Oil & Natural Gas Technology

DOE Award No.: DE-FC26-06NT15568

Research and Development Concerning Coalbed Natural Gas

Submitted by:

William D. Ruckelshaus Institute

of Environment and Natural Resources

University of Wyoming

Department 3971

1000 E. University Ave.

Laramie, WY 82071

Office of Fossil Energy

DISCLAIMER

TABLE OF CONTENTS

EXECUTIVE SUMMARY

The Powder River Basin in northeastern Wyoming is one of the most active areas of coalbed natural gas (CBNG) 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 co-produced with the gas during depressurization of the coal seam.

Beginning with a few producing wells in Wyoming's Powder River Basin (PRB) in 1987, CBNG well numbers in this area increased to over 13,600 in 2004, with projected growth to 20,900 producing wells in the PRB by 2010. CBNG development is continuing apace since 2004, and CBNG is now being produced or evaluated in four other Wyoming coal basins in addition to the PRB, with roughly 3500-4000 new CBNG wells permitted statewide each year since 2004. This is clearly a very valuable source of clean fuel for the nation, and for Wyoming the economic benefits are substantial. For instance, in 2003 alone the total value of Wyoming CBNG production was about $1.5 billion, with tax and royalty income of about $90 million to counties, $140 million to the state, and $27 million to the federal government.

In Wyoming, cumulative CBNG water production from 1987 through December 2004 was just over 380,000 acre-feet (2.9 billion barrels), while producing almost 1.5 trillion cubic feet (tcf) of CBNG gas statewide. Annual Wyoming CBNG water production in 2003 was 74,457 acre-feet (577 million barrels). Total production of CBNG water across all Wyoming coal fields could total roughly 7 million acre-feet (55.5 billion barrels), if all of the recoverable CBNG in the projected reserves of 31.7 tcf were produced over the coming decades.

Pumping water from coals to produce CBNG has been designated a beneficial water use by the Wyoming State Engineer's Office (SEO), though recently the SEO has limited this beneficial use designation by requiring a certain gas/water production ratio. In the eastern part of the PRB where CBNG water is generally of good quality, most of it is discharged to surface drainages or to soil (for irrigation). CBNG water quality generally declines when moving from the Cheyenne River drainage northwestward to the Belle Fourche, Little Powder, and Powder River drainages and in the central and western part of the PRB, most CBNG water goes to evaporation-infiltration ponds or is discharged directly to surface drainages. Concerns center on the salinity of the water, usually measured as total dissolved solids (TDS), or electrical conductivity (EC) and sodium adsorption ratio (SAR). Other management options currently in use include injection, managed irrigation (with additives to mitigate the effects of high salinity), atomization, and treatment by reverse osmosis or ion exchange. A key water quality issue is the cumulative effect of numerous CBNG water discharges on the overall water quality of basin streams. This leads to one of the most contentious issues in CBNG development in Wyoming's PRB: Montana's concern about the potential downstream effects of water quality degradation on rivers flowing north into Montana.

Many of the benefits and costs associated with CBNG development have been debated, but dealing with CBNG water quantity and quality arguably has been the most difficult of all the issues. Given the importance of these issues for continued development of CBNG resources in Wyoming and elsewhere, the DOE-NETL funded project presented here focuses on CBNG co-produced water management.

The research was organized around nine separate, but interrelated, technical project tasks and one administrative task (Task 1). The nine technical project tasks were pursued by separate research teams at the University of Wyoming, but all nine tasks were coordinated to the extent possible in order to maximize information gained about CBNG co-produced waters. In addition to project management in Task 1, the key research tasks included: (2) estimating groundwater recharge rates in the PRB; (3) groundwater contamination of trace elements from CBNG disposal ponds; (4) use of environmental tracers in assessing water quality changes in ground and surface water systems; (5) development of a software toolbox to assess CBNG water treatment technologies; (6) potential value of CBNG water for enhanced oil recovery using low salinity waterflood; (7) evaluation of natural zeolites for low cost CBNG water treatment; (8) evaluation of aquatic toxicity testing methods required by regulatory agencies on some CBNG water discharges; (9) use of remote sensing to evaluate CBNG water discharges as habitat for West Nile Virus transmitting mosquitoes; and (10) a summary of lessons learned from historic CBNG management in Wyoming.

Some of the most important conclusions drawn from the research in this project include the following (see individual task reports for additional key research conclusions):

- Investigators estimated that recovery times for PRB groundwater levels from CBNG water production may be as much as 10 times longer than BLM's 2003 EIS estimate of ~30 years – the new estimate is based on researcher's analysis using the Surface Water Assessment Tool (SWAT) to calculate recharge rates and uncertainty levels (Task 2).
- Stable isotopes of carbon show excellent potential for tracing CBNG production water, with a signal that is easily distinguished from natural surface waters – this method allowed investigators to identify CBNG contributions to Wyoming surface waters, but also led to their conclusion that Powder River samples from Montana are little affected or unaffected by CBNG production upstream even during low flow conditions (Task 4).
- The CBNG treatment toolbox software developed in Task 5 allows cost comparison estimates for 5 demineralization technologies, showing that treatment costs may range from \$0.036/bbl to \$0.190/bbl depending on technology and local conditions – overall the Toolbox results indicate that treatment cost is directly impacted by the amount of sodium removed regardless of technology used (Task 5).
- Injection of CBNG water in Tensleep Formation cores resulted in significantly improved oil recovery following injection of high salinity formation water, supporting a conclusion that, depending on the proximity of CBNG wells and targeted oil reservoirs, use of CBNG water can improve oil recovery in waterflood applications (Task 6).
- Wyoming zeolites modified with calcium additions had a much higher CBNG water treatment potential for removal of sodium than natural Ca-zeolites from New Mexico and Idaho, and Task 7 experiments led investigators to estimate Wyoming zeolite material costs at \$0.05/bbl to \$0.10/bbl of treated CBNG water (Task 7).
- Chemical constituents in Beaver Creek, Wyoming, CBNG discharge water did not cause acute toxicity to 11- to 15-d-old fathead minnows either in in-stream or lab toxicity tests, and field observations of aquatic plants and animals suggested no overt adverse effects from CBNG effluent discharged to Beaver Creek during 2006-07 study periods (Task 8).
- Ammonification of organic nitrogen in CBNG effluents can occur during transport of unpreserved effluent samples, thus potentially biasing Whole Effluent Toxicity tests by increasing ammonia concentrations by the time the samples arrive at the lab (Task 8).

REPORT DETAILS

Task 1: Project Management and Outreach

Harold Bergman[1], Ann Boelter and Jill Lovato

<u>Project Initiation:</u>

The current project, funded by the National Energy Technology Laboratory (NETL) of the Department of Energy's (DOE) Office of Fossil Energy under project number DE-FC26-06NT15568, is titled "Research and Development Concerning Coalbed Natural Gas (CBNG)," with an emphasis on issues related to management of CBNG co-produced water in Wyoming's Powder River Basin. The project was initiated as a Congressionally directed grant for ~$1.5 million to the University of Wyoming's Office of Research and Economic Development, which delegated responsibility for project initiation, organization and management to UW's Ruckelshaus Institute of Environment and Natural Resources.

To identify the specific research elements to pursue under this grant, the UW Research Office and the Ruckelshaus Institute issued a Request for Proposals (RFP) to UW and Wyoming Community College faculty and staff in February 2006. The steps taken prior to and following the RFP release to identify the potentially most important and needed research included the following:

- An invitation to all relevant federal and Wyoming state agencies responsible for developing, managing, monitoring and/or regulating CBNG development to submit priorities for needed research on CBNG issues, particularly related to management of CBNG co-produced water.
- A total of 17 categories of specific research needs were identified and included in the UW RFP under the following 7 groupings:
  - Enhanced CBNG production and relationship with water production,
  - CBNG and water resource assessment and reservoir management,
  - Groundwater hydrology and quality,
  - Surface water hydrology and quality,
  - CBNG water management and disposal,
  - Reclamation of CBNG disposal ponds and stream channels, and
  - Fish and wildlife impacts.
- A total of 27 proposals were received from UW and Wyoming Community College faculty, including proposals that addressed elements within each of the 7 categories of research needs identified by agencies.
- Each of the received proposals was reviewed by up to 5 independent experts from federal and state agencies, non-participating UW faculty and outside experts.
- A peer review panel was convened to review each of the proposals and the compiled outside reviews, to discuss strengths and weaknesses of each proposal, and to select the proposed project tasks to be submitted to DOE for funding consideration.

---

[1] Department of Zoology and Physiology. University of Wyoming, Laramie, WY. email: bergman@uwyo.edu

- A total of 9 proposed project tasks, plus a project management and outreach task (Task 1), were selected for consideration of funding in a UW proposal to be prepared for submission to DOE.
- UW's compiled proposal with 10 tasks was submitted for approval to DOE on April 24, 2006, with a proposed DOE cost of $1,443,837, UW cost share of $473,635 and additional industry match of $16,491, giving a total proposed project cost of $1,933,963.

Subsequently, the project was approved by DOE with a project start date on June 2, 2006 and a completion date of June 1, 2008. During early 2008, UW requested and DOE approved a no cost extension of this project through September 30, 2008.

Project Management:

During the completion of the Scope of Work for this project, the purpose of Task 1 was to manage and monitor the progress of the other tasks and to assure integration among the tasks and encourage cooperation among the investigators. The principal investigator accomplished this by holding quarterly meetings among the co-principal investigators to discuss research progress, results, and administrative requirements, such as quarterly and annual reports. The PI also communicated via email and phone to all task Co-PIs, UW administration, the DOE-NTEL project manager, and others to ensure that all research tasks and administrative and technical progress reports were moving smoothly. The PI's office also fulfilled requests from the DOE-NETL program manager for specific information concerning individual tasks, including papers written or presented by project investigators.

Throughout the life of this grant, nine progress reports were submitted to DOE. Table 1-1 describes each of these reports.

Table 1-1: Report type and submission dates

Report type	Date submitted to Department of Energy
Quarterly report 1: June – September 2006	October 17, 2006
Quarterly report 2: October – December 2006	January 12, 2007
Quarterly report 3: January – March 2007	April 7, 2007
Annual report 1: June 2006 – June 2007	June 28, 2007
Quarterly report 4: July – September 2007	October 1, 2007
Quarterly report 5: October – December 2007	January 17, 2008
Quarterly report 6: January – March 2008	April 17, 2008
Quarterly report 7: April – June 2008	July 21, 2008
Annual report 2: WAIVED by DOE	N/A

Project Outreach:

In an effort to convey information about the project and project findings to the scientific community, agencies, industry, NGOs and the public, project investigators presented information through numerous formal and informal briefings, meetings and other traditional professional outlets. To date, the project investigators have successfully submitted numerous manuscripts for peer reviewed publication and presented their results at numerous regional, national and international conferences (please see the BIBLIOGRAPHY section, where a partial list is presented including 29 peer reviewed journal articles or proceedings chapters, 2 books, 34 formal presentations and at least 3 theses and dissertations. Note that more publications, presentations and theses/dissertations are anticipated as investigators complete and submit articles and as in-progress graduate students defend their work that is based in whole or in part on this project.).

The co-principal investigators for each task also presented interim results of their research at a special session organized for the annual meetings of the American Society of Mining and Reclamation in Gillette, Wyoming, in June 2007. To assure that interested parties, including agencies, industry, NGOs and others, were aware of this special CBNG session it was widely advertised regionally, with special announcements sent to numerous CBNG stakeholders. The special session was well attended, particularly by industry and agency representatives. And the DOE-NETL project officer for this project at the time, John Ford, attended as well.

In the spring of 2009, on a date yet to be determined, the co-principal investigators will present their final results and conclusions for each task at a public co-produced water symposium that is now being organized for the University of Wyoming campus in Laramie, Wyoming (note that this conference will be conducted with no cost to DOE).

Task 2 – Estimation of Recharge in the Powder River Basin of Wyoming with Uncertainty Bounds

Fred L. Ogden[2] and Kerri A. Puckett

The semi-arid environment of Wyoming makes water of utmost importance, and therefore, the ability to accurately predict the movement of water is of high importance as well. Recently, waters related to Coal Bed Natural Gas (CBNG) production have been of concern, both in quality and quantity. The groundwater produced as a by-product of CBNG extraction in the Powder River Basin (PRB) is of varying quality, with a predominance of calcium, magnesium, and sodium cations and bicarbonate, chloride, and sulfate anions (Bartos and Ogle, 2002). Depending on the water quality and Department of Environmental Quality (DEQ) regulations, it is placed in infiltration/evaporation ponds or discharged into the surface flow.

From 1987-2004, approximately 370,000 acre-ft ($0.46km^3$) of groundwater was withdrawn from the PRB. By 2017, between 51,000 and 139,000 CBNG wells are expected to be installed, each pumping between 10 gpm and 100 gpm (BLM, 2003). Over the life of the CBNG project, it is projected 5,700,000 acre-feet ($7.0km^3$) will be removed from the groundwater storage in the Powder River Basin (Ruckelshaus Institute, 2005).

As part of the Environmental Impact Statement (EIS) for the PRB, the Bureau of Land Management (BLM, 2003) predicted that recovery will occur by 2030 (except in very localized areas of the basin) in the deep aquifer to within 50-100 feet of pre-development water levels, or 84-94 percent recovery in 27 years. Water levels in the deep aquifer are predicted to recover to within 10-50 feet of pre-operational levels by 2060, or 94-99 percent recovery in 57 years. The BLM estimated recovery of more than 50 percent in the deep Fort Union Formation occurring by 2030 (BLM, 2003).

However, the recharge estimation methodology used in the PRB EIS contains assumptions that are not fully justified by the physiography and geology of the basin, necessitating further research to verify or reject the recovery time estimates. The assumptions employed in the PRB EIS include: 1) an infiltration rate of 0.03-0.04 in y^{-1} (0.76-1.0 mm y^{-1}) applied uniformly across the PRB, 2) an increased infiltration rate of 0.60 in y^{-1} (15.2 mm y^{-1}) applied in areas of increased CBNG development, and 3) 72 in y^{-1} (1830 mm y^{-1}) of infiltration occurring from evaporation/infiltration impoundments (BLM, 2003).

In response to the EIS by the BLM, commentaries were composed by Tyler (2003) and Monks (2003) offering professional opinions concerning the recharge estimates. Tyler (2003) and Monks (2003) state the BLM underestimated the hydrologic impact to the shallow aquifer and surface flow, and therefore, overestimated the recharge rates, perhaps as much as 16 fold. Additionally, Monks (2003) and Tyler (2003) believe the water stored in evaporation/infiltration impoundments will likely evaporate or be discharged as base flow to streams rather than infiltrate to the deep coalbed aquifer. Given the contradiction between the comments provided by Monks (2003) and Tyler (2003) and the BLM EIS (2003), additional research is necessary to

---

[2] Department of Civil & Architectural Engineering and the Haub School of Environment and Natural Resources, University of Wyoming, Laramie, WY. email: fogden@uwyo.edu

provide independent estimates regarding the recharge time. Further details about the research reported for this Task are discussed in Puckett (2008).

The overall objective of the current study was to develop a methodology for estimating groundwater recharge in semi-arid regions using available models and data sources and to demonstrate model analysis in the context of uncertainty of climatic forcing, with spatially-varied geology and surfacial materials.

Methods:

Study Area Description and Hydrogeologic Setting of the Wyoming Powder River Basin

When the Powder River Basin is generally discussed, the land being referred to is the structural basin, an asymmetric syncline extending from Wyoming northward into Montana covering more than 57,000 km^2 (22,000 mi^2). The formation is bounded by the Bighorn Mountains to the west, the Black Hills to the east, the Casper Arch, Laramie Mountains, and the Hartville uplift to the south, and the Cedar Ridge anticline to the north.

Two major geological formations define the structural basin, the Wasatch Formation and Fort Union Formation; the Eocene Wasatch overlays the Paleocene Fort Union, which emerges at the basin margins. These formations dip sharply to the east along the western margin of the basin and dip by 0.5°-1° to the west along the eastern margin (Frost et al. 2002). The general direction of groundwater flow is south to north (Hinaman 2005). Portions of the Platte, Tongue, Belle Fourche, Little Powder, Cheyenne, and Powder rivers flow over the basin.

The hydrologic and structural PRBs do not coincide. Hydrologically, the PRB includes drainages of the Tongue, Belle Fourche, Little Big Horn, Little Powder, and Powder Rivers. The Platte River drainage is not included. Flow originates in the high elevations of the Big Horn Mountains, generally flowing northeast, but east in the southernmost portion of the basin. The area contributing to groundwater flow in the Wyoming Powder River Basin is a combination of the hydrologic and structural basins.

The geology of the Wyoming PRB is defined by two major formations, the Wasatch and Fort Union, and alluvium veins. Throughout the majority of the basin, the Fort Union Formation lies below the Wasatch Formation, sometimes over 430 m (1400 ft) below (WRDS 2007). The Fort Union Formation daylights at the eastern edge of the structural PRB and the base of the Bighorn Mountains on the western margin of the structural PRB. Further details regarding the hydrological and geological considerations of the Powder River Basin are presented in Puckett (2008).

