

Task 4 – Environmental Tracers Applied to Quantifying Causes in Water Quality Along the Powder River, Wyoming

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The Powder River Basin in northeastern Wyoming is one of the most active areas of coalbed natural gas development in the western United States. This resource 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. This task was composed of three subtasks that investigated a) the fate of produced water in the surface water system, b) the infiltration of this water into the shallow ground water system, and c) beneficial use of produced water in agriculture in the Powder River Basin:

- Task 4a sought to determine whether coalbed natural gas produced water is a source of salinity in the Powder River. We used environmental tracers including stable isotopic compositions of carbon, oxygen and hydrogen, $^{87}\text{Sr}/^{86}\text{Sr}$ of river water and $^{143}\text{Nd}/^{144}\text{Nd}$ of river particulate and bedload in addition to standard water quality measurements to answer this question. We collected from 30 sample sites along the entire length of the Powder River, from its headwaters near Casper, Wyoming, to its confluence with the Yellowstone River in Montana. Samples were collected both during low flow (September) and high flow (June).
- Task 4b investigated whether stable isotopes of carbon are effective in tracing infiltration of coalbed natural gas produced water into the shallow groundwater system in the Powder River Basin. We determined that carbon isotopes are particularly sensitive monitors of coalbed natural gas produced water input, building upon our earlier work documenting that $^{87}\text{Sr}/^{86}\text{Sr}$ is also an extremely useful environmental tracer.
- Task 4c evaluated the effectiveness of sulfur and gypsum applications to CBNG-irrigated fields. Strontium isotopes were used to analyze the effect of sulfur and gypsum applications on Powder River Basin soils undergoing irrigation with the sodium/bicarbonate CBNG water. Strontium's chemical similarity to calcium allowed us to investigate biologically-driven calcium cycles at the ecosystem scale and to assess the effectiveness of sulfur and gypsum amendments designed to treat the high sodium adsorption ratio (SAR) of CBNG produced water.

Also as a culmination of this research, we summarized the geochemical evolution of CBNG produced water throughout the whole 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 (Brinck et al. 2008). An understanding of this entire geochemical system is key to drafting appropriate regulations, preventing environmental degradation and anticipating potential remediation after cessation of CBNG production. Currently, most regulation is based upon the initial chemical composition of the CBNG produced water (Buccino and Jones 2004). Our work in this project, however, clearly demonstrated that in most situations the subsequent changes to the water caused by its interaction with the atmosphere

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and local soils ultimately will determine the impact upon the environment of the Powder River Basin.

Task 4 partially supported the PhD research of two students, Elizabeth Brinck (PhD 2007) and Jason Mailloux (PhD in progress). It also supported the MS research of Shaun Carter (MS 2008). Technical assistance by Michael Meredith and Jack Fenner was also partially supported by this project. Senior personnel include co-PI Frost and Assistant Research Scientist Dr. Shikha Sharma. To date, this task has resulted in 6 published abstracts, 2 published extended abstracts, and 4 refereed journal articles.

Methods:

Sample Collection

This study involved the collection of water from CBNG discharge points, shallow monitoring wells, ponds and streams. Water samples were collected in accordance with Wyoming Department of Environmental Quality grab sample collection procedure (Wyoming Department of Environmental Quality 2001). Temperature and pH were measured in the field; samples were filtered through a 0.45 micron filter and kept cool and dark until laboratory analysis. Half of each sample was acidified to pH 2 for major ion analysis. Suspended sediment samples were collected from the filter paper used in the water sample preparation; bedload samples were collected with a bedload sampler from the bottom of the main channel of the river. Sediment samples were dried in a 150°C oven for ~24 hours and bedload samples powdered using to 200 mesh grain size using a ring mill.

Sample Analysis

Elemental Analyses

Major cations and trace elements were measured by ICP-MS, sodium (Na) by flame atomic absorption, anions by ion chromatography and alkalinity by potentiometric titration at the University of Wyoming. TDS was calculated by summing the major ionic constituents and converting bicarbonate into equivalent carbonate (Drever 1997).

Strontium Isotopic Analyses

Strontium was isolated from a 3 ml aliquot of each un-acidified water sample using Teflon columns filled with Eichrom® Sr-Spec resin and the strontium isotopic composition determined by thermal ionization mass spectrometry at the University of Wyoming. The internal precision of $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratio measurements is ± 0.00001 . Seventy-six analyses of NBS 987 strontium standard measured during the course of this study gave an average value of $^{87}\text{Sr}/^{86}\text{Sr} = 0.71026 \pm 0.00002$ (2 standard deviations). All analyses were normalized to an $^{86}\text{Sr}/^{88}\text{Sr}$ ratio value of 0.1194. Analytical blanks were less than 0.2 ng, negligible compared to sample sizes of at least 0.1 microgram strontium. An additional 1-ml aliquot of each sample was spiked with an ^{84}Sr -enriched tracer and strontium concentration determined by isotope dilution. Strontium concentrations are reproducible at the 1% level. Replicates show that $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are reproducible within the error expected from the precision of the instrument.

Neodymium Isotopic Analyses

Neodymium and samarium were isolated from suspended sediment and bedload samples from the Powder River. Samples were dissolved in HF-cHNO₃. One aliquot was spiked with a ¹⁴⁶Nd and ¹⁴⁹Sm-enriched tracer and Nd and Sm concentrations were determined by isotope dilution. Rare earth elements were separated using standard cation chromatography techniques. REE-specific exchange resin was used to separate Nd and Sm from the other rare earth elements. Samples were loaded on triple filament assemblies and the isotopic compositions of Nd and Sm were obtained by thermal ionization mass spectrometry at the University of Wyoming. An average ¹⁴³Nd/¹⁴⁴Nd ratio of 0.511846 ± 11 (2 standard deviations) was measured on 20 analyses of the La Jolla Nd standard. Uncertainties in the individual Nd isotopic ratio measurements are 0.00001 (2 sigma). Blanks are less than 50 picograms and no blank correction was made.

