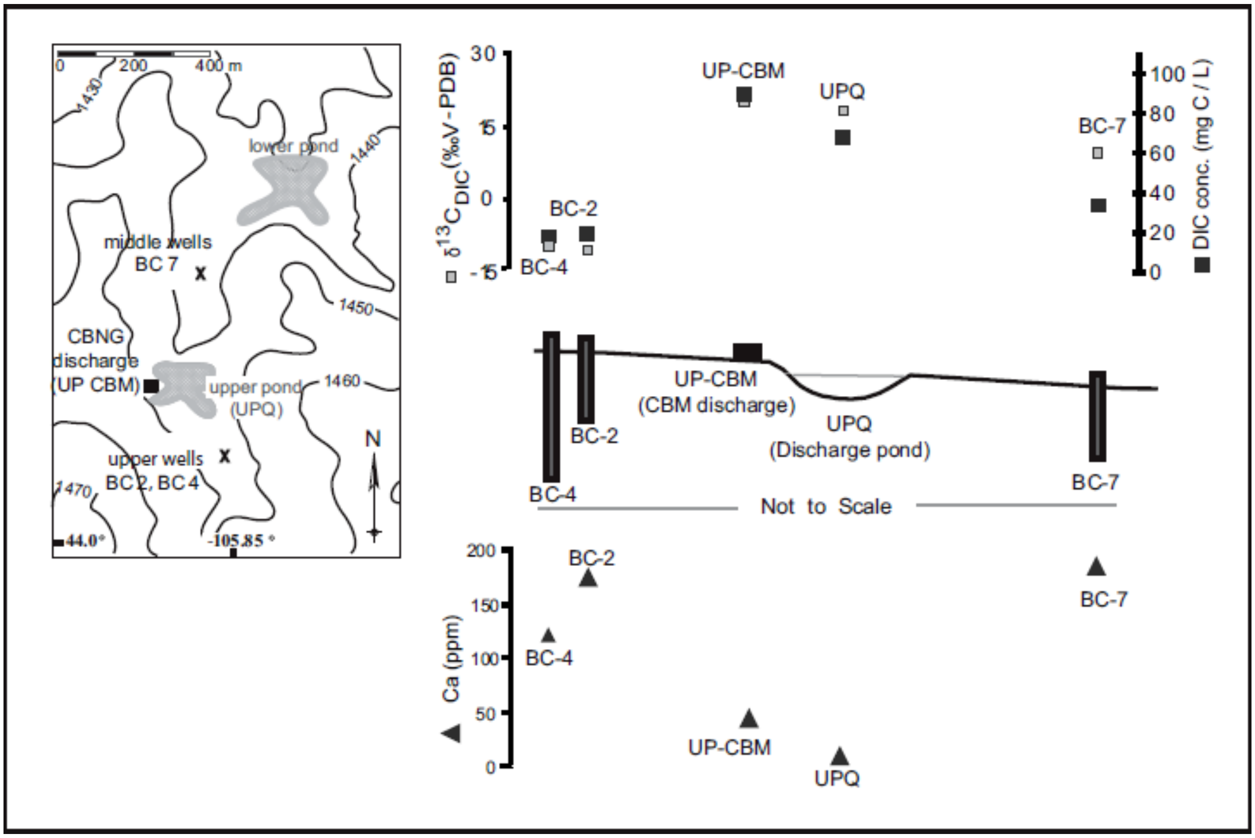
Brinck and Frost (2007) showed that CBNG produced water in the Powder River Basin has a higher $^{87}Sr/^{86}Sr$ than local alluvial water. This measureable difference allows the strontium isotope ratio and concentration to be used as tracers of coalbed natural gas produced water following its discharge on the surface. At the Beaver Creek site (latitude 44.0, longitude -105.85) produced water is discharged directly into the Beaver Creek drainage. Monitoring wells installed above and below the discharge points allowed Brinck and Frost (2007) to use Sr isotopic data to calculate that produced water contributes roughly 70% of alluvial water monitored at the "middle well site" downstream of the upper CBNG discharge point, and 30% is contributed by the local ground water (Figure. 7). Strontium isotopic data also provided evidence that CBNG water may mobilize local salts in the soil, increasing the TDS of the ground water (Wheaton and Brown, 2005; Payne and Saffer, 2005; Frost and Brinck, 2005).