Studies performed by Bartos and Ogle (2002) and Frost et al. (2002) report the Fort Union and Wasatch aquifers are chemically and hydrologically dissimilar. Bartos and Ogle (2002) and Frost et al. (2002) each performed a series of chemical analyses on groundwater samples retrieved from the Wasatch and underlying Fort Union coalbed aquifers. The major-ion chemistry was compared between the aquifers to establish aquifer connection and interaction. Bartos and Ogle (2002) found the concentrations of fluoride and sulfate to be qualitatively and statistically different between the Wasatch and Fort Union aquifers. Additionally, Bartos and

Ogle (2002) show many of the major-ion compositions have a distinct relationship to well depth. Water analyzed from the shallow Wasatch aquifer is different in chemical composition from those sampled deeper in the Wasatch and underlying Fort Union aquifer. This may suggest the conclusions offered by Bartos and Ogle (2002), as follows:

"... little vertical hydraulic connection is present between the successively deeper sandstone lenses in the Wasatch Formation and the underlying coalbed aquifer; very little flow, and therefore, intermixing of waters between the shallow and deep geochemical zones would occur."

Frost et al. (2002) performed a tracer test for the stable strontium (Sr) isotope. By analyzing the difference in Sr isotope composition, Frost et al. (2002) are able to determine locations where water from the upper sandstone Wasatch Formation was drawn into the underlying coalbed aquifer and where the aquifers are hydraulically disconnected. Frost et al. (2002) summarize their study with the following:

"The fact that Sr isotope ratios of water from coal and sandstone aquifers are distinct suggest that these aquifers are not hydraulically connected…"

Based on the research of Bartos and Ogle (2002) and Frost et al. (2002), the area of the PBR covered by the Wasatch formation was removed from the study area because negligible recharge to the deeper Fort Union formation is expected there.

Modeling Methods -- SWAT Model Overview

The land surface scheme chosen to model the Wyoming Powder River Basin groundwater recharge is the Soil and Water Assessment Tool (SWAT), version 2005. SWAT development was lead by Dr. Jeff Arnold of the USDA Agricultural Research Service (ARS), with contributions from Texas A&M University, the US Environmental Protection Agency (US EPA), National Resources Conservation Service (NRCS), National Oceanic and Atmospheric Associate (NOAA), and the Bureau of Indian Affairs. The SWAT model contains components of several ARS models including the Simulator for Water Resources in Rural Basins (SWRRB) (Williams et al., 1985 and Arnold et al., 1990), Chemical, Runoff, and Erosion from Agricultural Management Systems (CREAMS) (Knisel, 1980), Groundwater Loading Effects on Agricultural Management Systems (GLEAMS) (Leonard et al., 1987), Erosion-Productivity Impact Calculator (EPIC) (Williams, 1990), and the Enhanced Stream Water Quality Model (QUAL2E) (Brown and Barnwell, 1987; Neitsch et al., 2005).

SWAT capabilities include simulating the water balance, snow melt processes, nutrient cycling, bacteria transport, erosion, in-stream water quality, and pesticide routing. The model is designed to operate using readily available inputs provided by government agencies (Neitsch et al., 2005). These inputs include the digital elevation model (DEM), land use and land cover (LULC) dataset, and soil characteristics. Additional input data, including streamflow, water quality, land management practices, pesticide, nutrients, and irrigation data, and pond/reservoir storage, may also be used. SWAT simulations may use either historic climate data, including precipitation, air temperature, relative humidity, and wind speed, or the climate may be simulated using the WXGEN weather generator model (Sharply and Williams, 1990).

SWAT is a physically-based watershed scale model. In contrast to conceptual land surface schemes that rely on regression equations to relate inputs to output, SWAT models the physical processes associated with sediment movement, water movement, nutrient transport, etc. using the required inputs (Neitsch et al., 2005). SWAT is a continuous time model and is designed to be a long-term yield model. For this reason, it is not recommended to be used to simulate single storm-event flood routing or short term simulations.

The Wyoming Powder River Basin model utilizes only the water balance component of SWAT; the major water balance components, including sub-basin division, surface runoff, evapotranspiration, soil/plant water movement, snow melt, channel routing, and other elements pertaining to groundwater recharge estimation are discussed in detail by Puckett (2008).

SWAT Modeling Runs

A total of 225 model simulations were conducted. Each simulation ran for 75-years, with annual output being recorded. Simulation output was analyzed using two methods. First, the output for the 75 single years in each simulation was analyzed. Second, each simulation was summarized using the average results over all 75-years. SWAT results presented here are derived from two datasets: 1) annual results for every year simulated (225 simulations x 75 years/simulation = 16875 simulation-years) and 2) one average result for every simulation (225 simulations). Results derived from the annual results (the 16875 simulation-years) are referred to as 'Annual Average' results. Analysis based on the 75-year average annual results (the 225 simulations) is referred to as '75-year Annual Average' results.

Each of the 225 simulations was run for 75 simulation-years, with all modeling parameters remaining constant. Simulations varied only by the daily weather received, generated by the WXGEN weather generator. Within statistical limits derived from historical data records, the WXGEN weather generator creates weather/climate patterns to drive the SWAT model. The seed number input into WXGEN was randomly varied before each simulation was begun. WXGEN uses the random seed number to randomly determine the initial weather parameters for each simulation. Given the initial weather parameters, the daily weather over the length of the simulation was derived using the procedures described by Neitsch, et al. (2005).

Recharge Uncertainty Quantification

Because of the size and semi-arid nature of the Wyoming PRB, small quantities of recharge have great significance towards replenishing the groundwater supply. As the recharge expected basin-wide is very small, any deviations away from the expected mean can produce large changes in recharge time. Better stated, if the recharge in a humid region decreased by 1mm annually, it would likely go unnoticed. In the Powder River Basin, however, 1mm might account for 100% of the recharge in any given year. For this reason, it is especially important to attempt to quantify the uncertainty associated with the recharge estimates.

Recharge, and the associated uncertainty, was analyzed with respect to precipitation for two reasons, 1) precipitation is the most common climate measurement and 2) precipitation is commonly forecast in hydrologic models. If a relationship between precipitation and recharge can be established, the relationship could be used to predict recharge based on measured or

simulated precipitation. Five methods of determining uncertainty were used to analyze the stochastic simulations: 1) bounds established by the standard deviation, 2) certainty of the mean using the 95% confidence interval, 3) box and whisker plot analysis, 4) the coefficient of determination on exponential and linear regressions, and 5) the maximum recharge limit.

Results and Discussion:

SWAT Modeling Results

Results of the recharge area model simulations are presented at the basin level, by east side and by west side, where the land east of the Wasatch Formation is termed East Side and the land west of the Wasatch Formation is termed West Side. Basin-wide and East Side and West Side results were analyzed using two methods.   For the purposes of this report, a summary of results is presented.   For more detailed results, see Pucket (2008).

Basin-wide Annual Results

The annual average recharge histogram for almost 17,000 years, derived from 225 simulations, is shown in Figure 2-1. Three bins (between 0.80 mm y^{-1} and 1.399 mm y^{-1}) contain 44% of the values.
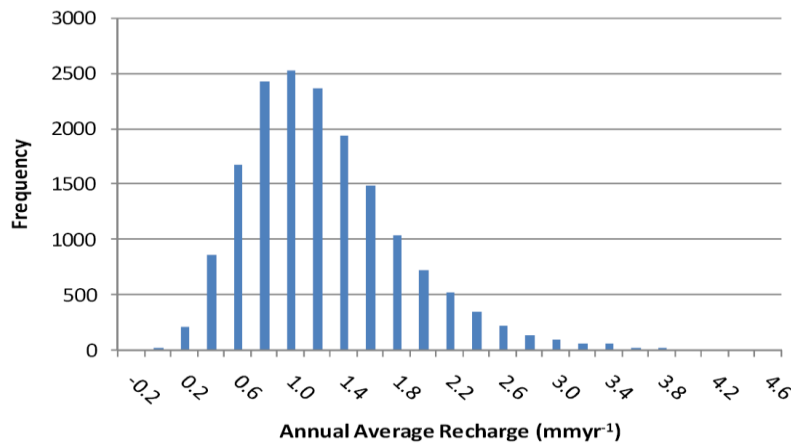
Figure 2-1: Annual Basin-wide Recharge Histogram

Figure 2-2 shows the probability density function (PDF) and cumulative density function (CDF) for the simulated basin-wide recharge. The maximum basin-wide recharge for any single year is 4.49 mm y^{-1} and minimum is -0.18 mm y^{-1}. Mean recharge for the recharge area is 1.14 mm y^{-1} with a standard deviation of 0.59 mm y^{-1}. The 95% confidence interval about the mean is 0.01 mm y^{-1}.
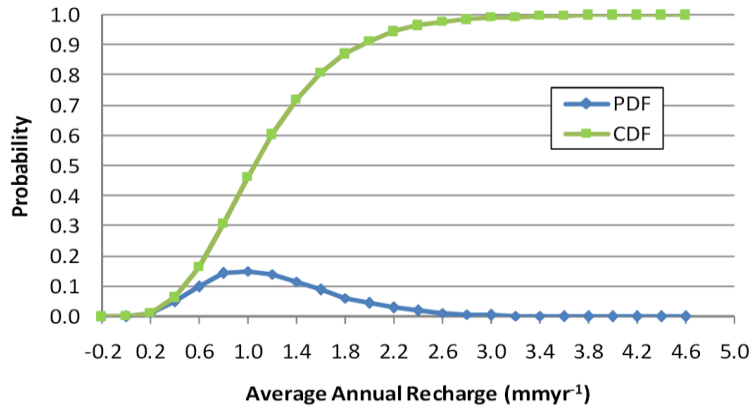
Figure 2-2: Annual Basin-wide Recharge PDF and CDF

A clear trend of increasing recharge with increasing precipitation was observed as shown in Figure 2-3. Maximum basin-wide precipitation for any single year is 583 mm y^{-1} and minimum is 208 mm y^{-1}. Mean precipitation for the recharge area is 371 mm y^{-1} with a standard deviation of 51 mm y^{-1}. The 95% confidence interval about the mean is 0.77 mm y^{-1}.
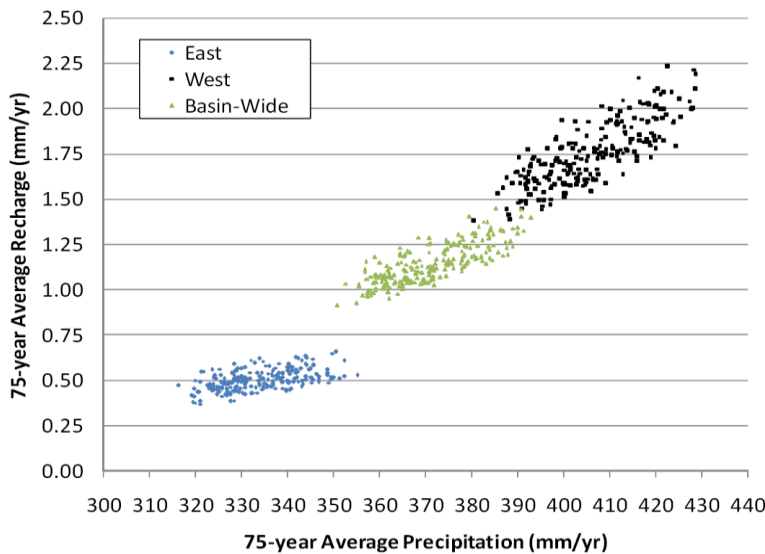
Figure 2-3: 75-year Average Annual East, West, and Basin-wide Precipitation vs. Recharge

Spatial Distribution of Recharge
Recharge is observed in concentrated areas on both sides of the recharge zone (Figure 2-3). Simulations show increased recharge in the high mountains and near perennial streams while little or no recharge is observed over large portions of the rest of the basin. SWAT results for recharge and precipitation for each of the 502 sub-basins were averaged from the 225 75-year average annual results.

The majority of the sub-basins on the east side receive no recharge (less than 0.01mm y^{-1}). Measureable recharge is observed in three areas on the east side: 1) near the Cheyenne River to the south, 2) near the Belle Fourche in the center, and 3) near the Little Powder River to the north.

11

Overall, minimal recharge (less than 0.10 mm/year) is seen in the southern portion of the west side, although recharge increases slightly near the South Fork of the Powder River. Two other rivers serve as major recharge zones for the west side, the North Fork of the Powder River and the Tongue River. The remainder of the west side sees an increase in recharge in the high elevation of the Bighorn Mountains.

Recharge Uncertainty Quantification Results

Recharge is strongly correlated with precipitation. The annual simulation outputs were divided into 12 bins spanning the range of precipitation observed and the annual recharge statistics within the bins were analyzed. The mean annual recharge increases with each increasing precipitation bin, with an average of 0.57 mm y^{-1} in the 200 mm y^{-1}-275 mm y^{-1} bin to an average of 2.86 mm y^{-1} in the 550 mm y^{-1}-600 mm y^{-1} bin. The standard deviation of the annual recharge increases as precipitation increases, implying a larger range of annual recharge is observed in bins of higher precipitation as well as increased scatter.

Initially, the uncertainty bounds on the annual recharge are presented using the standard deviation. The average annual recharge is bounded by one and two standard deviations for each precipitation bin. Assuming the distribution between precipitation and recharge is normal, the expected recharge for any annual precipitation may be bounded by the standard deviation. For a given precipitation, 68% of recharge values will fall within one standard deviation and 95% of the recharge values will lie within two standard deviations.

Next, the confidence interval (CI) was studied. The 95% confidence interval about the mean was used for this analysis. The CI is a test on the mean of a sample; in this case, if a series of precipitation in a given range was observed, the mean of the sample would fall within one CI above and one CI below the predicted mean 95% of the time. SWAT simulations predict a very narrow CI for recharge at low precipitations and larger recharge CIs as precipitation increases.

The box and whisker plot derived from the precipitation and recharge predictions is shown in Figure 2-4. The horizontal line in the center of each box is the median of the data set, while the outer edges of each box mark the first and third quartiles.   The first quartile is the median of the upper half of the dataset and the third quartile is the median of the lower half of the dataset. The vertical whiskers extending from each box show the maximum and minimum values. Extreme outliers are marked with an asterisk.
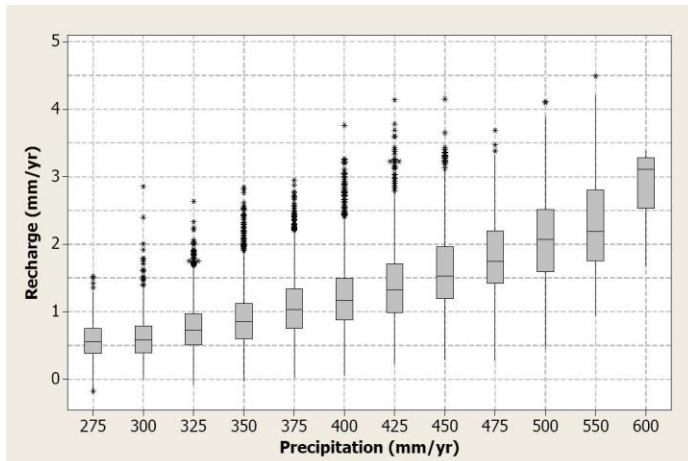
Figure 2-4: Annual Basin-wide Box and Whisker Plot for Recharge

Most bins have a number of outliers, almost all of which are on the extreme high side. The outliers may be caused by the interdependence of one year's recharge on precipitation during the previous year. For example, if a dry year was observed preceding a wet year, the water introduced during the wet year must first replenish the soil moisture deficit before recharge can occur. If the same wet year followed another wet year, more of the water would become recharge than before.

A regression analysis was performed on the annual precipitation versus annual recharge output. The regression line may be the most useful correlation between a known precipitation and predicted recharge, but says the least statistically. If an annual precipitation is obtained for the recharge area at the basin-wide scale, Equation 2-1 provides a relationship to estimate the annual recharge:

$$R = 0.159e^{0.0052 \cdot P}$$ **Equation 2-1**

where R is the annual recharge (mm y^{-1}) and P is the annual precipitation (mm y^{-1}). The equation is a low exponential regression with a coefficient of determination (R^2) of 0.9856. While R^2 is near 1.0, it is important to remember significant variability exists within the data used to generate the regression.

Use and Application of Results

The main objective of this study was to develop a methodology for determining recharge in semi-arid areas using existing models and readily available data sources. Of the available models that simulate groundwater recharge, SWAT was selected as the Land Surface Scheme for this project for numerous reasons. While SWAT is the most appropriate existing model for this research, it is not ideal. It is recommended alternative model formulations be explored or developed.

Given the mean response of the SWAT model, the recharge estimate is thought to be a likely representative of the actual recharge occurring in the Wyoming Powder River Basin. However, given the limitations of the modeling framework, including insufficient data for

13

parameterization, poor spatial resolution of input climate data, lack of long-term historical climate records, and the uncertainty associated with SWAT, the absolute magnitude of the recharge estimate may be in error.

Tyler (2003) stated the original estimates of 30 years for recovery time by the BLM (2003) were underestimated, perhaps as much as 16 times. The estimates provided here are approximately 10 times longer than the BLM estimates. The recharge estimates presented here are in reasonable agreement with the statements by Tyler (2003) and Monks (2003) with respect to recharge in semi-arid regions.

Conclusions:

The overall objective of this study was to develop a methodology for estimating groundwater recharge in semi-arid regions using available models and data sources and to demonstrate model analysis in the context of uncertainty of climatic forcing. This objective was met using existing computer modeling capabilities and data sources. The analysis presented in this report aims to describe a methodology that considers local climatic data as well as surfacial datasets and subsurface geological conditions. Each of these three factors are very important, as hydrology is by nature very spatially variable.