Stable Oxygen and Hydrogen Analyses

Samples to be analyzed for oxygen and hydrogen isotopic values were stored in an 8 dram glass vial. Vials were filled completely to the top and sealed with a special cone-in-cap lid, to prevent evaporation and isotopic exchange with air in head space. ²H/H ratios were measured using off-line Zn reduction methodology and oxygen and hydrogen isotopic compositions analyzed using a Micromass Optima dual inlet mass-spectrometer at the University of Wyoming's stable isotope laboratory.

Dissolved Inorganic Carbon Isotopic Analyses

Samples collected for dissolved inorganic carbon analyses were passed through a Cameo 0.45 micron nylon pre-filter attached to 60 cc Luer-lock syringe. The water sample was then transferred in 30 ml Wheaton glass serum vials with teflon septa and sealed with Al caps using a crimper. Few drops (2-3) of benzalkonium chloride were added to each vial before filling it with water to halt any metabolic activity. Samples were analyzed for d¹³C_{DIC} on a GasBench-II device coupled to a Finnigan DELTA plus mass spectrometer in the central Stable Isotope Facility at the University of Wyoming. The reproducibility and accuracy was monitored by replicate analysis of samples and internal lab standards and was better than ± 0.1 ‰. The d¹³C_{DIC} values are reported in per mil relative to V-PDB. The DIC concentrations in samples were also quantified from the mass spectrometry data. Three NaHCO₃ stock solutions of different DIC concentrations were prepared for this purpose. DIC concentrations were then quantified based on the peak areas of the mass 44-ion trace of these standards. Plotting peak area of CO₂ vs. concentration of DIC in these standards gives an excellent correlation (r²=0.995), indicating that DIC concentrations of the samples could be quantified using this method. The relative standard uncertainty of the DIC concentration measurement in this study was ± 3%.

Results and Discussion:

Task 4a: Fate of Produced Water in the Surface Water System

We analyzed surface water samples from the Powder River and several tributaries to evaluate whether CBNG produced water discharged to surface drainages can be traced geochemically and isotopically into major river systems. Sampling along Powder River was done from its headwaters west of Casper, Wyoming to its confluence with the Yellowstone River in Montana (Fig. 4-1). The initial sampling took place from September 21 to 24, 2006 when the river was

near its lowest flow but when a heavy rain temporarily increased flow and muddy roads prevented us from sampling all locations. Sampling was completed between June 30-July 4, 2007 when the river was near high flow conditions, and August 31-September 3, 2007 at low flow, and these sample sets are the basis for our interpretations. The sample set includes 5 samples of headwater tributaries, 22 samples of the main stem of the Powder River and 3 samples from tributaries in Wyoming and Montana. The tributaries sampled are Beaver Creek (PR8) Flying E (PR11) and Little Powder River (PR 24).

Geochemical Results and Discussion

The data gathered for this study are presented in Carter (2008). In this report we summarize the results on Fig. 4-2, which plots electrical conductivity as a proxy for total dissolved solids in the river water samples. The natural salinity of the river is similar or higher than the salinity measured in the produced water, so no contribution from produced water is readily observed in the electrical conductivity of the river water.

The main impact of CBNG produced water on the Powder River appears to be an increase in sodicity and resulting increase in SAR in the portion of the river north of Sussex, Wyoming (PR6) (Fig. 4-3). Minor ions of concern are not present in significant concentrations; water directly from the river is fully suitable for livestock and wildlife to consume.

Montana's numeric standards for EC and SAR 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. The quality of water in the river, as it relates to the Montana standards, depends strongly on the flow of the river. Some CBNG water is present in the Powder River. However, the current Montana standards are not well-suited to identify this component because they do not account for the natural seasonal variability of water quality in the Powder River. We suggest that the regulatory periods be revised better to correspond to natural flow variations in the Powder River. At present both maximum dilution at high flow and maximum concentration both fall within the same current regulatory period.