Figure 7. Beaver Creek water budget for the week of August 5-11, 2003. Values are in liters per second. Downward, upward, and horizontal arrows represent infiltration, evaporation, and surface flow respectively. Parenthetical values in gray are the $^{87}Sr/^{86}Sr$ ratios for the sample set collected in August, 2003. From Brinck and Frost (2007).



Sharma and Frost (2008) analyzed the carbon isotopic ratio of dissolved inorganic carbon from a subset of samples from the Beaver Creek site, including the CBNG discharge point, the retention ponds, ambient shallow ground water, and ground water from the middle monitoring well site. The ambient shallow ground water samples collected from the two up-gradient monitoring wells at Beaver Creek, upper well site wells BC-2 and BC-4, show low $\delta^{13}C_{DIC}$ values of -10.3‰ and -10.0‰, respectively (Figure 8). These are within the range of expected values for sub-surface waters in most natural systems. Water samples collected from the CBNG discharge point (UP-CBM) and the corresponding CBNG produced water retention pond (UPQ) yielded values of +19.8‰ and +17.8‰ respectively, within the range of $\delta^{13}C_{DIC}$ for the produced water samples discussed previously. The water from the shallow ground water monitoring well below the retention pond at Beaver Creek (BC-7) shows an intermediate $\delta^{13}C_{DIC}$ value of +9.3‰, between the values of ambient ground water and CBNG produced waters (Figure 8). The intermediate $\delta^{13}C_{DIC}$ value of this water also corroborates the Sr isotopic results suggesting a mixed system containing both CBNG water and ambient water. Although complicated by processes of carbonate dissolution and precipitation, the proportions of each end member suggested by the $\delta^{13}C_{DIC}$ values (approximately two-thirds CBNG, one-third ambient ground water) are similar to the proportions calculated from Sr isotopic data. The DIC concentrations are high in the UP-CBM (CBNG discharge point) and UPQ (retention pond) samples (Figure 8) compared to other samples. The high DIC concentrations do not appear to be related to higher $CaCO_3$ dissolution from source rocks because the two samples showing the highest DIC concentration (UP-CBM and UPQ) have the lowest Ca concentrations (Brinck and Frost, 2007). Therefore, the high DIC concentration in these samples is indicative of methanogenic processes occurring in the coal beds.

Figure 8. Carbon isotopic composition and concentration of dissolved inorganic carbon (DIC) and Ca concentration in water samples collected from the Beaver Creek site. BC-2 and BC-4 are ground water monitoring wells upstream of the CBNG discharge point UP-CBM. UPQ is the pond that holds the CBNG-produced water and BC-7 is a ground water monitoring well installed downstream of the pond. The location map of sampling sites is shown in the inset at the left upper corner. Modified from Sharma and Frost (2008).