The quantitative results shown are typical of the results that can be obtained using the proposed methodology for estimating groundwater recharge.   The magnitudes of the results are presented as an indicator of likely recharge rates.   However, the methodology is based on a computational model that has known inadequacies for estimating groundwater recharge and are unverified by direct observations. Numerical results for recharge rates presented herein must be interpreted with caution. This methodology could be used with any model of groundwater recharge. Studies performed by Bartos and Ogle (2002) and Frost et al. (2002) report that the Fort Union and Wasatch aquifers are chemically and hydrologically dissimilar. Bartos and Ogle (2002) and Frost et al. (2002) each performed a series of chemical analyses on groundwater samples retrieved from the Wasatch and underlying Fort Union coalbed aquifers. The major-ion chemistry was compared between the aquifers to establish aquifer connection and interaction. Bartos and Ogle (2002) found the concentrations of fluoride and sulfate to be qualitatively and statistically different between the Wasatch and Fort Union aquifers. Additionally, Bartos and Ogle (2002) show many of the major-ion compositions have a distinct relationship to well depth. Water analyzed from the shallow Wasatch aquifer is different in chemical composition from those sampled deeper in the Wasatch and underlying Fort Union aquifer. Frost et al. (2002) performed a tracer test for the stable strontium (Sr) isotope. By analyzing the difference in Sr isotope composition, Frost et al. (2002) are able to determine locations where water from the upper sandstone Wasatch Formation was drawn into the underlying coalbed aquifer and where the aquifers are hydraulically disconnected. Based on the research of Bartos and Ogle (2002) and Frost et al. (2002), the recharge area is the land where the Fort Union Formation daylights at the margins of the Wyoming Powder River Basin. Consideration of the geological setting is extremely important when modeling groundwater recharge from confined aquifers.

Modeling result showed that the majority of recharge to the Fort Union Formation occurs on the west side of the recharge area in the Bighorn Mountains and other areas that directly benefit from

the snowpack in the higher elevations, like the Tongue River drainage. Additional recharge is observed in smaller quantities on the east side of the recharge zone. East side recharge is primarily observed as streambed infiltration on the Belle-Fourche, Little Powder, and Cheyenne Rivers.

If an annual precipitation is obtained for the recharge area at the basin-wide scale, the following relationship can be used to estimate the annual recharge:

$$R = 0.159e^{0.0052 \cdot P}$$

where R is the annual recharge (mm y^{-1}) and P is the annual precipitation (mm y^{-1}). The equation is a low exponential regression with a coefficient of determination (R^2) of 0.9856. While R^2 is near 1.0, it is important to remember significant variability exists within the data used to generate the regression.

Tyler (2003) stated the original estimates of 30 years for recovery time by the BLM (2003) were underestimated, perhaps as much as 16 times. The estimates provided here are approximately 10 times longer than the BLM estimates. The recharge estimates presented here are in reasonable agreement with the statements by Tyler (2003) and Monks (2003) with respect to recharge in semi-arid regions.

Several future research needs were identified during this study. Mountain-front recharge phenomena deserve additional consideration. To better estimate the distribution of recharge at higher elevations, the mechanisms of mountain-front for the Bighorn Mountains should be examined. SWAT parameters would need to be adjusted on a sub-basin by sub-basin level to properly model large fractures, cases of extremely high water tables, and seasonal stream-flow. Measurements of evapotranspiration (ET) should be made in the study area. New technologies should be implemented to provide data to researchers and producers alike as well as to initiate the creation of a long-term ET dataset. These new technologies would include remote sensing using satellite observations such as the METRIC approach (Allen et al., 2007), supported by ground observations of actual ET and the components of the energy balance. Finally, the SWAT model has deficiencies with regard to estimation of groundwater recharge.   Development of model formulations to better simulate groundwater recharge in semi-arid regions is needed. These developments should be supported by field data collection efforts to assist in model calibration and formulation verification/validation.

References:

Allen, R.G., M. Tasumi, and R. Trezza, 2007, Satellite-based energy balance for mapping evapotranspiration with internalized calibration (METRIC) model, *J. Irrig. Drain. Engrg.*, DOI: 10.1061/(ASCE)0733-9437(2007)133:4(380).

Arnold, J.G., J.R. Williams, A.D. Nicks, and N.B. Sammons. 1990. SWRRB: A basin scale simulation model for soil and water resources management. Texas A&M Univ. Press, College Station, TX.

Bartos, T. T. and K. M. Ogle. 2002. Water quality and environmental isotopic analyses of ground-water samples collected from the Wasatch and Fort Union formations in areas of coal

bed methane development – implications to recharge and ground-water flow, Eastern Powder River Basin, Wyoming. *U.S. Geological Society.* Water-Resources Investigations Report 02–4045, 88 pp.

BLM, Bureau of Land Management. 2003. Final Environmental Impact Statement and Proposed Plan Amendment for the Powder River Basin Oil and Gas Project. *Wyoming State Office*: WY-070-02-065.

Brown, L.C. and T.O. Barnwell, Jr. 1987. The enhanced water quality models QUAL2E and QUAL2E-UNCAS documentation and user manual. EPA document EPA/600/3-87/007. USEPA, Athens, GA.

Frost, C.D., B.N. Pearson, K.M. Ogle, E.L. Heffern, and R.M. Lyman. 2002. Sr isotope tracing of aquifer interactions in an area of accelerating cola-bed methane production, Powder River Basin, Wyoming. *Geology.* **30**: 923:926.

Hinaman, K. in cooperation with the Bureau of Land Management. 2005. Hydrogeologic framework and estimates of ground-water volumes in tertiary and upper cretaceous hydrogeologic units in the Powder River Basin, Wyoming. *U.S. Geological Survey*. Scientific Investigations Report 2005-5008.

Knisel, W.G. 1980. CREAMS, a field scale model for chemicals, runoff and erosion from agricultural management systems. USDA ConservationResearch Rept. No. 26.

Leonard, R.A., W.G. Knisel, and D.A. Still. 1987. GLEAMS: Groundwater loading effects on agricultural management systems. Trans. ASAE 30(5):1403-1428.

Monks, J. 2002. Comments on Draft Environmental Impact Statement and Draft Planning Amendment for the Powder River Basin Oil and Gas Project. *Powder River Basin.org. Powder River Basin Resource Council*.<http://www.powderriver basin.org/cbm/expert_monk.shtml>.

Narasimhan, B., R. Srinivasan, J. G. Arnold, and M. Di Luzio. 2005. Estimation of long-term soil moisture using a distributed parameter hydrologic model and verification using remotely sensed data. *Trans. ASABE* 48(3): 1101-1113.

Neitsch, S.L., J.G. Arnold, J.R. Kiniry, and J.R. Williams. 2005. Soil and Water Assessment Tool theoretical documentation, version 2005.

Puckett, K.A., 2008, Uncertainty quantification in predicting deep aquifer recharge rates, with applicability in the Powder River Basin of Wyoming, M.S. Thesis, University of Wyoming, Laramie, WY 82071, USA.

Ruckelshaus Institute of Environmental and Natural Resources. 2005. Water production from coalbed methane development in Wyoming: A summary of quantity, quality and management options. Report prepared for the Office of the Governor, State of Wyoming.

Sharpley, A.N. and J.R. Williams, eds. 1990. EPIC-Erosion Productivity Impact Calculator, 1. model documentation. U.S. Department of Agriculture, Agricultural Research Service, Tech. Bull. 1768.

Tyler, S.W. 2003. Comments on the Powder River Basin Oil and Gas Project DEIS. *Powder River Basin.org, Powder River Basin Resource Council.* http://www.powderriver basin.org/cbm/expert_tyler.shtml.

Water Resources Data System, 2008. Digital data, accessed March 21, 2008, at URL http://www.wrds.uwyo.edu/wrds/wsc/climatology.html.

Williams, J. R. 1990. The erosion productivity impact calculator (EPIC) model: A case history. *Phil. Trans. R. Soc. London* 329(1255): 421- 428.

Williams, J.R., A.D. Nicks, and J.G. Arnold. 1985. Simulator for water resources in rural basins. Journal of Hydraulic Engineering 111(6): 970-986.

Task 3 – Monitoring and Modeling of Groundwater Contamination of Trace Elements from CBNG Disposal Ponds, Powder River Basin, Wyoming

K.J. Reddy[3] and Cindy Milligan

Coalbed natural gas is formed through biogeochemical processes in confined coal seams which also serve as CBNG reservoirs. The methane is extracted through drilling and fracturing of that coal seam, followed by pumping the groundwater to the surface. Methane is separated from the water and most of the water is discharged into unlined disposal ponds or stream channels. Each CBNG well in the PRB can produce 8 to 80 L/min of water depending on the aquifer and number of wells drilled into the aquifer. The CBNG drilling is commonly done by placing 2-10 CBNG wells together in a manifold system discharging to a single outfall that flows into a disposal pond. These amounts of water are not trivial as the Wyoming State Geological Survey has projected that approximately 7.01 billion m^3 of water will be discharged from CBNG development in Wyoming (DeBruin 2004). Once the produced water is discharged, it is designated as class 4C waters by the Wyoming Department of Environmental Quality (WYDEQ); such designation allows water to be used for recreation, wildlife, agriculture, industry, and scenic value.

The CBNG produced water in disposal ponds undergoes geochemical processes such as ion complexation, adsorption, and precipitation. These processes in turn control the concentration of elements and compounds that precipitate into the sediments of disposal ponds. Trace elements that are identified as a concern in CBNG produced water include arsenic (As), barium (Ba), chromium (Cr), selenium (Se), copper (Cu), molybdenum (Mo), boron (B), and manganese (Mn) (Jackson and Reddy 2007a). These trace elements in sediment, with time, could migrate into shallow aquifers. Several studies were conducted (Jackson and Reddy 2007a, McBeth et al. 2003a, McBeth et al. 2003b, Jackson and Reddy 2007b) in the PRB to examine the biogeochemical processes of CBNG produced water in disposal ponds. However, these studies did not investigate the accumulation and leaching potential of trace elements in CBNG disposal pond sediments. Such information is necessary to predict contamination of shallow aquifers. Thus, the objectives of this study were to determine the chemistry of disposal pond water and the leaching potential of trace elements from the disposal pond sediments in the Powder River Basin, Wyoming.

Methods:

Study Area Description

The PRB, located in northeastern Wyoming and southeastern Montana, is part of the Great Plains Missouri Plateau (Fig. 3-1). The basin is a semi-arid ecosystem with an average annual precipitation that ranges from 30 to 60 cm. The basin is bounded by the Yellowstone River to the north, the Laramie Mountains to the south, the Black Hills to the east, and Big Horn Mountains to the west. Elevation of the PRB ranges from 1,640 to 1,800m above sea level and

[3] Department of Renewable Resources and School of Energy Resources. University of Wyoming, Laramie, WY. email: katta@uwyo.edu

its topography is characterized by high plains with rolling hills that are capped with clinker (BLM 2003, Jackson and Reddy 2007a, McBeth et al. 2003a, McBeth et al. 2003b). The predominate soils in the PRB consists of clay loam, fine loam, and loam (USGS 1986). These soils sustain different plant communities in different parts of the PRB. Eastern parts of the basin are dominated by grass and sagebrush communities. Central and western parts have more diverse landscapes and plant communities (McBeth et al. 2003b).
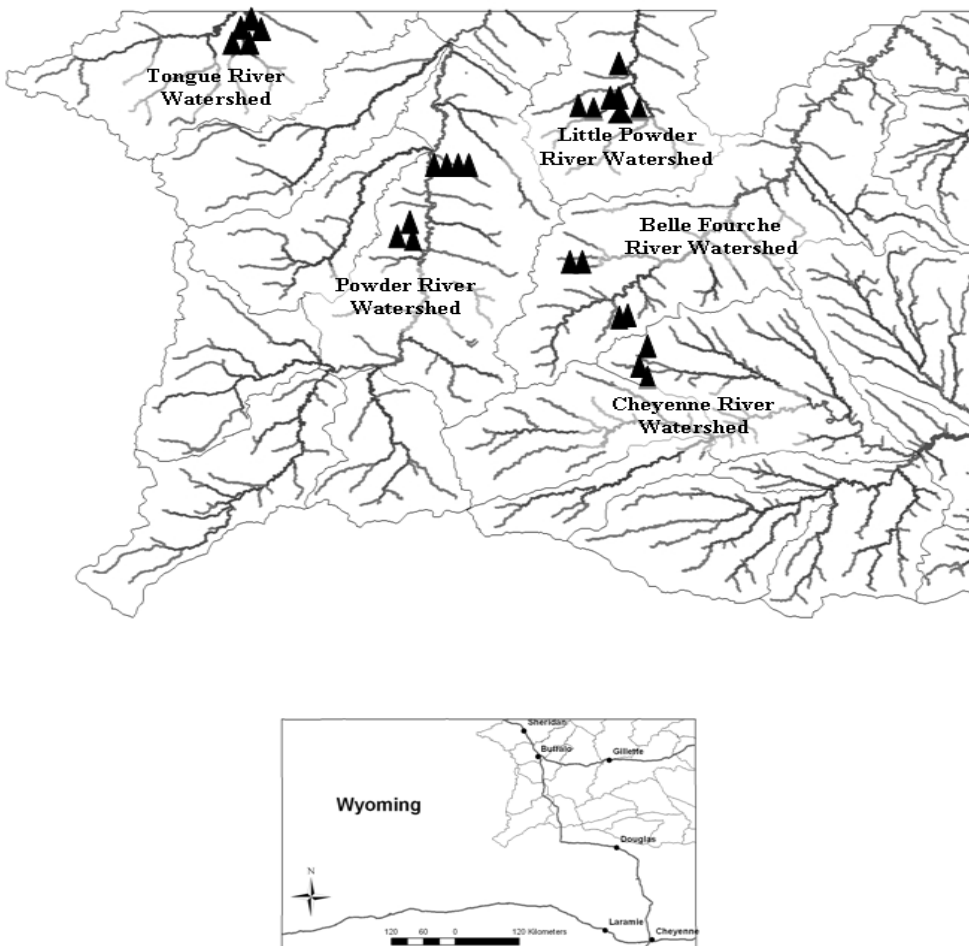
Figure 3-1: Sample site locations in the Powder River Basin, Wyoming. Reprinted with permission from McBeth et al. 2003b. Copyright 2007 American Chemical Society.

The major coal formations in the area include the Wasatch Formation and the Tertiary Tongue River Member of the Fort Union Formation (BLM 2003). The major river systems in the PRB include the Cheyenne River (CHR), which drains the southeast area of the PRB, the Belle Fourche (BFR), which drains the eastern area, the Little Powder River (LPR), which drains the northwestern area of the basin, the Powder River (PR), which drains the northwestern area, and the Tongue River (TR), which flows north out of Wyoming to the Yellowstone River (Fig.3-1). These rivers are tributaries of the Missouri River.   These rivers have intermittent and/or ephemeral flows from snowmelt or storm events introduced by surface streams. Therefore,

extraction of CBNG will increase overall flows in upland and basin streams of the PRB, which could eventually influence vegetation, soils, geology, and water uses. This could also affect the major land uses in the various watersheds of the PRB, which include agriculture, livestock production, and coal mining.

Site Selection

Site selection occurred over a period of seven years in the PRB. The initial fourteen sites, selected by McBeth et al. in 1999 (McBeth et al. 2003a, McBeth et al. 2003b), were in just three watersheds. Three of these were located in CHR watershed, four were located in BFR watershed, and seven were located in the LPR watershed. These sites were used in subsequent studies along with others that were added by Jackson and Reddy (2007b). A total of twenty-six sites in five watersheds were studied by Jackson and Reddy (2007b) (Fig. 3-1). They included 7 sites from each of the LPR and PR watersheds, 3 sites from the CHR watershed, 4 sites from the BFR watershed, and 5 from the TR watershed (Jackson and Reddy 2007a, Jackson and Reddy 2007b). For this study, we monitored 4 sites in each of the CHR and BFR watersheds, 5 sites in the TR watershed, 6 sites in the LPR watershed, and 7 sites in the PR watershed.

Sample Collection and Analysis

Water Sampling
CBNG produced water samples were collected from both outfall and disposal pond, at each chosen site in July of 2006 and 2007. Before collecting water samples, pH, dissolved oxygen (DO), oxidation-reduction potential (ORP), electrical conductivity (EC), and temperature were measured in the field using a Thermo Five-Star Field Probe. Before field measurements were taken, the instrument was calibrated according to the procedures of the manufacturer. Outfall water samples were taken from the discharge pipe. Pond measurements and samples were then taken where CBNG water enters the pond and where the pH of the water was stable (Jackson and Reddy 2007a). Water samples were collected following protocols of the Wyoming Department of Environmental Quality (WYDEQ) which includes rinsing sample bottles three times and leaving no headspace in the sample bottle (WYDEQ 2004). Water samples were transported to the University of Wyoming Water Quality Laboratory in a cooler at 2ºC.

Water Chemistry Analysis
Water samples were filtered using a 0.45µm filter and subdivided. Fifteen (15) ml of each sample were placed in a centrifuge tube and acidified to a pH of 2 with concentrated HNO_3. Another 15 ml were taken from each sample and placed in another centrifuge tube and remained unacidified. Acidified samples were analyzed for Ca, Na, Mg, K, Fe, Al, Cr, Mn, Pb, Cu, Zn, As, Se, Mo, Cd, Ba, and B by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES), and unacidified samples were analyzed by Ion Chromatography (IC) for SO_4, Cl, F, NO_3, and PO_4. Another twenty-five mL were taken from the remaining sample and used to determine total alkalinity (mg/L $CaCO_3$) by acid titration using 0.01N HCL.