Powder River Sample Locations

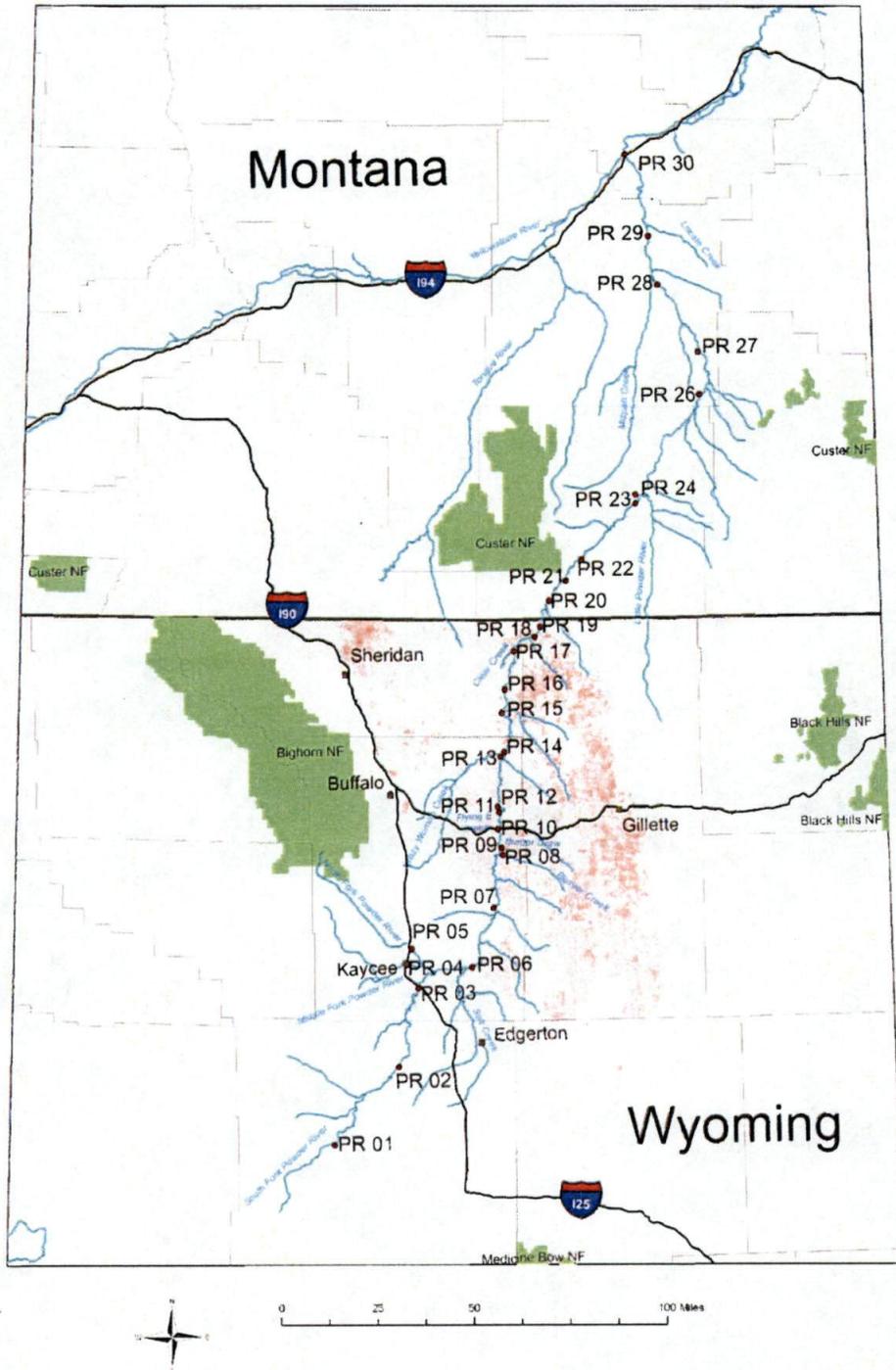


Figure 4-1: Location map of samples collected along the Powder River, Wyoming and Montana. Area in pink is the area of CBNG development. Map from Carter (2008).

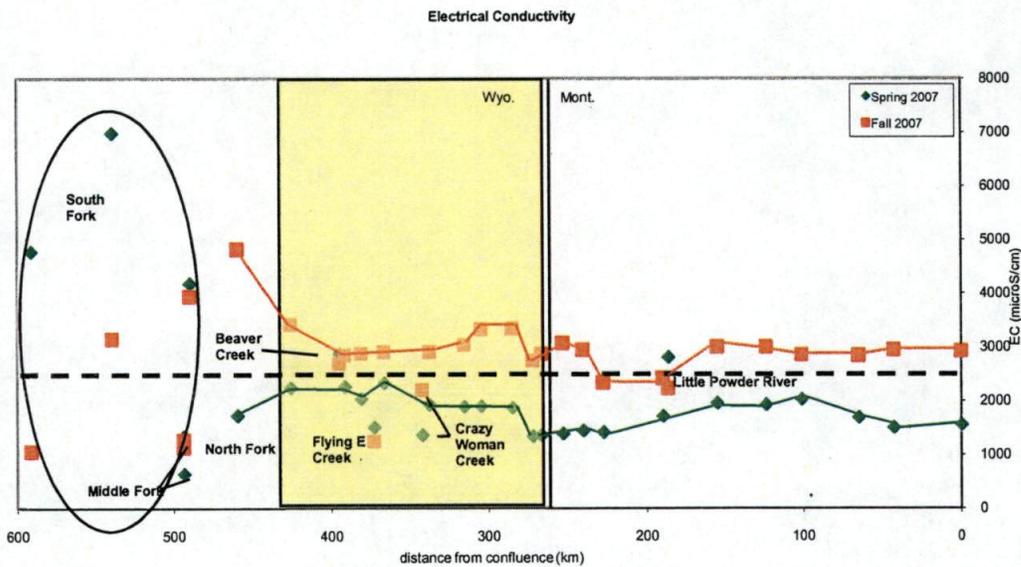


Figure 4-2: Electrical conductivity with position on the river. Shaded area indicates most intense CBNG development. The dashed line represents Montana's numeric standard for the time of year including both May and September samplings (2500 microS/cm). From Carter (2008).

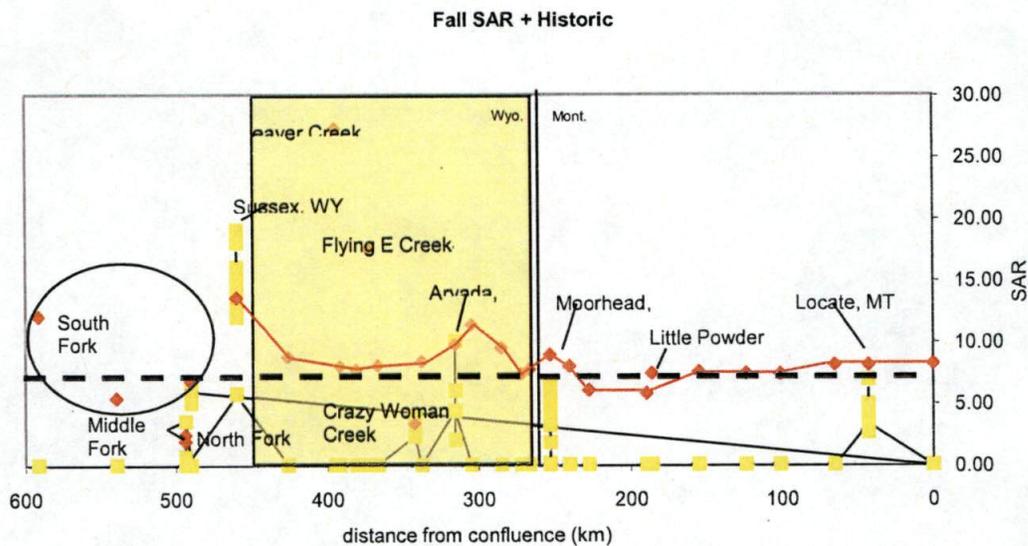


Figure 4-3: Sodium adsorption ratio at low flow compared to historic data (yellow symbols) with position on the river. Shaded area indicates area of most intense CBNG development. Dashed line represents Montana's limit at the time of sampling (7.5 instantaneous). Data from Hembree et al. (1952) and USGS (2008) from the beginning of record (~1940s) through 1989. From Carter (2008).