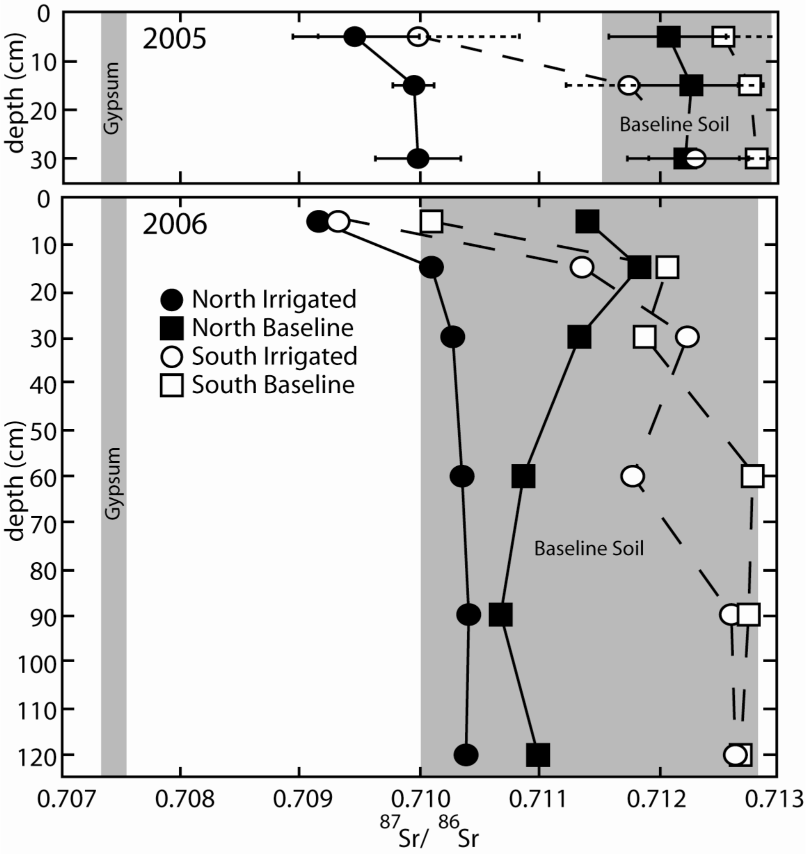
Case study 4: Isotopic identification of beneficial use of produced water for agriculture in the Powder River Basin. Gypsum and sulfur are applied to soils being irrigated with sodium-bicarbonate dominated CBNG produced water to protect soil structure and fertility. Because Wyoming law requires beneficial use of produced water, irrigation with CBNG produced water in the semi-arid Powder River Basin is becoming more common. Strontium isotopes have been used to evaluate the effectiveness of the gypsum and sulfur applications in preventing sodification of these irrigated soils.

Brinck and Frost (2009) studied two fields within the Powder River Basin in northeast Wyoming that were irrigated with CBNG produced water and received applications of gypsum and sulfur. The North Site is a 40-acre center pivot irrigated field near the Powder River. This site has undergone intermittent irrigation since the summer of 2002 and has been planted with alfalfa and barley. The South Site is a 20-acre center pivot irrigated field near the confluence of Beaver Creek and the Powder River. This site has undergone intermittent irrigation since June of 2005 and is planted with barley.

At each site, Sr isotopic and major ion geochemical data were collected on the gypsum and sulfur amendments, irrigation water (which was obtained from CBNG retention ponds), soil samples from depth profiles (including soluble salts and the exchangeable fraction based upon measurements of ammonium acetate extractions and the saturated paste extractions) and vegetation (irrigated and non-irrigated).

As shown on Figure 9, the strontium isotope ratio of strontium on the cation exchange complex of irrigated soil falls between that of the gypsum amendment and that of local soil. In 2005 samples, approximately half the strontium on the cation exchange sites is from the addition of gypsum to a depth of 30 cm at the North irrigated site and at the surface (<5 cm) of the South irrigated site. Deeper samples at the South irrigated site show less influence of gypsum with only 20% and 10% of the strontium coming from gypsum. In 2006 samples, approximately half the strontium on the exchange sites comes from gypsum from 0 to 30 cm on the North irrigated site. Progressively less strontium on the exchange sites comes from gypsum in deeper samples with 10 to 20% originating from gypsum in soil deeper than 30 cm. South irrigated site samples from 2006 are similar to South Site 2005 samples in that only the surface sample has a significant contribution of strontium from gypsum. The strontium in South irrigated site surface sample in 2006 is approximately 30% from gypsum; less than the 50% strontium from gypsum measured in the 2005 surface sample.