Geochemical Modeling

The geochemical model MINTEQA2 (Brown and Allison 1992) was used to determine charge balance, speciation, and mineral saturation indices. Chemical data, pH, ORP, and reduction couples were used to calculate speciation and mineral saturation indices.

Sediment Sampling

Sediment samples were collected according to the procedures described for the Toxicity Characteristic Leaching Procedure (TCLP) (EPA 2005). One sediment sample was collected in each disposal pond directly under the site where water samples were collected and placed into a 250mL polypropylene bottle. Sediment samples were placed in a 2ºC cooler for transport back to the lab for analysis. Sediment samples were collected for two years and at the same time as the water samples were collected.

Toxicity Analysis

The sediment samples were transported to Paragon Analytics, Inc. in Ft. Collins, Colorado for the Toxicity Characteristic Leaching Procedure (TCLP) analysis. The TCLP protocol requires a minimum of 110 g per sample to complete the analysis. In this procedure trace elements including As, Ba, Cr, Se, Cu, Mo, B, and Mn were tested for leaching potential in each sediment sample. The leachates from TCLP were analyzed using method 3010A. For cold vapor AA, the leachates were digested using method 7470A (USEPA 2005).

Quality Control/Quality Assurance

To meet quality control/quality assurances, protocols such as duplicate sampling and analysis, trip blanks, and reference standards were included. Sampling procedures were performed following the WYDEQ Standard Operating Procedures for Sample Collection and Analysis *(*WYDEQ 2004*).*

Statistical Analysis

Sediment samples were grouped into watersheds and subjected to statistical analysis using a one-way analysis of variance set in a completely randomized design to determine statistical differences among watersheds ($\alpha=0.05$). Each trace metal detected had a separate ANOVA. To determine relationships between water and sediment samples, and parameters such as pH, ORP, DO, Temp, and alkalinity, multiple linear regressions were employed ($\alpha=0.05$) (SAS Institute 2000).

Results and Discussion:

Chemical data measured in the field for both outfalls and ponds are shown in Table 3-1. The pH of outfall water remained constant between 7 and 8 but increased to nearly 9 in disposal pond samples. The ORP values of outfalls were extremely low due to reducing conditions in the coal seam which is consistent with low dissolved oxygen levels. Temperature of the produced water at the outfall ranged between 17 and 20ºC and increased in the pond to nearly 25ºC.

Table 3-1: Field measurement data for outfalls and ponds for 2006 and 2007.

Watershed	Type	Temp Cº		pH		DO mMol/L		ORP mV		EC dS/m	
		2006	2007	2006	2007	2006	2007	2006	2007	2006	2007
CHR	Outfall	19.8	18.9	7.2	6.9	0.07	0.03	-92.8	-82.1	0.6	0.6
Std err±		0.7	*	0.0	*	0.06	*	8.8	*	0.0	*
CHR	Pond	24.4	26.3	9.4	9.3	0.15	0.27	69.5	20.5	1.3	0.6
std err±		0.1	1.6	0.6	0.3	0.15	0.08	14.0	65.0	0.4	0.1
BFR	Outfall	17.5	20.2	7.4	7.1	0.01	0.01	-18.7	-40.2	0.6	0.6
std err±		2.0	*	0.0	*	0.00	*	17.0	*	0.0	*
BFR	Pond	28.4	30.2	9.4	9.3	0.43	0.56	61.3	109.4	0.8	0.6
std err±		3.3	*	0.2	*	0.04	*	5.3	*	0.0	*
LPR	Outfall	21.1	19.6	7.3	7.1	0.02	0.02	-120.0	-63.2	1.4	1.5
std err±		1.4	6.0	0.1	2.2	0.01	0.01	36.0	43.3	0.1	0.0
LPR	Pond	21.3	22.3	8.4	9.3	0.11	0.32	47.2	104.0	1.5	1.7
std err±		1.4	0.8	0.4	0.2	0.03	0.05	23.0	15.9	0.1	0.2
PR	Outfall	17.5	24.3	8.6	7.7	0.16	0.09	-78.7	-33.2	1.1	2.2
std err±		2.3	1.4	0.2	0.3	0.14	0.06	140.0	27.7	0.1	0.4
PR	Pond	25.9	26.5	9.0	8.7	0.14	0.24	90.6	98.4	3.0	2.6
std err±		1.0	0.4	0.3	0.2	0.06	0.01	17.0	11.8	0.5	0.4
TR	Outfall	18.7	20.6	8.2	8.7	0.01	0.02	-222.0	-72.8	1.8	1.8
std err±		0.9	*	0.1	*	0.01	*	36.0	*	0.0	*
TR	Pond	22.4	23.8	8.8	9.1	0.16	0.16	73.6	69.2	1.9	2.2
std err±		0.5	0.4	0.3	0.3	0.05	0.01	27.0	18.8	0.2	0.3

BFR Watershed,CHR Outfall, and TR Outfall do not have standard errors due to no outflow.

Dissolved concentrations of major and trace elements for outfalls and ponds are shown in Table 3-2.   In 2006 the overall trend for all elements was an increase in concentration from outfall to disposal pond. In 2007 most element concentrations remained similar or decreased. For example in 2006, the Ca concentrations in CHR, PR, and TR did not change substantially from outfall to disposal pond. For BFR and LPR, the Ca concentrations decreased from outfall to disposal pond. Moreover in 2007, Ca concentrations did not change substantially from outfall to disposal pond. However, there were some exceptions. Aluminum concentrations increased substantially from outfalls to disposal ponds in 2007. Anion concentrations for outfalls and disposal ponds are presented in Table 3-3. Overall, major anions remained similar between outfalls and disposal ponds over both years, including alkalinity. These results are consistent with the findings of other studies (McBeth et al. 2003a, McBeth et al. 2003b).

Table 3-2: Major and trace element concentrations in outfall and ponds for 2006 and 2007.

Watershed	Type	Na mMol/L		Mg mMol/L		Al µMol/L		K mMol/L		Ca mMol/L		Zn µMol/L	
		2006	2007	2006	2007	2006	2006	2006	2007	2006	2007	2006	2007
CHR	Outfall	5.78	5.90	0.26	0.16	0.20	0.07	0.21	0.11	0.36	0.29	0.07	0.21
	std err±	0.20	*	0.10	*	0.01	*	0.01	*	0.07	*	0.01	*
CHR	Pond	13.90	5.84	0.34	0.20	37.30	36.33	0.28	0.23	0.33	0.28	0.21	0.15
	std err±	4.45	1.39	0.10	0.06	19.76	22.69	0.12	0.06	0.19	0.08	0.10	0.00
BFR	Outfall	5.52	5.61	0.24	0.25	0.20	0.04	0.16	0.18	0.42	0.46	0.06	0.06
	std err±	0.29	*	a	*	0.01	*	a	*	0.01	*	0.01	*
BFR	Pond	7.35	5.97	0.24	0.23	8.87	7.10	0.19	0.19	0.24	0.20	0.06	0.05
	std err±	0.10	*	0.02	*	3.73	*	0.03	*	0.07	*	0.01	*
LPR	Outfall	13.00	14.10	0.70	0.85	0.21	0.03	0.23	0.29	0.92	1.16	0.05	0.11
	std err±	0.97	0.26	0.11	0.08	a	0.01	0.03	0.01	0.13	0.09	a	0.02
LPR	Pond	15.70	13.60	0.69	1.52	3.48	6.15	0.28	0.34	0.45	1.59	0.06	0.09
	std err±	2.28	3.53	0.09	0.64	2.76	3.81	0.04	0.05	0.16	0.92	0.02	0.03
PR	Outfall	11.90	25.50	0.06	0.42	0.28	0.08	0.06	0.25	0.15	0.58	0.12	0.05
	std err±	0.73	4.74	0.01	0.12	0.01	0.03	a	0.07	0.01	0.15	0.08	a
PR	Pond	37.00	30.40	0.52	0.41	3.25	6.63	0.41	0.39	0.18	0.31	0.02	0.13
	std err±	5.74	4.28	0.12	0.08	0.33	4.71	0.13	0.12	0.02	0.09	0.01	0.04
TR	Outfall	20.80	21.10	0.07	0.09	0.27	8.59	0.10	0.14	0.11	0.12	0.03	0.05
	std err±	0.26	*	0.01	*	0.03	*	a	*	0.01	*	0.01	*
TR	Pond	26.80	25.40	0.21	0.15	11.74	23.95	0.13	0.14	0.17	0.16	0.05	0.14
	std err±	2.30	3.39	0.02	0.02	3.41	11.95	0.01	a	0.01	0.02	0.01	0.01

*BFR watershed, CHR, and TR outfall do not have standard error due to only one sample was obtained; [a] concentration was undetectable

Table 3-3: Anion concentrations for outfalls and disposal ponds for 2006 and 2007.

Watershed		Type	F $mMol/L$		Cl $mMol/L$		NO$_3$ mMol/L		PO$_4$ $mMol/L$		SO$_4$ mMol/L		Alkalinity mMol/L#	
			2006	2007	2006	2007	2006	2007	2006	2007	2006	2007	2006	2007
CHR		Outfall	0.056	0.041	0.258	0.300	0.002	0.002	a	a	0.002	a	3.2	3.1
	std err±		0.017	*	0.018	*	a	*	a	*	a	*	0.1	*
CHR		Pond	0.145	0.085	0.463	0.274	0.029	0.003	0.004	0.001	0.024	0.304	6.3	2.9
	std err±		0.007	0.011	0.027	0.006	0.020	0.001	0.004	0.001	0.003	0.270	2.1	0.8
BFR		Outfall	0.051	0.059	0.305	0.408	0.002	0.014	0.005	a	0.001	0.007	3.1	3.3
	std err±		a	*	0.024	*	a	*	0.005	*	a	*	0.1	*
BFR		Pond	0.075	0.066	0.377	0.395	0.019	0.009	a	a	0.199	0.034	3.5	3.0
	std err±		0.000	*	0.032	*	0.008	*	a	*	0.135	*	0.0	*
LPR		Outfall	0.041	0.060	0.226	0.310	0.002	0.005	a	0.007	0.049	a	7.4	8.8
	std err±		0.008	0.005	0.024	0.015	a	0.001	a	0.005	0.047	a	0.7	0.3
LPR		Pond	0.047	0.071	0.272	0.239	0.021	0.002	0.002	0.023	0.064	3.407	8.6	6.4
	std err±		0.006	0.020	0.044	0.056	0.012	0.001	0.002	0.021	0.042	2.116	1.2	2.1
PR		Outfall	0.081	0.133	0.265	0.428	0.003	0.006	a	0.006	0.085	0.006	5.6	13.0
	std err±		0.001	0.013	0.015	0.045	a	0.001	a	0.002	0.079	0.003	0.5	2.5
PR		Pond	0.113	0.150	0.409	0.602	0.005	0.006	0.001	0.002	0.221	0.122	17.7	14.7
	std err±		0.008	0.008	0.046	0.199	0.001	0.001	0.001	0.002	0.134	0.068	2.9	2.0
TR		Outfall	0.111	0.129	0.479	0.672	0.001	0.007	a	a	0.143	0.153	9.2	9.4
	std err±		0.010	*	0.001	*	a	*	a	a	0.111	*	0.2	*
TR		Pond	0.145	0.178	0.486	0.742	0.012	0.008	a	a	0.587	0.544	11.2	11.2
	std err±		0.015	0.032	0.002	0.107	0.005	0.004	a	a	0.096	0.101	0.6	1.4

alkalinity expressed as CaCO$_3$

*BFR Watershed,CHR Outfall, and TR Outfall do not have standard errors due to no outflow

[a] Denotes concentration was below detectable levels.

The trace elements (As, Ba, Cr, Se, Cu, Mo, B, and Mn) measured were also detected in the disposal ponds (Table 3-4). Boron, Cr, As, Se, and Mo concentrations increased from outfall to disposal pond. However, concentrations of Mn, Cu, and Ba all differed among watersheds. There are no specific patterns for Mn concentrations when comparing watersheds. The Cu concentrations increased from outfalls to ponds. Conversely, Ba concentrations decreased from outfall to disposal pond. The MINTEQA2 model predicted that as much as 30% of the Ba concentration in the disposal pond is being bound by carbonates according to MINTEQA2 modeling, suggesting $BaCO_3$ precipitation. This was confirmed by comparing saturation index values for $BaCO_3$ calculated by MINTEQA2 . Overall, the differences between outfalls and ponds for Mn, Cu, and Ba appeared to depend on watershed.

Table 3-4: Trace metal concentrations in outfall and disposal pond for 2006 and 2007.

Watershed		Type	B µMol/L		Cr µMol/L		Mn µMol/L		Cu µMol/L		As µMol/L		Se µMol/L		Mo µMol/L		Ba µMol/L	
			2006	2007	2006	2007	2006	2007	2006	2007	2006	2007	2006	2007	2006	2007	2006	2007
CHR		Outfall	4.18	3.16	0.02	0.08	0.13	0.14	0.13	0.05	0.02	0.01	0.01	a	a	a	1.62	1.26
	std err±		0.53	*	0.01	*	0.01	*	0.05	*	0.01	*	a	*	a	*	0.44	*
CHR		Pond	15.00	11.20	0.05	0.05	0.14	0.11	0.45	0.15	0.12	0.12	0.01	0.01	0.08	0.05	1.19	2.19
	std err±		4.03	0.68	0.00	0.02	0.08	0.08	0.20	a	0.02	0.01	a	a	0.05	0.02	0.41	0.71
BFR		Outfall	4.78	4.34	0.02	0.03	0.09	0.11	0.08	0.09	0.01	0.01	0.01	a	a	a	2.16	2.43
	std err±		0.04	*	a	*	a	*	0.02	*	a	*	a	*	a	*	0.07	*
BFR		Pond	10.60	6.50	0.04	0.05	0.07	0.03	0.24	0.08	0.05	0.02	0.01	a	0.03	a	0.56	1.46
	std err±		2.68	*	0.01	*	0.03	*	0.07	*	0.02	*	a	*	0.02	*	0.04	*
LPR		Outfall	8.45	7.73	0.08	0.21	0.25	0.34	0.08	0.10	a	a	0.01	a	a	a	4.09	5.90
	std err±		0.82	0.16	0.01	0.02	0.07	0.07	0.01	0.01	a	a	a	a	a	a	0.69	0.46
LPR		Pond	12.40	8.06	0.05	0.07	0.02	0.30	0.16	0.15	0.03	0.08	0.01	0.01	0.01	0.03	2.52	1.39
	std err±		2.62	1.59	0.01	0.03	0.01	0.22	0.05	0.04	0.02	0.04	a	a	0.01	0.02	0.62	0.18
PR		Outfall	6.33	9.31	0.05	0.26	0.10	0.29	0.31	0.17	a	0.01	a	a	0.01	a	1.11	4.98
	std err±		0.80	0.89	0.01	0.07	0.06	0.09	0.21	0.03	a	a	a	a	a	a	0.28	1.42
PR		Pond	18.20	14.50	0.39	0.25	0.03	0.09	0.24	0.27	0.08	0.06	0.01	0.01	0.04	0.03	1.19	2.45
	std err±		2.78	2.66	0.14	0.06	0.01	0.05	0.04	0.04	0.02	0.01	a	a	0.01	0.01	0.31	0.64
TR		Outfall	9.76	10.92	0.07	0.16	0.05	0.11	0.10	0.17	a	0.01	0.01	a	a	a	1.81	1.56
	std err±		0.44	*	0.01	*	0.01	*	0.01	*	a	*	a	*	a	*	0.11	*
TR		Pond	13.50	12.40	0.08	0.13	0.16	0.45	0.24	0.29	0.02	0.04	0.01	0.01	0.03	0.06	0.62	1.36
	std err±		0.90	0.85	0.01	0.01	0.14	0.37	0.07	0.09	0.01	0.02	a	0.01	0.02	0.05	0.16	0.33

BFR Watershed, CHR Outfall, and TR Outfall do not have standard errors due to no outflow.

^{a} *Denotes concentration was below detectable levels.*

The data from the TCLP analysis of sediment samples is shown in Table 3-5. Among the eight trace elements tested, only Ba and Mn were detected in the sediment leachate for 2006 and 2007. One exception was Se which was detected only in one pond sediment leachate sample in LPR in 2006 (0.12 µMol/L). Barium and Mn leachate concentrations from 2006 were not significantly different among the five watersheds in the PRB (p=0.06, df=4, F=2.95) and (p=0.587, df=4, F=2.85), respectively. It is important to determine if the sediment leachates within basin are similar or different to establish separate protocols to implement for individual watersheds in the PRB. Our results suggest that sediment trace metal leachate can be regulated on a PRB scale. In 2007, barium sediment leachate concentrations once again were not significantly different among watersheds (p=0.06, df=4, F=2.95). However, manganese was determined to be significantly different among watersheds (p=<0.01, df=4, F=5.81) Upon further analysis, the TR and LPR watersheds means were significantly greater in Mn leachate concentrations than the CHR watershed.

Table 3-5: Sediment trace metal leachate concentrations.