Carbon Isotope Results and Discussion

Stable isotopes of carbon show good potential for tracing water produced with coalbed natural gas. Produced water has a strongly positive $\delta^{13}\text{C}$ that is easily distinguished from the negative per mil values of surface water. The major sources of dissolved inorganic carbon in this system each have distinct values, from approximately -23‰ for soil CO_2 to greater than +10‰ for produced water (Sharma and Frost 2008).

The $\delta^{13}\text{C}$ values of the Powder River clearly identify the area of greatest CBNG activity, between sites PR7, north of Sussex, and PR16, north of Arvada (Fig. 4-4). Samples collected during high and low flow show the same trends, although the $d^{13}\text{C}_{\text{DIC}}$ of the Powder River samples at high flow are not as strongly positive as during low flow, reflecting the greater proportion of water from snowmelt during the spring runoff. Of note is the Beaver Creek drainage, which receives significant produced water discharge. The $d^{13}\text{C}_{\text{DIC}}$ of water from Beaver Creek (PR8) is +16.4‰, which is within the range of $d^{13}\text{C}_{\text{DIC}}$ that we analyzed for CBNG produced water directly from wellheads. It appears that in the fall, the water in the Beaver Creek tributary is dominated by CBNG discharge.

The highly positive $d^{13}\text{C}_{\text{DIC}}$ 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 $d^{13}\text{C}_{\text{DIC}}$. Only sample PR23, from the Powder River at Broadus, Montana, has $d^{13}\text{C}_{\text{DIC}}$ (-5.58‰) above the ambient value of approximately -10‰. This suggests that surface waters in Montana are little to unaffected by CBNG production during the low flow conditions.

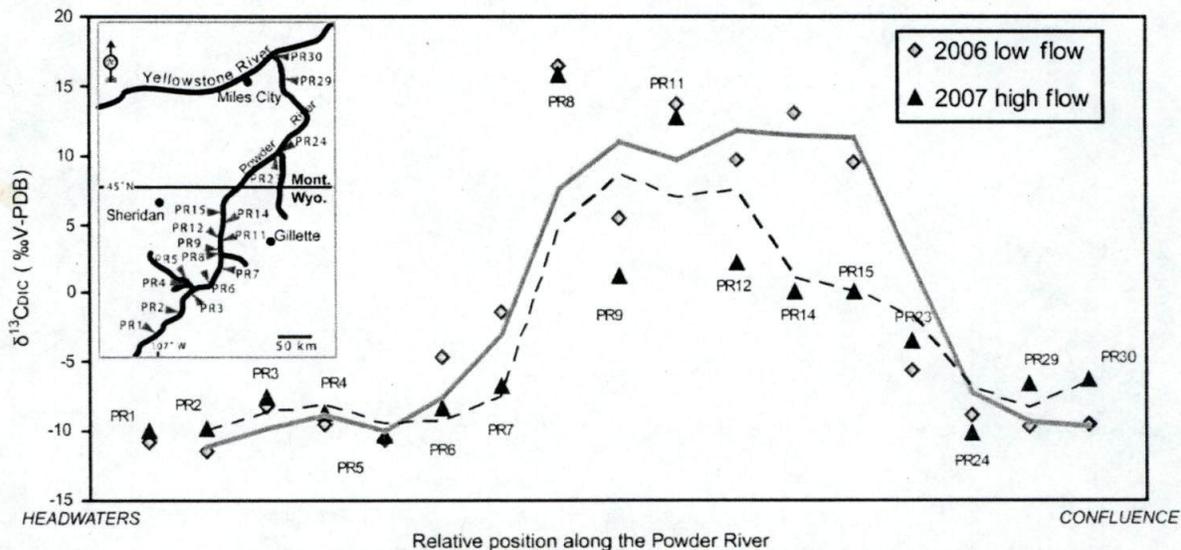


Figure 4-4: Carbon isotopic compositions of dissolved inorganic carbon in surface water samples collected from the Powder River and its tributaries. The high values correspond to the region where CBNG production is concentrated (Sharma and Frost 2008).

Sr Isotopic Results and Discussion

We undertook a Bayesian 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 (Mailloux et al., submitted). Using the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio and $[\text{Sr}]$ ($[\text{Sr}]$) of water collected from the Powder River at 30 locations, we implemented a four end-member mixing model that accounts for the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio and $[\text{Sr}]$ 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 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 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, our work shows that it is possible for even a small amount of water to affect water quality parameters such as the sodium adsorption ratio (SAR) and electrical conductivity (EC), which affect the irrigation quality of water.

Nd Isotopic Results and Discussion

On a plot of $^{143}\text{Nd}/^{144}\text{Nd}$ versus $^{147}\text{Sm}/^{144}\text{Nd}$, Powder River sediment has typical Sm-Nd isotopic compositions typical of river and aeolian particulate matter (Fig. 4-5). These data suggest that the suspended and bedload sediment carried by the Powder River is representative of that carried by world rivers. The $^{143}\text{Nd}/^{144}\text{Nd}$ of the suspended sediment in the Powder River is slightly more radiogenic on average than that of the bed load, resulting in slightly older Nd depleted-mantle model ages for the bed load compared to suspended load (1.9 Ga vs 1.7 Ga). There is no variation in Sm-Nd isotopic characteristics as a function of location along the river, suggesting that Nd has been efficiently recycled from Precambrian basement into younger sedimentary rocks such that all sources of fine and coarse sediment carried by the Powder River have nearly indistinguishable Nd isotopic compositions. This extensive sediment recycling leads to the conclusion that the zircon population in the Powder River Basin has also been repeatedly recycled, which is in fact observed (Mailloux, PhD thesis in progress). Because Nd dissolved in river water and in CBNG produced water is in very low concentrations, its isotopic ratio does not fingerprint either water source but instead Nd isotopic data yields insight into the effectiveness of sedimentary recycling processes in the Rocky Mountain region.