Figure 9. Strontium isotope ratios of exchangeable strontium with depth. North irrigated and baseline site samples are solid circles and squares, respectively. South irrigated and baseline site samples are open circles and squares, respectively. Grey shaded areas represent the range of strontium isotope ratios measured for the gypsum amendment and the exchangeable strontium in baseline soil. Shaded areas for baseline soil represent the range of isotope ratios measured for the respective years.



Also through use of strontium isotopes, plant uptake of strontium originating from the gypsum amendment was determined (Brinck and Frost, 2009). Vegetation growing on the irrigated fields had ^{87}Sr/^{86}Sr ratios similar to the gypsum amendment indicating calcium and strontium from the gypsum amendment is being incorporated onto the soils' cation exchange complex and is in a plant available form.

Despite having a source of calcium that is incorporated onto the exchange sites of the soil, the amount of sodium occupying exchange sites increased following irrigation with CBNG produced water. This is reflected in the SAR value of the irrigated field's soil water, which was elevated over baseline. It is possible that in the event of a heavy rain or the cessation of irrigation, the EC may drop below the threshold needed to maintain soil structure. To avoid degradation in soil structure, care should be taken to keep SAR levels low enough that natural salt levels will maintain a compressed double layer in the clays. Baseline EC values indicate that natural salt levels are around 1-2 dS m^{-1}. At these EC levels, soil may have SAR values around 10-15 with low to moderate risk of dispersion (Richards, 1954; Rengasamy et al., 1984; Hanson et al., 1999); however a soil specific study would need to be done to ensure the correct threshold SAR and EC values have been identified. To achieve these lower soil SAR levels, it may be necessary to lower the initial sodium levels of the irrigation water prior to application (Brinck and Frost, 2009).

CONCLUSION

From the foregoing summaries of case studies it is clear that stable isotope ratios of carbon and strontium show excellent potential for tracing water produced with coalbed natural gas. Produced water has a strongly positive $\delta^{13}C$ value that is easily distinguished from the negative carbon isotope values of surface water. The major sources of dissolved inorganic carbon in this hydrologic system have distinct carbon isotope values, from approximately -23‰ for soil CO_2 to greater than +10‰ for produced water. This difference in $\delta^{13}C$ values enabled Sharma and Frost (2008) and Carter (2008) to identify the area of greatest impact of CBNG activity on surface flows, which lies between Sussex and Arvada, Wyoming. The influence of CBNG produced water was readily identified both in samples collected at high and low flow. The Powder River samples collected in Montana all have $\delta^{13}C_{DIC}$ values similar to baseline. This suggests that the contribution of CBNG water to total discharge is low.

Baysian statistical analysis of the Sr isotopic data from the dissolved load samples of the Powder River allowed Mailloux et al. (submitted) to quantify the amount of CBNG produced water in the Powder River. Using the $^{87}Sr/^{86}Sr$ ratio and Sr concentration data of water collected from the Powder River at 30 locations, they implemented a four end-member mixing model that accounts for the $^{87}Sr/^{86}Sr$ ratio and strontium concentration of lithology encountered in the Powder River Basin, as well as produced water. Model results confirm that two of the tributaries associated with high CBNG activity, Flying E Creek and Beaver Creek, are dominated by CBNG produced water. Importantly, the results indicate that CBNG produced water is volumetrically an insignificant fraction of water carried by the Powder River. However, these studies show that it is possible for even a small amount of water to be fingerprinted using carbon isotopes, and for this volume of produced water to affect water quality parameters such as the sodium adsorption ratio (SAR), which affects the irrigation quality of water.

In addition to investigating the effect of CBNG produced water on surface flows of the Powder River, several studies have used carbon and strontium isotopes to trace the infiltration of product water into the shallow ground water system. Both carbon and strontium isotopic data can identify ground water that originated in part from infiltrated CBNG produced water. These studies establish $\delta^{13}C$ and $^{87}Sr/^{86}Sr$ as particularly powerful fingerprints for tracing CBNG on the surface and subsurface, and makes it possible to monitor the fate of CBNG produced water into ground water and streams of the region.