Watershed		Type	Mn µMol/L		Ba µMol/L	
			2006	**2007**	**2006**	**2007**
CHR		Sed	34.60	40.00	32.80	29.10
	std					
	err±		10.00	5.46	6.38	8.74
BFR		Sed	80.70	20.60	10.20	9.47
	std					
	err±		24.90	4.91	9.66	2.18
LPR		Sed	51.30	51.00	57.70	34.50
	std					
	err±		10.80	5.38	18.00	12.20
PR		Sed	91.00	89.20	28.00	15.40
	std					
	err±		8.80	9.28	7.79	3.44
TR		Sed	104.00	98.30	14.40	13.40
	std					
	err±		31.50	42.30	3.83	2.16

Specific field measurements and trace element concentrations in disposal ponds can be used to explain the concentration of trace elements in the sediment. The regression model ($r^2 = 0.45$) for Ba sediment leachate ($\hat{Y}$) was as follows:

$$\hat{Y} = 0.42102 - 0.02281 \times \text{pond Ba} - 0.04891 \times \text{year} + 0.0101 \times \text{temperature} - 0.04266 \times \text{pH [1]}$$

With regard to regression model [1], we noted that all coefficients were statistically significant (p <0.05). We also note that regression model predicted that Ba sediment leachate ($\hat{Y}$) decreased with increasing pond Ba concentration and increasing pH. Conversely increased Ba sediment leachate with increasing temperature. Also, Ba concentrations decreased from the year 2006 to 2007.

In contrast to the regression model that explained the concentration of Ba in sediment leachates, the regression model ($r^2 = 0.40$) for leachable Mn has just two predictors:

$$\hat{Y} = 3.58918 + 1.04311 \times \text{pond Mn} - 0.0489 + 0.000451 \times \text{alkalinity}$$

With regard to this model we again note that all coefficients were statistically significant ($p < 0.05$). The model predicted that Mn sediment leachate concentration ($\hat{Y}$) increased when both pond Mn concentration and alkalinity increased. A possible explanation why alkalinity was important for explaining the amount of Mn in sediment leachate is that under alkaline conditions Mn is shown to co-precipitate as MnO_2 with $CaCO_3$ or dependent upon pH and ORP (Stumm et al. 1996, Deutsch 1997).

Conclusions:

The findings of this research are important not only for estimating if shallow groundwater systems are being contaminated by trace elements from the CBNG disposal ponds, but also for determining if the sediments are toxic. If the sediments are toxic, future reclamation practices of CBNG disposal ponds must remove sediment for a appropriate disposal. Over all findings of this research are useful for state, federal, and local agencies in managing CBNG produced water disposal ponds.

References:

Brown, D. S.; Allison, J. D. 1992. MINTEQA2: An equilibrium metal speciation model. Athens, Georgia: Environmetnal Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency.

Bureau of Land Management. 2003. *Final Environmental Impact Statement and Proposed Plan Amendment for the Powder River Basin Oil and Gas Project;* Buffalo Field Office: Buffalo, WY, Vol. 1-3.

De Bruin, R. 2004. Coalbed Methane in Wyoming. First Annual CBM Research, Monitoring and Applications Conference, University of Wyoming, Laramie, WY, August 17-19.

Jackson, R.E.; Reddy, K.J. 2007a. Trace Element Chemistry of Coal Bed Natural Gas Produced Water in the Powder River Basin, Wyoming. *Environ. Sci. & Tech.* 2007a. 41, 5953-5959.

Jackson, R.E.; Reddy, K.J. 2007b. Geochemistry of coalbed natural gas (CBNG) produced water in Powder River Basin, Wyoming: salinity and sodicity. *Water, Air, Soil Pollut.* http://www.springerlink.com/content/e11m0777845n722/fulltext.html

McBeth, I.H.; Reddy K.J.; Skinner, Q.D. 2003a. Chemistry of coalbed methane product water in three Wyoming watersheds. *J. Am Water Res.* 39, 575-585.

McBeth, I.H.; Reddy, K.J.; Skinner, Q.D. 2003b. Chemistry of trace elements in coalbed methane product water. *Water Res.*, 37,884-890.

SAS (SAS Institute). 2000. SAS Proprietary Software Release 9.0. SAS Institute, Raleigh, NC.

U.S. Environmental Protection Agency. 2005. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods. SW-846 Manual Fourth Edition. http://www.epa.gov/epaoswer/hazwaste/test/sw846.htm

U.S. Geological Survey. 1986. Hydrology of Area 50, Northern Great Plains and Rocky Mountain Coal Provinces, Wyoming and Montana. Water Resources Investigations Open-File Report 83-545.

Wyoming Department of Environmental Quality/Water Quality Division. 2004. Manual of Standard Operating Procedures for Sample Collection and Analysis. Wyoming Department of Environmental Quality, Water Quality Division, Watershed Program, Cheyenne, WY.

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

Carol Frost[4], Elizabeth Brinck, Jason Mailloux, Shaun Carter and Shikha Sharma

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, $^{87}Sr/^{86}Sr$ of river water and $^{143}Nd/^{144}Nd$ 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 $^{87}Sr/^{86}Sr$ 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

---

[4] Department of Geology and Geophysics. University of Wyoming, Laramie, WY. email: frost@uwyo.edu

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 $^{87}Sr/^{86}Sr$ 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 $^{87}Sr/^{86}Sr = 0.71026 \pm 0.00002$ (2 standard deviations). All analyses were normalized to an $^{86}Sr/^{88}Sr$ 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 $^{87}Sr/^{86}Sr$ 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-cHNO$_3$. One aliquot was spiked with a ^{146}Nd and ^{149}Sm-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 ^{143}Nd/^{144}Nd 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. ^{2}H/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 d^{13}C$_{DIC}$ 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 d^{13}C$_{DIC}$ values are reported in per mil relative to V-PDB. The DIC concentrations in samples were also quantified from the mass spectrometry data. Three NaHCO$_3$ 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 CO$_2$ vs. concentration of DIC in these standards gives an excellent correlation (r^2=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.
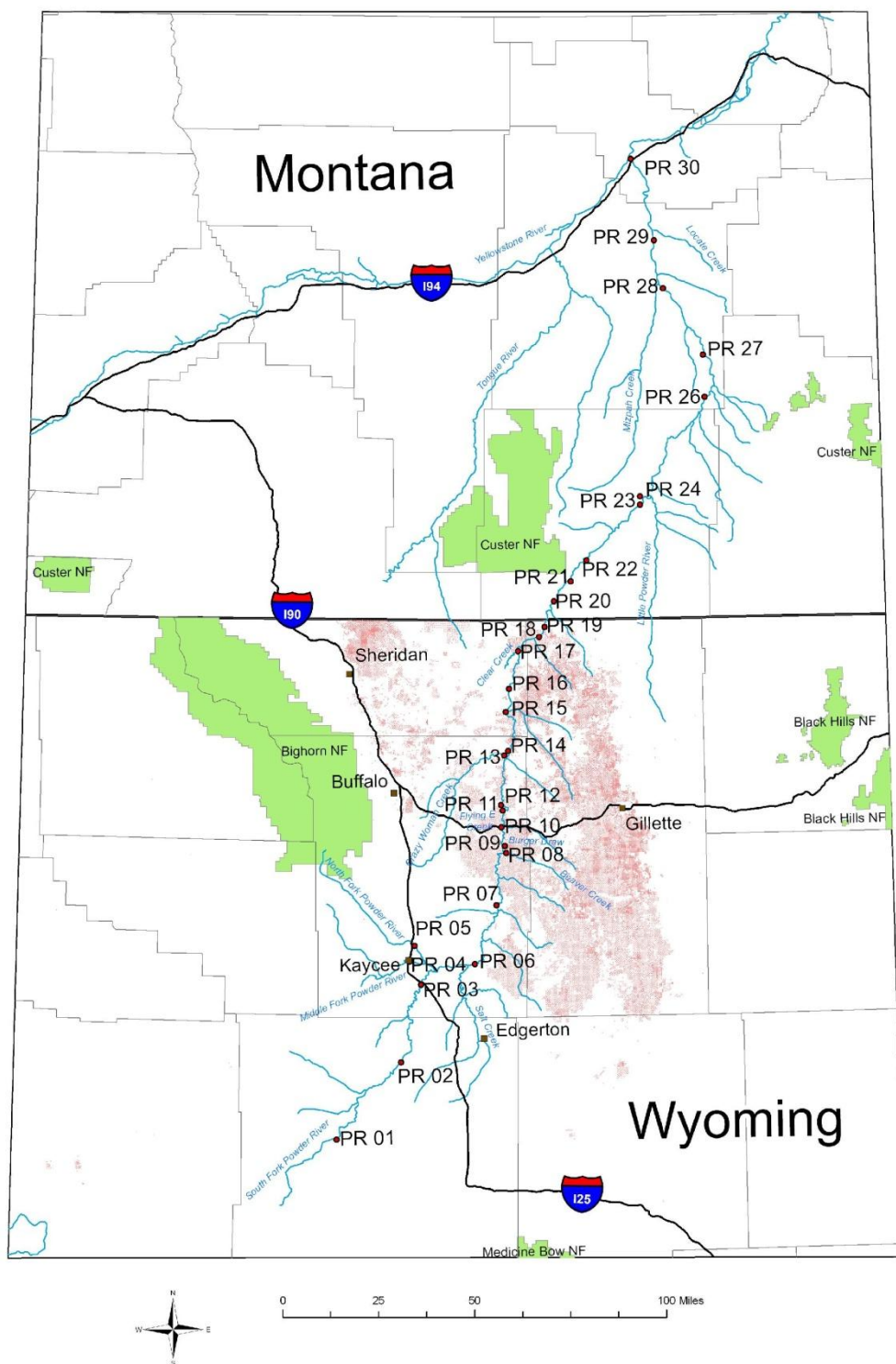
Figure 4-1: Location map of samples collected along the Powder River, Wyoming and Montana. Area in pink is the area of CBNG development. Map from Carter (2008).
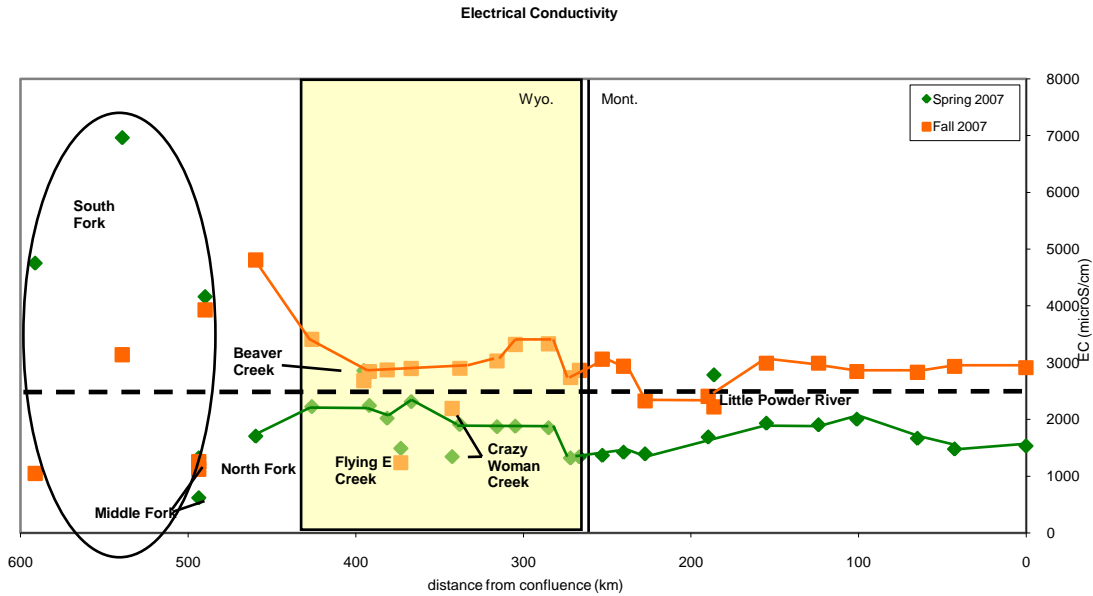
Figure 4-2: Electrical conductivity with position on the river. Shaded area indicates most intense CBNG development. The dashed line represents Montana's numeric standard for the time of year including both May and September samplings (2500 microS/cm). From Carter (2008).
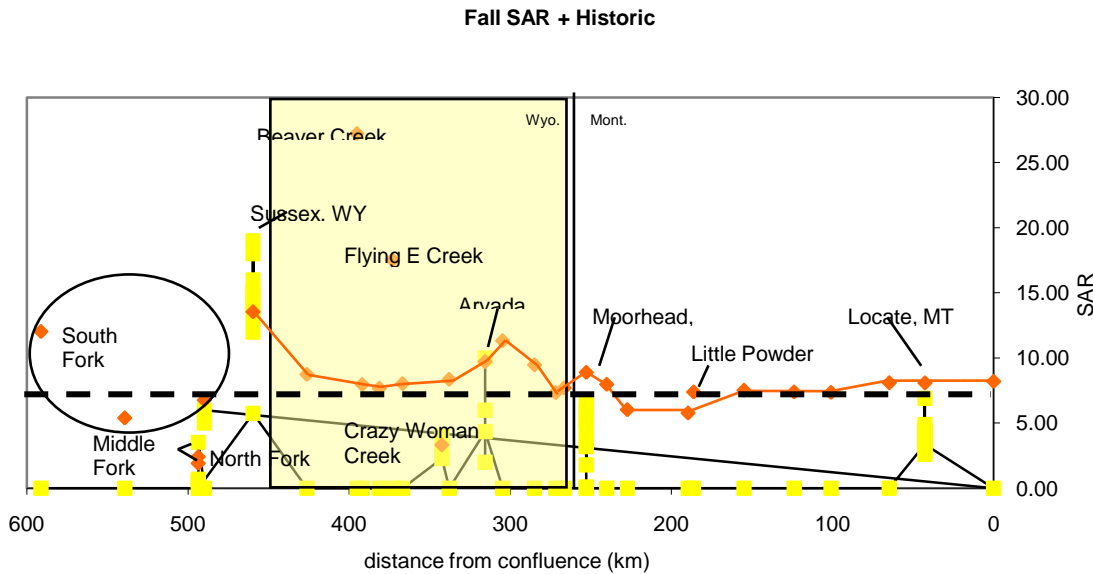

Figure 4-3: Sodium adsorption ratio at low flow compared to historic data (yellow symbols) with position on the river. Shaded area indicates area of most intense CBNG development. Dashed line represents Montana's limit at the time of sampling (7.5 instantaneous). Data from Hembree et al. (1952) and USGS (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 $\delta^{13}C$ 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 $\delta^{13}C$ 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 $d^{13}C_{DIC}$ 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 $d^{13}C_{DIC}$ of water from Beaver Creek (PR8) is +16.4‰, which is within the range of $d^{13}C_{DIC}$ 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 $d^{13}C_{DIC}$ 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 $d^{13}C_{DIC}$. Only sample PR23, from the Powder River at Broadus, Montana, has $d^{13}C_{DIC}$ (-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.
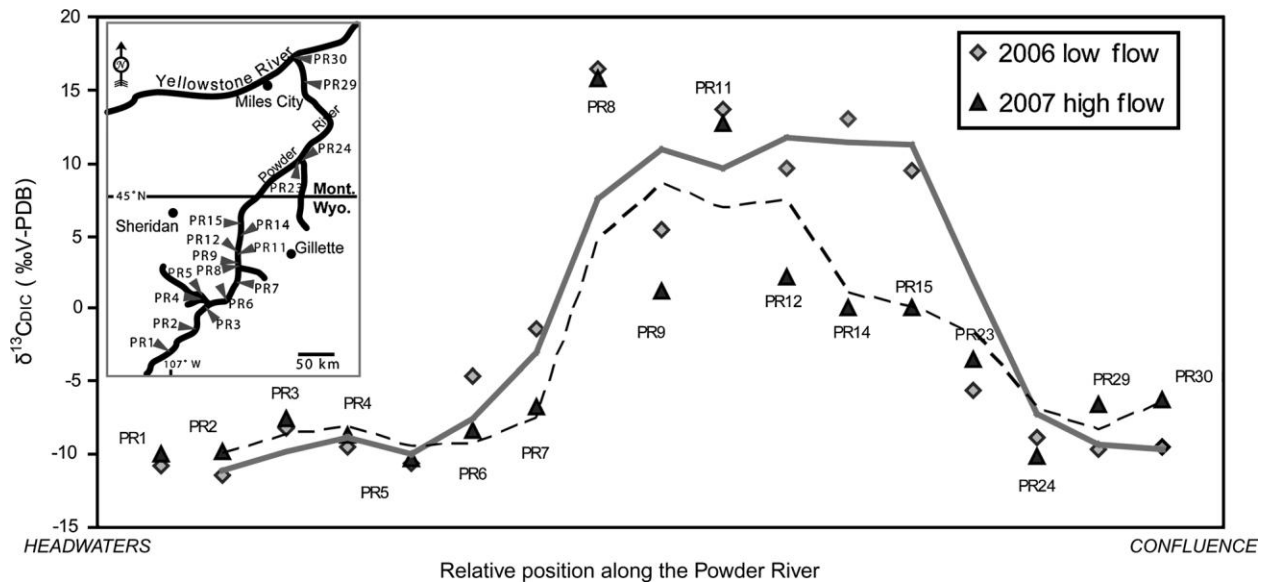

Figure 4-4: Carbon isotopic compositions of dissolved inorganic carbon in surface water samples collected from the Powder River and its tributaries. The high values correspond to the region where CBNG production is concentrated (Sharma and Frost 2008).