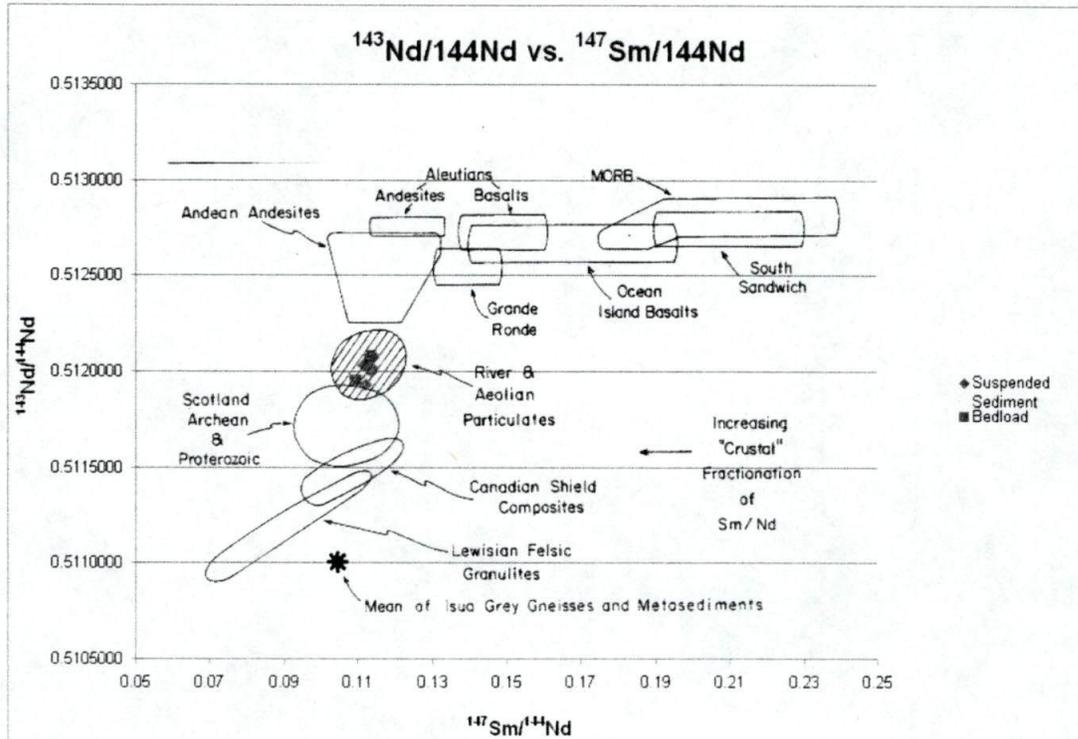


Figure 4-5: Plot showing Powder River sediment isotope values compared to reference geologic materials from Goldstein et al. (1984).

Task 4b: Infiltration of CNG Produced Water into the Shallow Ground Water System

In this subtask, we built upon earlier work of Brinck and Frost (2007) that showed Sr isotopes are effective fingerprints of the aquifer from which water originates. Specifically, CBNG produced water has a higher $^{87}\text{Sr}/^{86}\text{Sr}$ than local alluvial water. This measurable difference allows the strontium isotope ratio and concentration to be used as tracers of CBNG water following its discharge on the surface. At the Beaver Creek site (44.0 latitude, -105.85 longitude) CBNG water is discharged directly into the Beaver Creek drainage. Monitoring wells were installed above and below the discharge points by the Western Resources Project as part of a study of the effects of CBNG development on surface and shallow ground water systems in the Powder River Basin (Wheaton and Brown 2005, Payne and Saffer 2005, Frost and Brinck 2005). We calculated from Sr isotopic data that CBNG water contributes roughly 70% of the water in the “middle well site” downstream of the upper CBNG discharge point, and 30% is contributed by the local ground water (Fig 4-6). We also showed from Sr isotopic data that CBNG water may mobilize local salts in the soil, increasing the ion concentrations in the water.

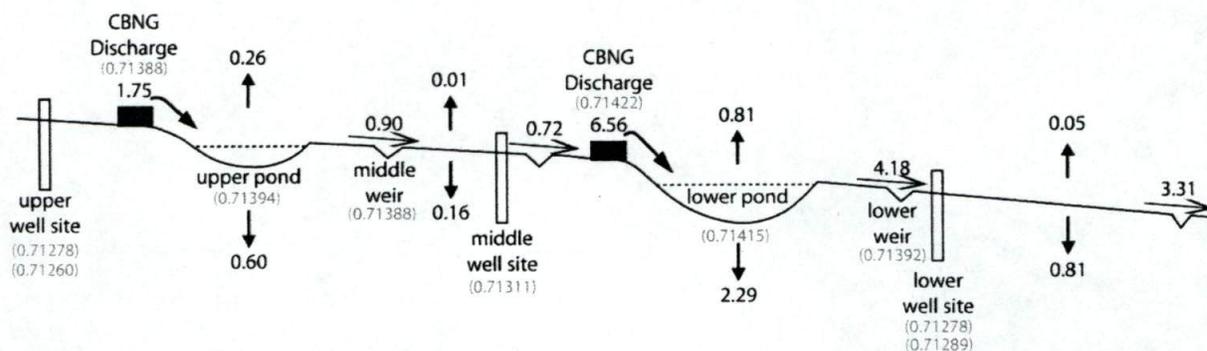


Figure 4-6: Beaver Creek water budget for the week of August 5-11, 2003. Values are in liters per second. Downward, upward, and horizontal arrows represent infiltration, evaporation, and surface flow respectively. Parenthetical values in gray are the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for the sample set collected in August, 2003. From Brinck and Frost 2007.

In subtask 4b, we analyzed the carbon isotopic ratio of dissolved organic carbon from CBNG produced water from several different coal zones. In addition, we analyzed some of the same water 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 CBNG wellhead samples collected from different coal zones and different parts of the basin show positive $d^{13}\text{C}_{\text{DIC}}$ values of +12 to +22‰ and high DIC concentrations of above 100mg C/L (Sharma and Frost 2008). The positive $d^{13}\text{C}_{\text{DIC}}$ values reflect preferential removal of ^{12}C from the carbon pool by the methanogens present in the formation waters. The DIC concentrations are similar in the CBNG produced water from both coal zones. However, the $d^{13}\text{C}_{\text{DIC}}$ of the CBNG produced water from the Upper Wyodak coal zone, which vary from +18.4 to +22.1‰, is 7-8 ‰ more enriched in $d^{13}\text{C}_{\text{DIC}}$ than water being produced from the Lower Wyodak coal zone, which yielded $d^{13}\text{C}_{\text{DIC}}$ of 12.2 to 14.3‰ (Sharma and Frost 2008). This difference in the $d^{13}\text{C}_{\text{DIC}}$ values could reflect differing conditions under which methanogenesis is taking place and/or the reaction progress/degree of methanogenesis in these coal zones or the Lower Wyodak water might be affected by leakage of groundwater from other aquifers with lower $d^{13}\text{C}_{\text{DIC}}$ values.