Brinck and Frost (2007) showed a connection between changes in water quality and strontium concentration at an on-channel coalbed natural gas produced water discharge site. They suggested that on-channel discharge shows promise for future disposal in that there are fewer salts in existing channels due to annual flushing. However, the amount and duration of CBNG discharge may exceed the water mounding caused by annual flooding; in which case stream bank salts may be mobilized. Additionally, the change in vegetation species and biomass that occurs due to the creation of a perennial stream may be of concern to landowners if the local vegetation, adapted to semi-arid conditions, is out-competed by undesirable riparian vegetation or by a floral community that is not stable when the source of water is removed (Stearns et al., 2005). The conclusions drawn by those authors that existing ephemeral channels have fewer soluble salts than the associated floodplain imply that ponds excavated off existing channels will probably also experience the mobilization of local salts.

In situations where CBNG produced water is used for irrigation, strontium isotopes are useful for following changes to soil health caused by the high sodium levels in the CBNG water. Potential chemical and physical changes to soil caused by irrigation with CBNG produced water are of concern to ranchers in the Powder River Basin. A study by Brinck and Frost (2009) of two sites along the Powder River between Beaver Creek and I-90 showed that CBNG produced water irrigated soil salinity and sodicity values varied from EC values around 3-10 dS/m and SAR values around 8-20 compared to 1-2 dS/m and <1 SAR for non-irrigated sites. 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 platelets to remain closer together (flocculated) because of the compressed double layer (Essington, 2004). Longer term studies (Brinck and Frost, 2009) found that after the initial increases in salinity and sodicity during the first two years, no further increases were found. However, care must be taken that salinity and sodicity levels are low enough prior to the cessation of CBNG-produced water irrigation to ensure that subsequent addition of low-salinity, low-sodicity rain water does not cause further reductions in soil quality (Brinck et al., 2008).

Future applications for strontium and carbon isotope ratio measurements in coalbed natural gas studies include corroborating ongoing and future research into produced water minimization and management. Several companies now use subsurface drip irrigation systems utilizing CBNG produced water. We anticipate that strontium isotopes could be a valuable tool to identify the final infiltration depth of the water, to track the chemical additions to the water, and to identify the source of salts in surface soils. Carbon isotopes would be a useful way to verify aerial surveys of ground water salinity (Hammack et al., 2008). Aerial identification of high salinity ground water may reflect natural variation or could indicate a contribution from CBNG produced water. Positive values of $\delta^{13}C_{DIC}$ would be a way to distinguish between these possibilities. We also recommend adopting a geospatial approach to interpreting regional strontium isotope ratios of produced water. Deviations from the regional trends in coalbed strontium isotope ratio, particularly when correlated with high water to gas ratios for individual wells, may help identify areas where coal seams are not well isolated from other aquifers and are thus not ideal areas for CBNG production. This approach may help segregate problems caused by improper well completion (which will show as isolated deviations) from natural problems such as high hydraulic-conductivity fractures (for which deviations in isotopic ratio and water to gas ratios will be widespread and may be associated with faults that may be identified through seismic surveys).

In summary, the research summarized in this chapter shows that strontium and carbon isotopic tracers can be very useful in understanding the geochemical evolution of CBNG produced water and for predicting potential environmental impacts. It is not enough to regulate the produced water based upon its initial chemical composition at the wellhead. 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. Understanding and mitigating potential environmental changes due to the discharge of produced water may determine the future of CBNG production not just in Wyoming and Montana but globally.

ACKNOWLEDGEMENTS

The case studies summarized here were funded by Department of Energy awards DE-FC26-06NT15568 Task 4, DE-FC26-05NT15549 Task 3 and by the Western Resources Project. These awards partially supported PhD dissertations by E. Brinck, and J. Mailloux, and M.S. theses by C. Campbell, S. Carter, and B. Pearson.

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