Sr Isotopic Results and Discussion

We undertook a 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 (Mailloux et al., submitted). Using the ^{87}Sr/^{86}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}Sr/^{86}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 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}Nd/^{144}Nd versus ^{147}Sm/^{144}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}Nd/^{144}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.
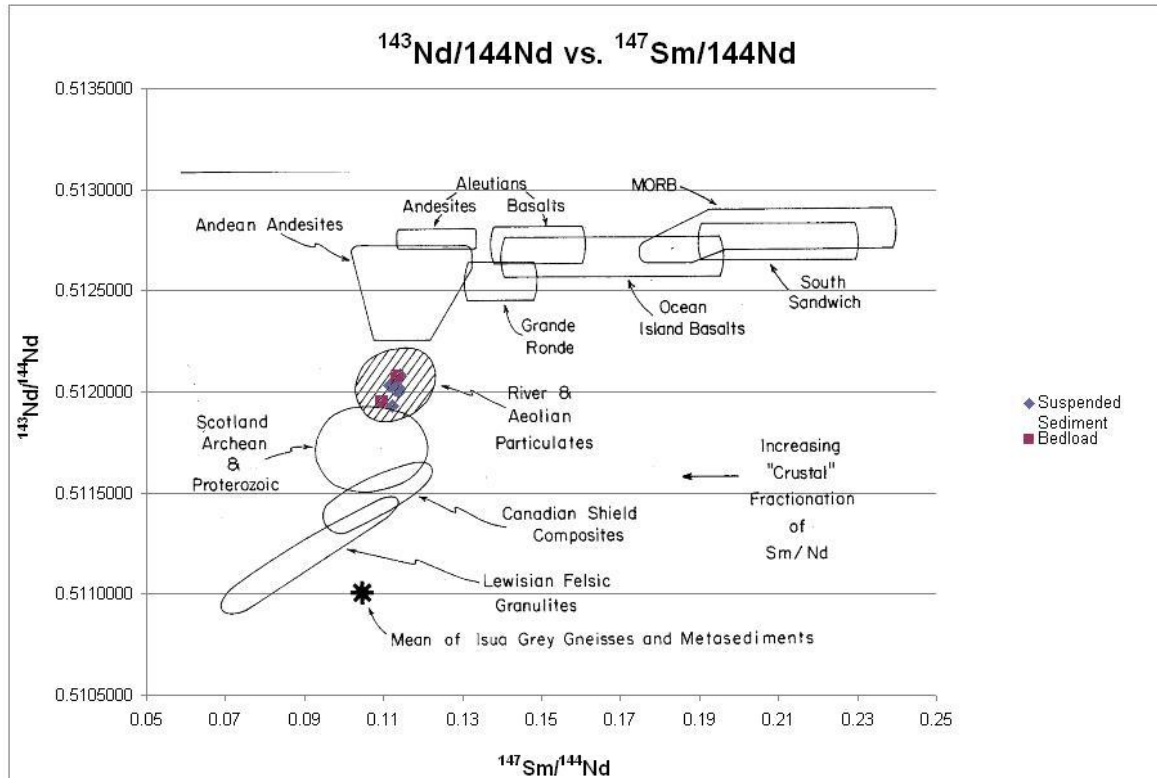
Figure 4-5: Plot showing Powder River sediment isotope values compared to reference geologic materials from Goldstein et al. (1984).

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 $^{87}Sr/^{86}Sr$ than local alluvial water. This measureable 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.
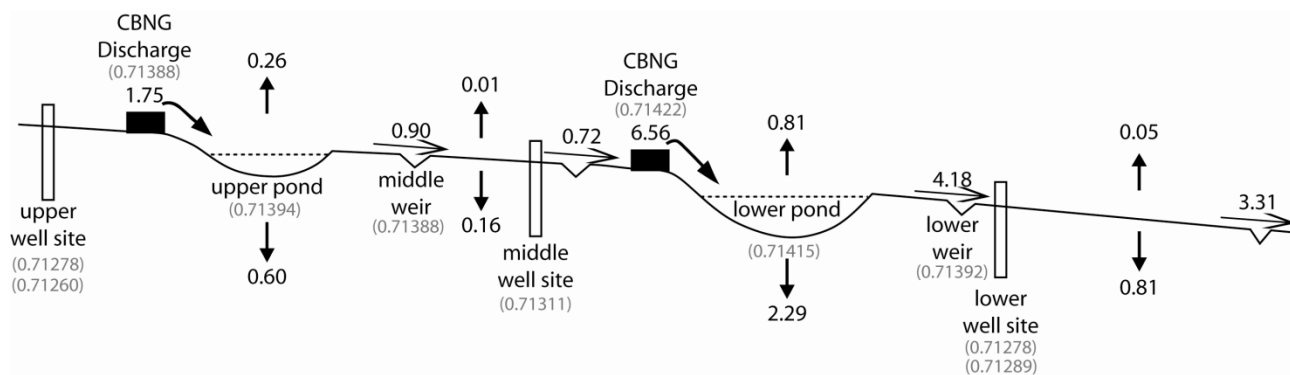
Figure 4-6: Beaver Creek water budget for the week of August 5-11, 2003. Values are in liters per second. Downward, upward, and horizontal arrows represent infiltration, evaporation, and surface flow respectively. Parenthetical values in gray are the $^{87}Sr/^{86}Sr$ ratios for the sample set collected 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 $d^{13}C_{DIC}$ values of +12 to +22‰ and high DIC concentrations of above 100mg C/L (Sharma and Frost 2008). The positive $d^{13}C_{DIC}$ 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 $d^{13}C_{DIC}$ 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 $d^{13}C_{DIC}$ than water being produced from the Lower Wyodak coal zone, which yielded $d^{13}C_{DIC}$ of 12.2 to 14.3‰ (Sharma and Frost 2008). This difference in the $d^{13}C_{DIC}$ 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 $d^{13}C_{DIC}$ 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 $d^{13}C_{DIC}$ 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 $d^{13}C_{DIC}$ 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 $d^{13}C_{DIC}$ value of +9.3 ‰, intermediate between the values of ambient ground water and CBNG produced waters (Fig. 4-7). Brinck and Frost (2007) used $^{87}Sr/^{86}Sr$ 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 $d^{13}C_{DIC}$ 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 $d^{13}C_{DIC}$ 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.
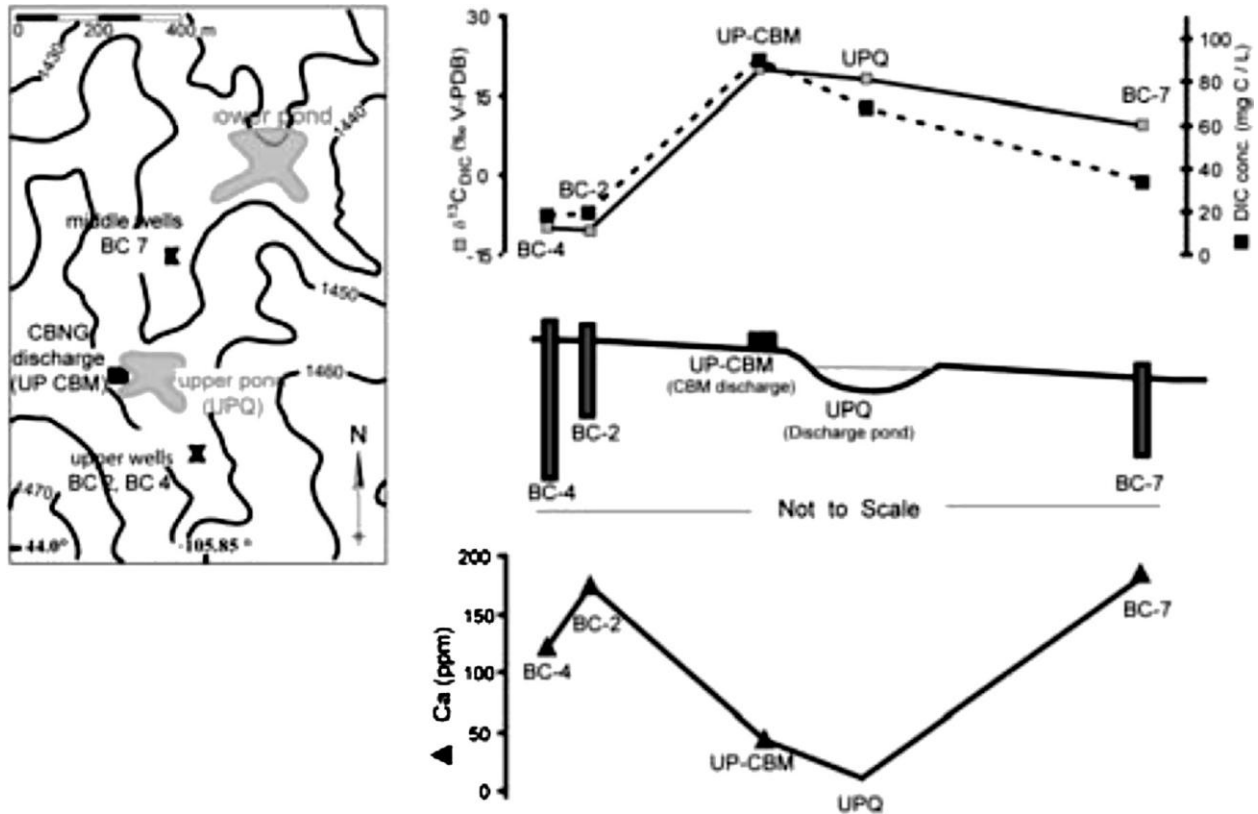

Figure 4-7: Carbon isotopic composition and concentration of dissolved inorganic carbon (DIC) and Ca concentration in water samples collected from the Beaver Creek site. BC-2 and BC-4 are ground water monitoring wells upstream of the CBNG discharge point UP-CBM. UPQ is the pond that holds the CBNG-produced 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.
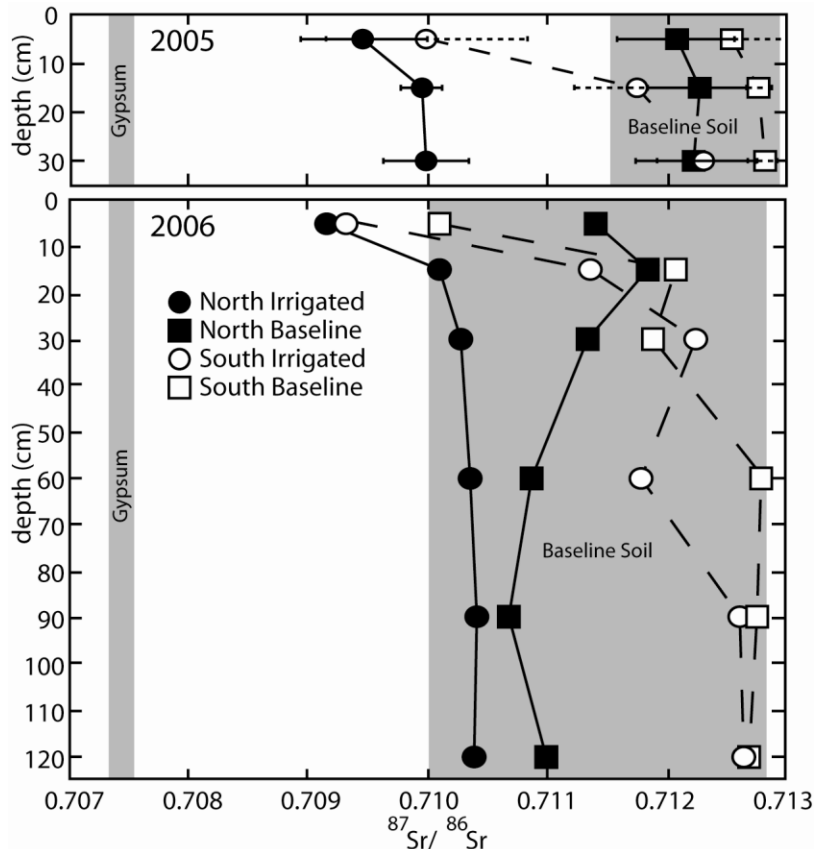
Figure 4-8: Strontium isotope ratios of exchangeable strontium with depth. North irrigated and baseline site samples are solid circles and squares, respectively. South irrigated and baseline site samples are open circles and squares, respectively. Grey shaded areas represent the range of strontium isotope 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).
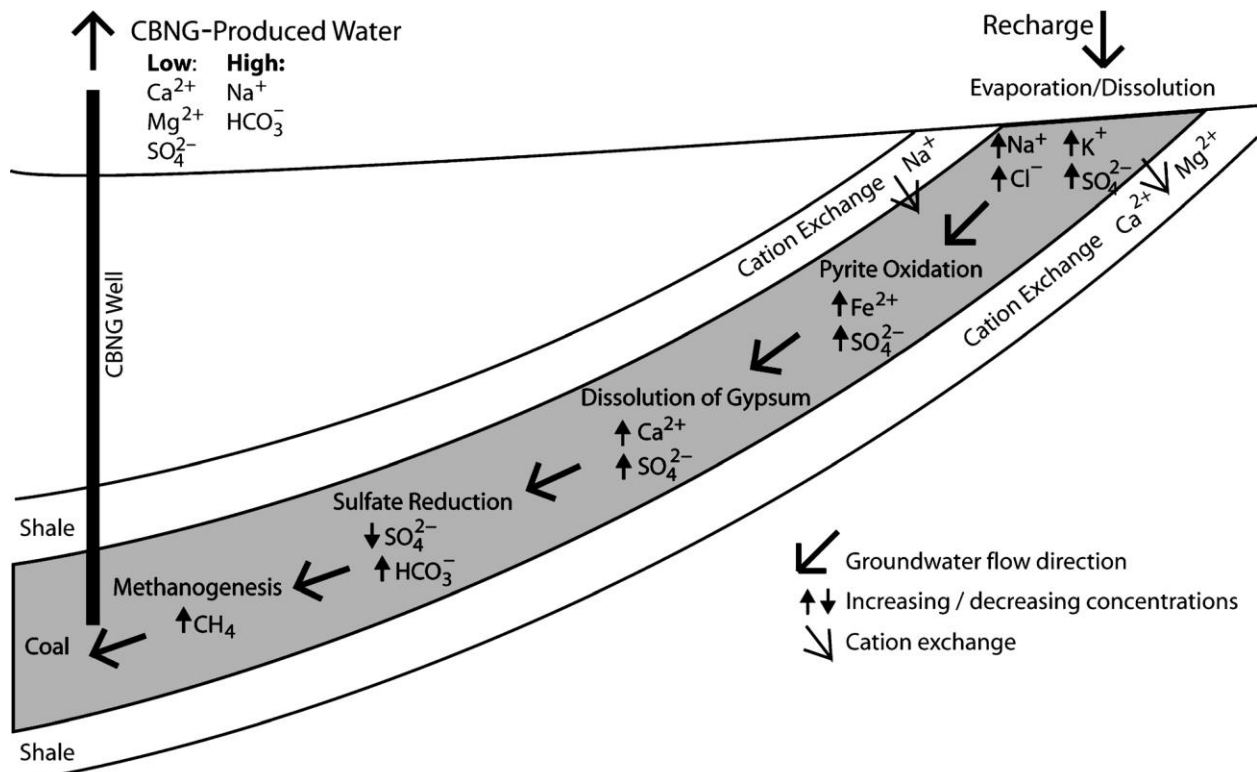

Figure 4-9: Summary of geochemical processes occurring in coal aquifers used for coalbed natural gas production. From Brinck et al. (2008).

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.
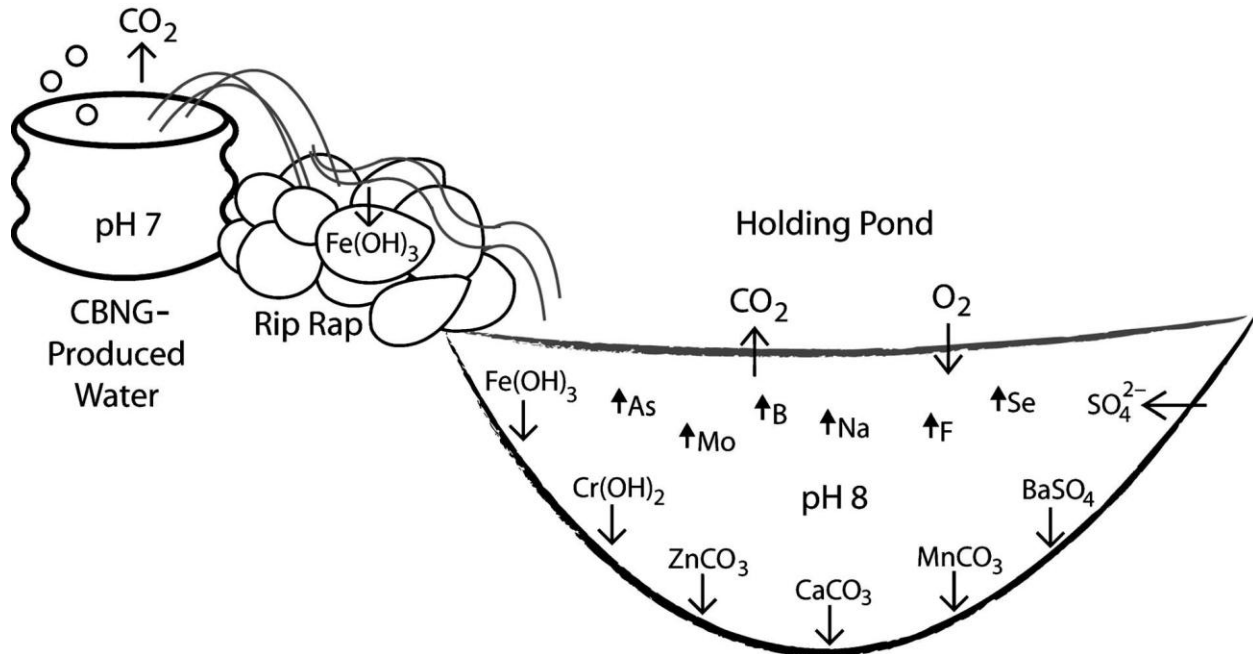

Figure 4-10: Summary of geochemical changes that occur when CBNG produced water is held in an impoundment. Arrows directed to the floor of the pond and rip rap indicate the precipitation of minerals out of water. Upward arrows indicate the loss to atmosphere of gas. Downward arrows across the surface 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 $\delta^{13}C$ 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 $\delta^{13}C$ 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 $d^{13}C_{DIC}$. This suggests that surface waters in Montana are little to unaffected by CBNG production during the low flow conditions.