The ambient shallow ground water samples collected from the two up-gradient monitoring wells at Beaver Creek, BC-2 and BC-4, show low $d^{13}\text{C}_{\text{DIC}}$ values of -10.3‰ and -10.0‰, respectively (Fig. 4-7). These are within the range of expected values for sub-surface waters in most natural systems. On the other hand 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 $d^{13}\text{C}_{\text{DIC}}$ for the produced water samples discussed above. The water from the shallow ground water monitoring well below the retention pond at Beaver Creek (BC-7) shows a $d^{13}\text{C}_{\text{DIC}}$ value of +9.3 ‰, intermediate between the values of ambient ground water and CBNG produced waters (Fig. 4-7). Brinck and Frost (2007) used $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and Sr concentrations of these same samples to calculate that a minimum of 70% of the water in monitoring well BC-7 originated from the CBNG discharge. The intermediate $d^{13}\text{C}_{\text{DIC}}$ value of this water also suggests 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 $d^{13}\text{C}_{\text{DIC}}$ values (approximately two-thirds CBNG, one-third ambient ground water) is similar to the proportions calculated from Sr isotopic

data. The DIC concentrations are also high in the Up-CBM (CBNG discharge point) and UPQ (retention pond) samples (Fig. 4-7) 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 also indicative of contribution of methanogenic processes to the DIC.

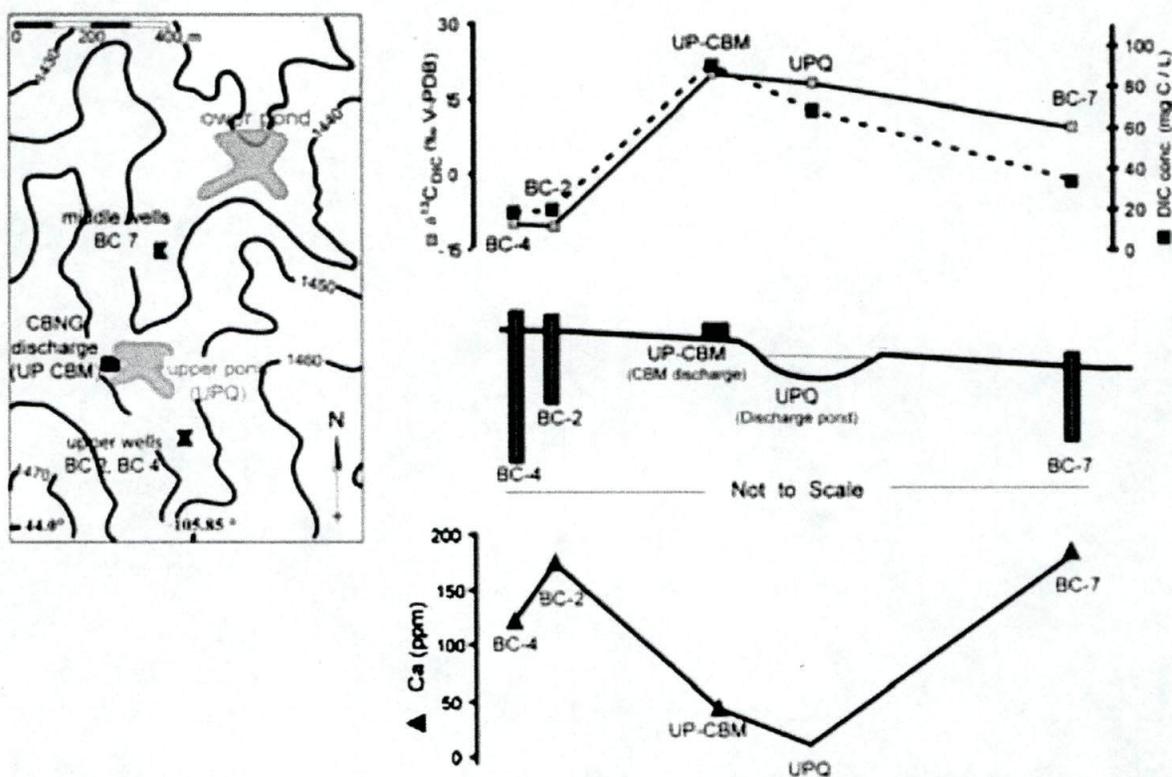


Figure 4-7: Carbon isotopic composition and concentration of dissolved inorganic carbon (DIC) and Ca concentration in water samples collected from the Beaver Creek site. BC-2 and BC-4 are ground water monitoring wells upstream of the CBNG discharge point UP-CBM. UPQ is the pond that holds the CBNG-produced 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.

Task 4c: Beneficial Use of Produced Water in Agriculture in the Powder River Basin

Gypsum and sulfur are applied to soils being irrigated with sodium-bicarbonate dominated coal bed natural gas (CBNG) produced water to protect soil structure and fertility. Wyoming law requires beneficial use of produced water and irrigation with CBNG produced water in the semi-arid Powder River Basin is becoming more common. Strontium isotopes were used to evaluate the effectiveness of the gypsum and sulfur applications in preventing sodification of these irrigated soils.

Research for this subtask was carried out on two fields within the Powder River Basin in northeast Wyoming that were irrigated with CBNG produced water and receive applications of gypsum and sulfur (Brinck and Frost, in revision). The North Site is a 40-acre center pivot irrigated field near the Powder River about five kilometers south of Interstate-90. The 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 about eleven kilometers south of Interstate-90. This site has undergone intermittent irrigation since June of 2005 and was 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 unirrigated).

As shown on Fig. 4-8, 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 30 cm at the North irrigated site and at the surface 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 at the surface of 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.

Effects of sulfur application are more ambiguous in that the pH of the amended soil in this study was not statistically lower than baseline soil nor was there a significant amount of local calcium mobilized. Also through use of strontium isotopes, plant uptake of strontium originating from the gypsum amendment was determined. There was no bioaccumulation of barium in irrigated vegetation and, in fact, both irrigated vegetation and soil water had lower concentrations of barium than the baseline vegetation and soil.

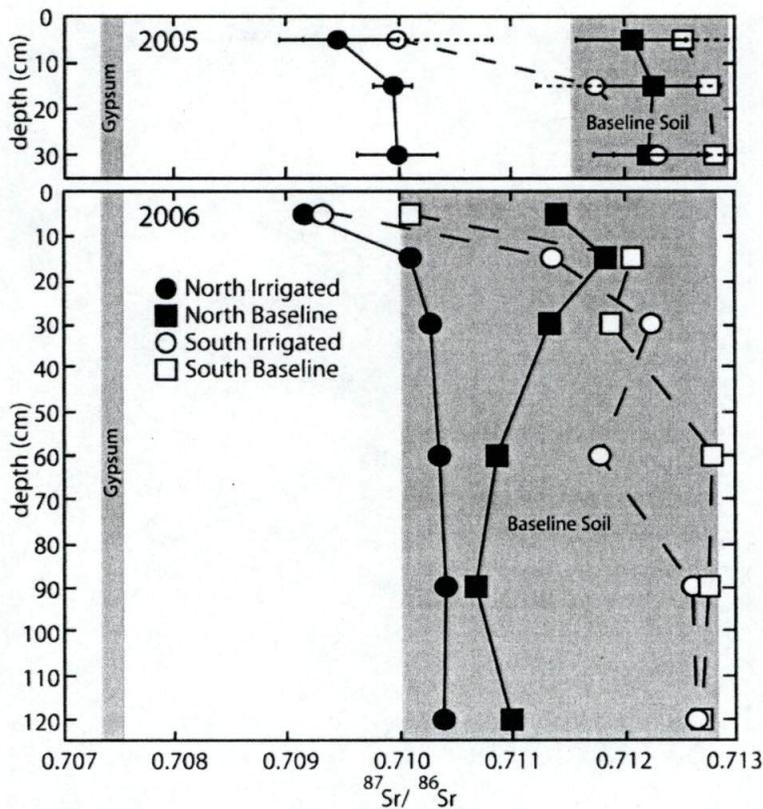


Figure 4-8: Strontium isotope ratios of exchangeable strontium with depth. North irrigated and baseline site samples are solid circles and squares, respectively. South irrigated and baseline site samples are open circles and squares, respectively. Grey shaded areas represent the range of strontium isotope 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. From Brinck and Frost (in revision).

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 event or the cessation of irrigation, the EC may drop below the threshold needed to maintain flocculation. 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. Baseline EC values measured in the baseline sites (Brinck and Frost, in revision) 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 risk of dispersion (Rengasamy et al. 1984); however a soil specific study would need to be done to ensure the correct threshold SAR 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.

Summary Research for Task 4: Geochemical Evolution of CBNG Produced Water in the Powder River Basin

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 upon the initial chemical composition of the CBNG produced water (Buccino and Jones 2004). Our work in this project, however, clearly demonstrated 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 upon the environment of the Powder River Basin.

In Brinck et al. (2008) we describe how water produced with coal bed 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 (Fig 4-9).

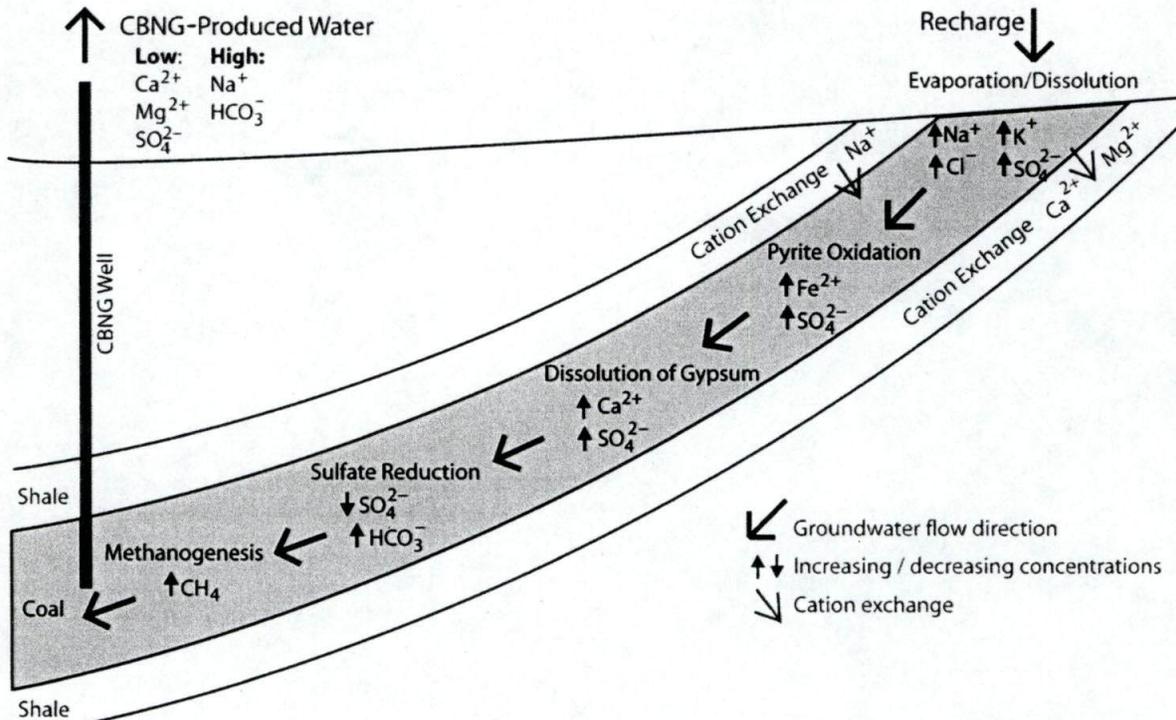


Figure 4-9: Summary of geochemical processes occurring in coal aquifers used for coalbed natural gas production. From Brinck et al. (2008).