Our Baysian 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 $^{87}Sr/^{86}Sr$ 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 $^{87}Sr/^{86}Sr$ 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 $d^{13}C_{DIC}$ 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.

References:

Brinck, E.L., and C.D. Frost. 2007. Detecting infiltration and impacts of introduced water using strontium isotopes. *Ground Water* 45, no.5: 554–568.

Brinck, E.L., Frost, C.D., Evaluation of amendments used to prevent sodification of irrigated fields. *Applied Geochemistry* , in revision, September 2008.

Brinck, E.L., Drever, J.I., and Frost, C.D., 2008. The geochemical evolution of water co-produced with coal bed natural gas in the Powder River Basin, Wyoming. *Environmental Geosciences,* in press, July 2008.

Buccino, S., and Jones, S., 2004. Controlling water pollution from coalbed methane drilling—an analysis of discharge permit requirements. *Wyoming Law Review*, 4, 559-583.

Carter, S.A., 2008. Geochemical analysis of the Powder River, Wyoming/Montana and an assessment of the impacts of coalbed natural gas co-produced water. M.S. thesis, University of Wyoming, 146 p.

Drever, J.I. 1997. *The geochemistry of natural waters, surface and groundwater environments,* 3rd ed. Upper Saddle River, NJ: Prentice Hall.

Essington, M.E. 2004. *Soil and water chemistry: an integrative approach*. Boca Raton, Florida: CRC Press LLC.

Frost C.D., and E. Brinck. 2005. Strontium isotope tracing of the effects of coal bed natural gas (CBNG) development on shallow and deep groundwater systems in the Powder river basin, Wyoming. In *Western Resources Project Final Report - Produced Groundwater Associated with Coalbed Natural Gas Production in the Powder River Basin*. Wyoming State Geological Survey Report of Investigations No. 55, ed. M.D. Zoback, 93-107, Laramie, Wyoming: WyGS.

Goldstein, S.L., O'Nions, R.K., and Hamilton, P.J., 1984. A Sm-Nd isotopic study of atmospheric dusts and particulates from major river systems. *Earth and Planetary Science Letters*, 70, 221-236.

Hembree, C. H., Colby, B. R., Swenson, H. A., Davis, J. R., 1952. Sedimentation and Chemical Quality of Water in the Powder River Drainage Basin Wyoming and Montana: *USGS Circular 170*, 92p.

Mailloux, J., Ogle, K., Frost, C., Using a Bayesian statistical model to determine the amount of coal bed natural gas co-produced water in the Powder River, Wyoming and Montana, manuscript submitted to *Water Resources Research*, September 2008.

Payne, A.A., and Saffer, D.M. 2005. Surface water hydrology and shallow groundwater effects of coalbed natural gas development, upper Beaver Creek drainage, Powder River Basin, Wyoming. In *Western Resources Project Final Report - Produced Groundwater Associated with Coalbed Natural Gas Production in the Powder River Basin*. Wyoming State Geological Survey Report of Investigations No. 55, ed. M.D. Zoback, 5-43. Laramie, Wyoming: WyGS.

Rengasamy, P., Greene, R.S.B., Ford, G.W., Mehanni, A.H., 1984. Identification of dispersive behavior and management of Red-Brown Earths. *Aust. J. Soil Res*. 24, 229-237.

Sharma, S., and Frost, C.D., 2008. Tracing coal bed natural gas co-produced water using stable isotopes of carbon. *Ground Water,* 46 no 2, 329-334.

Stearns, M., J.A. Tindall, G. Cronin, M.J. Friedel, and E. Bergquist. 2005. Effects of coal-bed methane discharge waters on the vegetation and soil ecosystem in Powder River Basin, Wyoming. *Water, Air, and Soil Pollution* 168, no. 1-4: 33-57.

United States Geologic Survey, 2008. National Water Information System URL:http://waterdata.usgs.gov/nwis

Wheaton, J., and Brown, T.H. 2005. Predicting changes in groundwater quality associated with coalbed natural gas infiltration ponds in Western Resources Project Final Report - Produced Groundwater Associated with Coalbed Natural Gas Production in the Powder River Basin. In *Western Resources Project Final Report - Produced Groundwater Associated with Coalbed Natural Gas Production in the Powder River Basin*. Wyoming State Geological Survey Report of Investigations No. 55, ed. M.D. Zoback, 45-69. Laramie, Wyoming: WyGS.

Wyoming Department of Environmental Quality, 2001. Water Quality Division, Watershed Program, Manual of Standard Operating Procedures for Sample Collection and Analysis, 373p.

Task 5 – Toolbox to Evaluate Treatment Technologies for Coalbed Natural Gas Co-Produced Water

Eric T. Sajtar and David M. Bagley[5]

As noted in earlier Task reports, above, waters associated with coalbed natural gas (CBNG or sometimes referred to as coalbed methane – CBM) are generally termed CBM co-produced waters. These waters must be withdrawn from the coal seam to desorb methane from the surface of the coal, thus allowing the methane to be removed (Western Resources, 2005). The water which is a by-product of CBM extraction then must be managed in a manner that will not adversely impact the environment.

Currently CBM co-produced waters are managed in five ways. These include: surface discharge to rivers or infiltration ponds, irrigation, livestock watering, atomization and road application for dust control (WYDEQ, 2007). None of these options return the water to the source aquifer. The primary concern is what is in the water.

PRB CBM waters contain excess sodium, and may be classified as being saline-sodic (water with a sodium adsorption ratio (SAR) greater than 12 and electrical conductivity (EC) greater than 4dS/m) (Keith et al., 2003). Waters with a SAR above 13 have the ability to cause soil to be hard and cloddy when dry, to crust badly, and to take water very slowly (Soltanpour and Follett, 1999) which makes the soil unusable or less suitable for growing crops. These waters also have the ability to alter ecosystems (Stearns et al., 2005) when managed with current methods.

These concerns have caused regulations to be imposed by the Wyoming Department of Environmental Quality and United States Environmental Protection Agency regarding the discharge of CBM co-produced waters in the PRB. Regulations have made it necessary for CBM waters to be treated before discharge if the water does not meet the discharge requirements (WYDEQ, 2007).

Processes that have the ability to treat these waters to meet discharge requirements related to elevated sodium concentration include: pressure driven membrane processes, electrical processes, ion exchange processes, and thermal processes (Arthur et al., 2005). Currently, reverse osmosis, a pressure driven membrane process, and ion exchange processes are used in the PRB to treat CBM waters (WYDEQ, 2007). These processes do treat these waters to meet discharge requirements (WYDEQ, 2007), but other processes and technologies may treat these waters more economically.

Yet another issue is how to dispose of waste products that are generated as a result of treating CBM produced waters. Currently, waste is either disposed of via deep well injection or through the use of evaporation ponds. Deep well injection requires the use of injection wells which are costly to install and have a set capacity (Mickley, 2001). In addition, the location of these wells is determined based on site geology to ensure drinking water sources do not become

---

[5] 5 Department of Civil & Architectural Engineering, University of Wyoming, Laramie, Wyoming. email: Bagley@uwyo.edu

contaminated. The other technique currently used is evaporation ponds. A major issue encountered with evaporation ponds is that the salts accumulate in the pond and the pond will eventually reach a capacity at which time the dried solids must be disposed of in some manner. These issues make it necessary to investigate other brine disposal techniques.

Currently no tool exists to compare the many technologies available to treat produced waters and wastes generated on an equal platform. Such a tool would make it possible to decide how best to treat a water based on the influent water characteristics, effluent water requirements, and the abilities of the technologies capable of removing sodium from water.

The objectives of Task 5 were to use publicly available data to: (1) determine what technologies can treat CBM co-produced waters to meet discharge and use requirements based on the characteristics of the water and; (2) to develop a toolbox which will aid producers and regulators when deciding how best to treat CBM produced waters based on the abilities and costs associated with each technology.

Methods:

The seven tasks identified in Table 5-1 provide the methodology for developing the Coalbed Methane-Demineralization Treatment Cost (CBM-DTC) toolbox. Details of the methods used are summarized below.

Table 5-1: Project tasks

Task	Description
5a	Interview and periodically meet with key public agency personnel
5b	Characterize CBNG waters to be treated and classify treated water quality by use
5c	Develop comprehensive list of existing water treatment technologies and preliminarily match possible treatment technologies to regional CBNG waters
5d	Identify treatment technology 'black box' characteristics
5e	Identify capital and operating costs to the extent possible
5f	Construct and validate the toolbox
5g	Provide the toolbox to the user community

Input from Public Agencies and Industry

Meetings with public agency and industry personnel were conducted as indicated below to determine the needs of public agencies for the CBM-DTC toolbox, to examine existing CBM treatment facilities, to meet selected treatment operators and owners and to identify the available data. The purpose of the tour and meetings was to examine CBM treatment facilities currently in place, meet selected treatment operators and owners, and develop contacts for additional work.
- Bagley and Johnson met with Wyoming Dept of Environmental Quality (WYDEQ), Water Quality Division, Cheyenne, July 13, 2006.
- Bagley met with Bureau of Land Management, Buffalo Field Office, July 18, 2006.

- Bagley and Johnson met with Dennis Lamb, Wyoming DEQ, Casper, July 24, 2006.
- Bagley, Johnson and Sajtar toured Powder River area with Dennis Lamb, WYDEQ, August 22, 2006.
- Bagley, Johnson and Sajtar met with Jeff Young, Siemens Water Technologies, on August 22, 2006 to discuss the Wild Turkey RO plant.
- Bagley, Johnson and Sajtar met with Doug Beagle, EMIT Technologies, Sheridan, August 23, 2006.
- Bagley contacted Jeff Cline, Anadarko, starting August 15, 2006 to request information.
- Bagley had a phone conference with Ron and Vivian Drake, Drake Water Technologies, on January 19, 2007 to discuss the Drake Process.
- Bagley and Sajtar met with Doug Beagle, EMIT Technologies, on February 28, 2007 at UW to further discuss the Higgins' Loop IX process.
- Bagley and Sajtar met with several industry and regulatory personnel at the ASMR annual conference on June 5, 2007.

Characterize CBNG Waters

Much work has been done to determine the characteristics of PRB CBM waters (Rice et al. 2000; McBeth et al. 2003, Patz et al. 2004, Patz et al. 2006, Jackson and Reddy 2007). The conclusion from research has shown that CBM water constituent concentrations vary from watershed to watershed in the PRB (McBeth et al. 2003). There are five primary watersheds in the PRB. The rivers that comprise these watersheds are the Cheyenne River, Belle Fourche River, Little Powder River, Powder River and Tongue River.

CBM water data for the five watersheds are outlined in Table 5-2. Data were compiled from numerous studies and databases to provide a range of values for constituents in CBM waters for each watershed. Water constituent data collection points were located on a USGS map which has the various watersheds of the PRB delineated on it. High, low, and mean water constituent concentrations where then determined for each watershed. Additional information about water constituents in PRB CBM waters is available from the Wyoming State Geologic Survey (http://ims.wrds.uwyo.edu/prb/prb.html). The Wyoming State Geologic Survey has done much research related to CBM water constituents in the PRB. Data available at the above link represents water constituents on a by-coal-formation basis.

Table 5-2: PRB CBM water constituents and concentrations by watershed. Data are adapted from Rice et al. (2000) unless otherwise noted.

Constituent	Units	Cheyenne River			Belle Fourche River			Little Powder River			Powder River			Tongue River [c]		
		Mean	High	Low	Mean	High	Low	Mean	High	Low	Mean	High	Low	Mean	High	Low
Temperature	°C	16.8	17.7	15.9	20.2	28.7	13.8	18.0	26.5	13.9	19.5	24.8	11.7			
Specific Conductance	µS/cm	705	770	640	1023	1640	470	1426	1660	1070	2097	3020	860	1800	1850	1750
Total dissolved solids	mg/L	430	470	390	666	1120	270	966	1260	720	1411	2010	540	1200[b]		
F^-	µg/L	1600	1600	1600	967	1700	500	760	1000	500	710	1400	420			
Cl^-	mg/L	8.2	10.0	6.3	14.7	64.0	5.2	9.9	12.0	8.9	11.7	18.0	6.4			
SO_4^{2-}	mg/L	8.9	17.0	0.7	2.5	12.0	0.0	1.2	3.0	0.1	1.5	8.1	0.1			
Br	µg/L	65	90	40	144	85	20	72	80	60	76	11	50			
Alkalinity (as $CaCO_3$)	mg/L	465	490	440	742	1170	290	1112	1520	810	1585	2320	580	775	950	600
NH_4^+	mg/L	2.4	2.4	2.4	2.1	3.2	1.1	3.4	5.3	2.1	2.7	4.8	1.1			
Ca^{2+}	mg/L	25.5	32.0	19.0	34.4	59.0	5.9	47.6	69.0	30.0	20.3	35.0	9.1	6	7	5
K	mg/L	6.6	7.3	5.9	8.1	14.0	3.8	11.7	15.0	8.1	8.4	18.0	3.9			
Mg^{2+}	mg/L	11	13	10	15	25	2	27	46	14	14	28	5	2.5	3	2
Na^+	mg/L	140	150	130	219	390	110	308	360	240	563	800	220	392	460	325
Ba^{2+}	µg/L	300	370	230	605	1300	140	988	1600	470	539	750	240	270	296	244
Fe	µg/L	1500	2400	580	484	490	120	554	820	270	569	2800	20	72	105	38
Si	mg/L	4.8	5.3	4.3	4.6	5.8	3.8	4.5	5.6	3.7	5.2	7.1	4.6			
Sr	µg/L	455	560	350	763	1800	100	1054	1900	450	415	840	250			
[a]Al	µg/L	6.7			5.4			11						1817		
[a]As	µg/L	2.3			1.5			4.7						0.7		

[a]Se	μg/L	0.71			0.75			0.83						0.8		
[a]B	μg/L	51			62			89						109		
[a]Cu	μg/L	10			13			24						10.8		
[a]Mo	μg/L	0.31			0.25			2.51						1		
[a]Mn	μg/L	11			10.6			29						7.7		
[a]Cr	μg/L	33.1			43.6			83.9						8.3		
[a]Zn	μg/L	4.5			6.2			26.9						11		
pH		7.1	7.1	7.1	7.2	7.5	6.9	7.2	7.6	6.8	7.5	7.7	7.4	7.4	7.9	6.9
SAR		5.9	6.0	5.7	8.0	12.0	6.1	9.1	11.0	7.7	23.6	32.0	13.0	40	45	35

[a]Data are adapted from McBeth et al. (2003)
[b]Data are adapted from Ruckelshaus Institute (2005)
[c]Data are adapted from Jackson and Reddy (2007)

Based on reviewed data, the primary constituents present in PRB CBM waters are sodium and alkalinity. Sodium and alkalinity concentrations can range from 110 to 800 mg/L and 290 to 2320 mg/L as $CaCO_3$, respectively.

Classify Waters By Use

PRB CBM waters are most commonly discharged to a river or infiltration pond (Lamb 2006). These waters can also be put to other beneficial uses including: drinking water, livestock watering, irrigation, enhanced oil recovery, and cooling water for electric generation. Each use has specific guidelines which may be followed, and/or regulations which must be followed. Discharge to surface water is regulated by the Wyoming Department of Environmental Quality (WYDEQ). A range of discharge limits are outlined in Table 5-3. Data used to develop concentration ranges for constituent discharge, were found by reviewing numerous Wyoming Pollutant Discharge Elimination System (WYPDES) permits (WYPDES 2006). Discharge points from the WYPDES permits were located on a USGS map which has the various watersheds of the PRB delineated on it. The data collected from the WYPDES permits did not appear to have significant differences from watershed to watershed. However, new watershed based permitting requirements are in the process of becoming law (WYDEQ 2007).