After CBNG produced water is discharged to the surface, interaction with the atmosphere will initiate precipitation of calcite, iron hydroxide and barite among other minerals (Fig. 4-10). The interaction of CBNG produced waters with semi-arid Powder River Basin soils can mobilize accumulated salts which, through infiltration, can then reach the water table, potentially affecting the quality of the groundwater. 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.

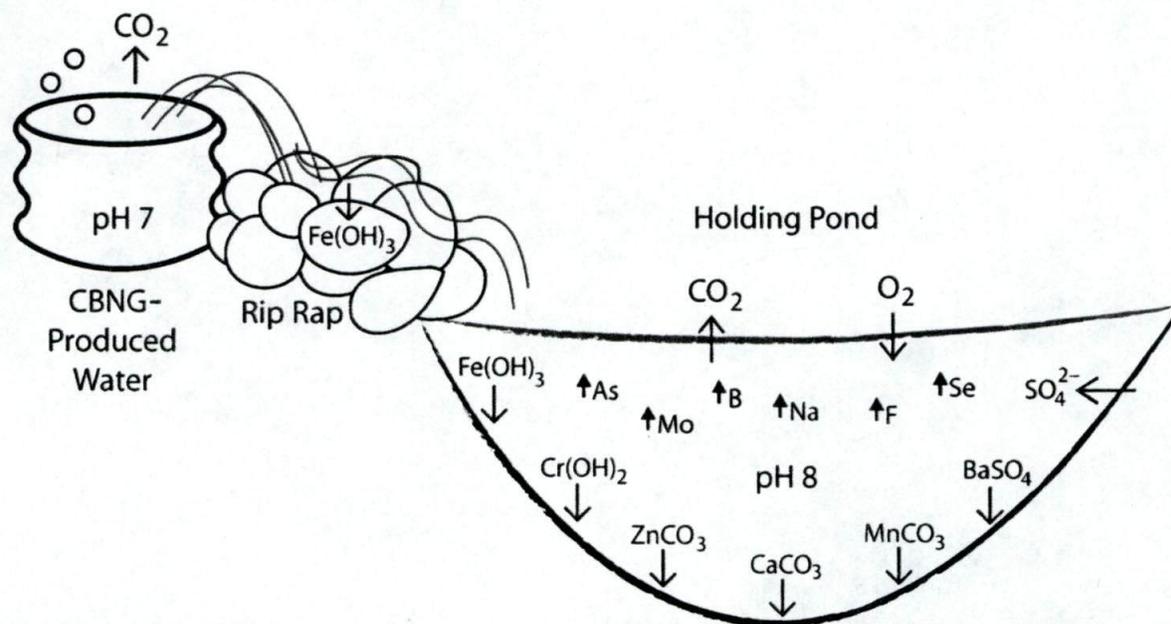


Figure 4-10: Summary of geochemical changes that occur when CBNG produced water is held in an impoundment. Arrows directed to the floor of the pond and rip rap indicate the precipitation of minerals out of water. Upward arrows indicate the loss to atmosphere of gas. Downward arrows across the surface of 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. Bold upward arrows represent increasing concentrations of the species in pond water. From Brinck et al. (2008).

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 (Brinck et al. 2008). The high sodium to calcium and magnesium ratio in CBNG produced water requires careful management when using as an irrigation source to prevent sodification of irrigated soils. 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.

Conclusions:

The research undertaken in this task focused on the fate of CBNG produced water following discharge at the surface in the Powder River Basin. Our carbon isotopic measurements show that some CBNG produced water does make its way to the Powder River. Its main impact on the water quality of the Powder River appears to be an increase in sodicity and resulting increase in SAR in the portion of the river where most CBNG is focused. Minor ions of concern are not

present in significant concentrations; water directly from the river in this area is fully suitable for livestock and wildlife to consume.

Stable isotopes of carbon show excellent potential for tracing water produced with coalbed natural gas. Produced water has a strongly positive $\delta^{13}\text{C}$ that is easily distinguished from the negative per mil values of surface water. The major sources of dissolved inorganic carbon in this system each have distinct carbon isotope values, from approximately -23‰ for soil CO_2 to greater than +10‰ for produced water. This difference in $\delta^{13}\text{C}$ values enabled us to identify the area of greatest CBNG activity, between Sussex and Arvada, Wyoming. The influence of CBNG produced water was readily identified both in samples collected and high and low flow. The Powder River samples collected in Montana all have negative $\text{d}^{13}\text{C}_{\text{DIC}}$. This suggests that surface waters in Montana are little to unaffected by CBNG production during the low flow conditions.

Our Bayesian statistical analysis of the Sr isotopic data from the dissolved load samples of the Powder River allowed us to quantify the amount of CBNG produced water in the Powder River (Mailloux et al., submitted). Using the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio and [Sr] ([Sr]) of water collected from the Powder River at 30 locations, we implemented a four end-member mixing model that accounts for the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio and [Sr] 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 indicate that CBNG produced water is volumetrically an insignificant fraction of water carried by the Powder River. However, our work shows that it is possible for even a small amount of water to be fingerprinted using carbon isotopes, and for this volume of SBNG 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 the Powder River, we also 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. Our study establishes $\text{d}^{13}\text{C}_{\text{DIC}}$ and DIC concentration as a particularly powerful fingerprint 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.

Our results show a connection between changes in water quality and strontium concentration at an on-channel CBNG disposal site. We suggest 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 here that existing ephemeral

channels have fewer soluble salts than the associated floodplain imply that ponds excavated off existing channels (off-channel) may also experience the mobilization of local salts.

In situations where CBNG product 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 is of concern to ranchers in the Powder River Basin. Our study (Brinck and Frost, in revision) 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. 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 ours (Brinck and Frost, in revision) 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).

In summary, our research shows that understanding the geochemical evolution of CBNG produced water is important 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. We suggest that further work is needed to understand the potential impact the cessation of CBNG produced water irrigation may have upon the fields to which it is being applied to avoid degradation of soil quality. Understanding and mitigating potential environmental changes due to the discharge of CBNG produced water may determine the future of CBNG production in Wyoming and Montana.

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