PRB CBM waters may be used for drinking water (municipal or bottled). The United States Environmental Protection Agency (EPA) has set standards for some constituent concentrations if a water is used as a source of drinking water. The Maximum Contaminant Level (MCL) is the highest allowable constituent concentration for water and is enforced by federal law. A secondary MCL is a guideline set by the EPA that is not enforced by law. The World Health Organization (WHO) has also set guidelines for drinking water (WHO recommended standards) which are not enforced by law. Both secondary MCLs and WHO recommended standards are guidelines that prevent aesthetic or odor problems from being present in drinking water (EPA 2006, WHO 2006). Drinking water standards and recommendations are outlined in Table 5-4.

Table 5-3: Constituent Limits for Discharging PRB CBM waters (WYPDES 2006).

Constituent	Units	High[1]	Low[2]
Specific Conductance	µS/cm	7500	465
Total Dissolved Solids	mg/L	5000	310
F^-	µg/L	4000	2000
Cl^-	mg/L	230	46
SO_4^{2-}	mg/L	3000	412
NH_4^+	mg/L	5	0.5
Na^+	mg/L	350	270
Ba^{2+}	µg/L	1800	1800
Fe	µg/L	1000	125
Al	µg/L	750	490
As	µg/L	150	3.1
Cu	µg/L	13.2	8.6
Mn	µg/L	820	629
Zn	µg/L	97	90
Radium 226	pCi/l	60	1
pH		9	6.5
SAR		24	10

[1]High = the highest value permitted in the discharge permits sampled at WYPDES (2006)
[2]Low = the lowest value that was permitted in the discharge permits sampled in WYPDES (2006).

PRB CBM waters have been and are being used for livestock watering and irrigation. Recommended constituent concentrations for both of these uses have been developed by Ayers and Westcot (1994). A key issue with using PRB CBM waters for irrigation is sodium adsorption ratios (SAR). SAR values above the recommendations may cause clay expansion of soils, making soils unusable to grow crops (Ayers and Westcot 1994).

Enhanced oil recovery (EOR) and cooling water for energy generation are two other possible uses for PRB CBM waters. Enhanced oil recovery is the process of pumping water into an underground geologic feature that contains oil for the purpose of recovering oil. The water requirements for this use have been developed by Royce et al. (1984). Royce et al. (1984) found that the water characteristics for EOR are a range of TDS concentrations and total hardness concentrations between 10,000 – 150,000 mg/L and 1 – 5,000 mg/L, respectively. Xie (2007) who is researching the use of PRB CBM waters for EOR stated that the water characteristics for EOR are flexible and depend primarily on the geologic formation from which oil will be extracted. Xie (2007) recommended TDS concentrations be less than 4000 mg/L for EOR.

CBM waters may also be used as cooling water for energy generation. Very pure water (TDS < 1) is required for this use to prevent corrosion and precipitate formation (Bueker 1997).The required water chemistry for this use is outlined in Table 5-4. These data have been adapted from Bueker (1997). PRB CBM waters are currently not being used as cooling water.

<u>Suitable Treatment Technologies</u>

Analysis of CBM waters and the current use requirements show that the primary constituent that must be removed is sodium. Water treatment technologies used to do this are generally termed demineralization technologies. A number of demineralization technologies can treat CBM produced waters including: electrodialysis (ED), electrodialysis reversal (EDR), high efficiency electro-pressure membranes (HEEPM™), electrodeionization, capacitive deionization, advanced zeolites, constructed wetlands, rapid spray evaporation, and several reverse osmosis (RO) and ion exchange (IX) configurations. Currently, only two of these technologies, reverse osmosis and ion exchange, are being used to treat PRB CBM water. Four of these demineralization technologies (IX, RO, EDR, and HEEPM) were investigated in detail. An overview is provided below. For more details, the reader is directed to Sajtar (2008).

Pretreatment is required to remove constituents that may be harmful to the demineralization technology or unsafe. Methane, iron and/or alkalinity are typically the constituents that should be removed during pretreatment. Table 5-5 outlines different pretreatments that may be required for selected demineralization technologies.

Equalization storage is required for all technologies to provide a uniform water flow rate and relatively consistent influent water concentrations to the demineralization technology. Equalization storage volume is dependent on the water flow rate to the facility, and is assumed to be equal to the daily water volume to the facility (Beagle 2007). This allows for continuous water treatment if CBM wells are temporarily shut down or other problems are encountered.

Table 5-4: Constituent limits for water uses

Constituent	Units	Drinking water High[a]	Low[b]	Livestock[c]	Irrigation[c]	Cooling High	Low
Specific Conductance	μS/cm	1661*	801*	5000	3000	5400	80
Total Dissolved Solids	mg/L	500		2000	2000	1	0.1
Dissolved Fluoride	μg/L	4000	2000				
Chlorides	mg/L	250[b]			1064	0.33	0.003
Sulfates	mg/L	250[b]			1920	0.33	0.003
Br (regulated BrO$_3$)	μg/L	10	10				
Alkalinity (as CaCO$_3$)	mg/L	216*	104*		510	350	100
Nitrate as N	mg/L	10	10	100	10		
Nitrite as N	mg/L	1	1	10			
Ca^{2+}	mg/L	300*	30*		800	150	0
K	mg/L				2		
Mg^{2+}	mg/L	300*	10*	400	122	150	0
Na (Dissolved Sodium)	mg/L	200[b]		4370	920	3.3	0.27
Ba (Total Barium)	μg/L	2000	2000	100			
Fe (Dissolved Iron)	μg/L	300[b]				100	10
Si	mg/L					150	0.01
Sr	mg/L						
Al	μg/L	200[b]		5000			
As	μg/L	10	0	200			
Se	μg/L	50	50	50			
B	μg/L			5000	2000		
Cu	μg/L	1300	1000	500		50	10
Mo	μg/L						
Mn	μg/L	50[b]		50			
Cr	μg/L	100	100	1000			
Zn	μg/L	5000*		2400			
Total Radium 226	pCi/l	5	5				
pH		8.5*	6.5*		8.5 - 6	10.5	8.3
Sodium Adsorption Ratio					15		

[a] Constituent value is USEPA MCL, unless otherwise noted
[b] Constituent value is either USEPA Secondary Standard or WHO recommended standard, unless otherwise noted
[c] Ayers and Westcot (1994)
[d] Bueker (1997)
* Recommendation or solubility limit

Table 5-5: Pretreatment required for selected technologies.

Technology	Methane	Iron	Alkalinity
Ion Exchange	x		
Reverse Osmosis	x	x	x
Electrodialysis	x	x	
HEEPM	x	x	x

Reverse osmosis (RO) is a demineralization technology that removes constituents from water by forcing water through a semi-permeable membrane. After pretreatment, the water is pressurized with high pressure pumps to a pressure greater than the osmotic pressure of the water, 15-25 bar for brackish water and 54-80 bar for seawater (Miller 2003). The water is then forced through a semi-permeable membrane that rejects a percentage of the salts in the feed solution. Rejected salts are then removed from the system in a brine, and the cleaned water is discharged or stored for other uses.

The chemical rejection efficiency for reverse osmosis depends primarily on the membrane being used (Yoon and Lueptow 2005, Dow 2005) but typically is greater than 95% for most constituents. Water recovery for RO is a function of several variables. The type of membrane used, feed pressure, number of membranes used in series (stages), and feed water characteristics all have an impact on the water recovery.

Ion exchange is the process of exchanging ions that are on an insoluble exchange material for ions that are dissolved in solution (Metcalf and Eddy 2003). This process is an adsorption phenomenon where the mechanism for adsorption is primarily electrostatic (Weber and DiGiano 1996). This process has been used in water and wastewater treatment for: demineralization, desalting, hardness removal, nutrient removal, and in the recovery of valuable waste products (Reynolds 1982, Weber and DiGiano 1996).

Ion exchange is generally performed in a vessel containing ion exchange material (referred to as resin unless otherwise noted). This process continues until the ion exchange material reaches its capacity (exhaustion or breakthrough) at which point the ion exchange material must be regenerated. Regeneration is performed by contacting the resin with a solution which contains the original ion, regenerant (Reynolds 1982). The regenerant typically contains a high (1-10% by weight) concentration of the original ion to ensure that the resin is restored to its original state (Wachinski 2006). For sodium removal, the regenerant solution must contain hydrogen ions because hydrogen ions have a lower selectivity than sodium ions, therefore, an acid is used, typically hydrochloric or sulfuric acid.

Water can contact the resin in four different configurations. Different water resin contacting techniques include: 1) batch, 2) fixed bed, 3) fluidized bed (Wachinski 2006), and 4) moving bed (Drake 2007). Batch mode ion exchange works well for laboratory testing of resin when performing isotherms, but is no longer employed beyond the lab (Wachinski 2006). Batch ion exchange was attempted at several locations in the PRB with zeolites, but was soon disbanded due to effluent requirements not being met (Lamb 2006).

During fixed bed ion exchange the resin bed does not move during the service step while during fluidized bed ion exchange the upward flow of water causes the resin bed to become fluidized (Wachinski 2006). In the moving bed configuration, the resin moves with the water to achieve a specified ion removal. A moving bed can have flow regimes that exhibit elements of fluidization, slip flow and elutriation (Drake 2007).

There are currently four ion exchange vendors in the PRB that are treating CBM water. These vendors include: EMIT Water Discharge Technology, Rohm and Haas Company, Catalyx Fluid Solutions Inc., and Drake Water Technology, LLC.

Electrodialysis (ED) is an electrochemical separation process in which ions are transferred through semi-permeable, ion-selective, charged membranes by means of an electrical potential difference (Schoeman and Thompson, 1996). Ion selective membranes allow only anions or cations to cross them and can become even more selective when increasing or decreasing the pore sizes in the membrane.

ED works by applying an electrical potential between two electrodes. The resulting current causes cations to migrate toward the negative electrode and anions to migrate toward the positive electrode. As the ions migrate toward their respective electrodes, the cation selective membrane allows cations to pass through the cation selective membrane, and the anion selective membrane allows anions to pass through the anion selective membrane, generating a concentrate stream. The ions do not diffuse back through the membrane because the current will not allow the ion to move against it.

Electrodialysis reversal (EDR) is the most commonly used ED configuration in water treatment (Reahl, 2006). EDR removes constituents from the water in the same manner as ED except the polarity of the stack is reversed every ten to fifteen minutes (Schoeman and Thompson 1996) to remove solids that may form on the membranes during normal operation.

The chemical rejection efficiency of an ED/EDR system is dependent on the number of stages operated in series, the membrane type, the feed TDS of the water, and the current applied (electrical potential across the stack). All of these variables have an impact on the effluent ion concentrations and vary from facility to facility.

High Efficiency Electro-Pressure Membranes (HEEPM) is a patent pending technology marketed by EET Corporation. This technology combines electrodialysis and reverse osmosis. After pretreatment, produced water is treated with electrodialysis then reverse osmosis. Electrodialysis is used to reduce the ion load to reverse osmosis, and is also used to treat the brine stream generated from reverse osmosis (EET 2006).

This process has been used for water flows ranging from 1,000 gpd to 10 mgd, and is adaptable to a wide range of influent TDS concentrations. A benefit to this process is higher water recovery than is possible with RO alone, with a smaller system size than is required for ED alone (Sferrazza, 2006). High recovery is achieved by recycling RO residuals through the electrodialysis process. This concentrates the brine which results in less brine production. The brine is removed from the system during electrodialysis.

All of the selected water treatment technologies generate a waste stream as a result of removing constituents from water. This waste stream is generally termed brine. The brine contains all of the constituents that were removed from the water and as a result must be managed in a manner that will not release these constituents into the environment.

Two brine management techniques are currently used in the PRB. These include deep well injection and brine evaporation ponds (Lamb 2006). Other techniques that may be used to manage brine in the PRB include: evaporation crystallization, bipolar electrodialysis, and membrane distillation. These processes were considered in the toolbox.

<u>Capital and Operating Costs</u>

Capital and operating costs were determined from the literature and through discussions with vendors. The details of this data collection and analysis are presented in Sajtar (2008).

<u>Constructing the Toolbox</u>

The Coalbed Methane Demineralization Treatment Cost (CBM-DTC) Toolbox was constructed in Visual Basic with the user interface being Excel based. The presence of visual basic macros are identified by a series of buttons located though out the spreadsheet. To use the toolbox the user must answer a series of questions by entering an answer in the adjacent cell. Then to run a specific macro the user must hit enter then click the mouse on the necessary button. The results will then be displayed in the output portion of the spreadsheet.

Default influent and effluent water characteristics data were embedded into the toolbox for users who do not know these parameters. The user may select and use these data when running analyses by answering a series of questions at the top of the spreadsheet.

Each demineralization technology was given its own button. Technologies include: reverse osmosis (RO), electrodialysis reversal (EDR), high efficiency electro-pressure membranes (HEEPM), ion exchange with hydrochloric acid regeneration (IX HCl), and ion exchange with sulfuric acid regeneration (IX H_2SO_4).

The user has the option, but is not required to, input some parameters that may be important to the costs associated with a technology. Optional user input includes: electrical cost ($/kW-hr), sulfuric acid cost ($/ton), hydrochloric acid cost ($/ton), facility life (yrs), ion exchange run time (hrs), and brine disposal cost ($/bbl of brine). If the user does not input values for these parameters, default values will be used.

The toolbox output appears below the toolbox input on the spreadsheet. Toolbox output includes: treated water, blended water and brine concentrations; feed, bypass, brine and final flow rate; itemized operating costs, capital costs, and overall treatment cost in $/bbl of water entering the facility.

Other output is displayed with input data. These output include a column that specifies if the water must be treated to meet an effluent requirement for each constituent. Unknown influent concentration approximations and unspecified effluent concentrations are output as well. The toolbox calculates the treated water constituent concentrations based on the technology's treatment capabilities and the influent water concentrations. The final treated water fraction is determined for each constituent from the treated water concentrations and the desired effluent concentrations. The limiting constituent (constituent that leads to the highest final treated water fraction) or constituent for which the water is being blended to meet a desired effluent concentration is then output.

With the final treated water fraction known, flow rates are determined. The feed and brine flow rates are determined with the technology's water recovery rate and other flow rates. The flows output include: treated water flow rate, bypass water flow rate, feed flow rate, brine flow rate, final flow rate, and initial treated fraction. Pretreatment residual flow is neglected.

Treatment costs are determined based on the feed flow rate. Amortized treatment costs are output in both dollars per year and dollars per barrel of water entering the facility. Costs that are output include: electrical, labor, chemical (which includes alkalinity removal), membrane replacement, resin replacement, iron removal pretreatment, total operating, total capital and total cost per barrel of water entering the facility. The capital cost per bbl of water entering the facility is amortized assuming straight line depreciation over the lifetime of the facility.

Brine disposal / management costs are calculated separately from treatment costs. After the user has selected a treatment technology, a brine management option must be selected otherwise the brine management cost will not be included in the total treatment cost. A brine management option is selected by clicking one of the buttons under "Click to Select Brine Management". The user has the option of selecting deep well injection, evaporation with crystallization, or evaporation pond brine management.

There are optional user inputs for brine management. These are located at the top right of the spreadsheet. Optional inputs include: deep well injection cost ($/bbl of brine), evaporation rate (ft/yr), evaporation pond unit cost ($/ft^2), brine facility life (yrs), and electrical cost ($/kW-hr). Default values may also be used.

Once a brine management option is selected (after a treatment technology has been selected) the toolbox calculates the total cost to treat the water entering the facility. This is output below the technology and brine output.

The toolbox also calculates different parameters for the brine management option selected. The cost per bbl of brine ($/bbl) and cost per bbl of water entering the facility ($/bbl) is the only output for deep well injection. Evaporation pond output includes: the required evaporative area (ft^2), the pond depth (assumed to be 1.5 ft (Mickley 2001)), the evaporation rate (bbl/yr), operating cost ($/bbl of brine), capital cost ($), total cost per bbl of brine ($/bbl) and brine management cost per bbl of water entering the facility ($/bbl). Evaporation with crystallization output includes: evaporator and crystallizer capital cost ($), and operating and maintenance cost

($/bbl), in addition to, the total cost per bbl of brine ($/bbl) and brine cost per bbl of water entering the facility ($/bbl).

<u>Validating the Toolbox</u>

The toolbox was reviewed by CBM producers, researchers and regulators to ensure user friendliness and result accuracy. Selected reviewers were sent the CBM-DTC Toolbox, user's manual and a short questionnaire via email on two separate occasions (August 16, 2007 and October 2, 2007). The first reviews (August 16, 2007) involved only researchers at the University of Wyoming. Twenty three CBM researchers working at UW were sent the above items via email and asked to reply with any questions and/or comments they had pertaining to the toolbox. Comments included minor errors such as typos and other issues pertaining to the clarity of some toolbox user input. These issues were resolved and the second set of reviews was conducted.

The second set of reviews (October 2, 2007) involved CBM producers and regulators. These reviews were conducted to allow the target user community (producers and regulators) to offer comments and provide actual treatment costs for toolbox validation; however, no actual treatment costs were provided. The above items were sent to twenty three producers and/or regulators familiar with PRB CBM water. The result was 17% of the recipients responding to the questionnaire.

Results and Discussion:

The principle result of this task was the production of the CBM-DTC toolbox. The toolbox and User's Manual are available to the user community at: ftp://ftp.wygisc.uwyo.edu/pub/clearinghouse/general/cbm_dtc_toolbox.zip. The results and discussion that follow arise from use of the toolbox by the researchers to examine specific issues. Additional information is presented in Sajtar (2008).

<u>Sensitivity Analysis</u>

Sensitivity analysis was used to determine which variable or variables have the largest and smallest effect on the toolbox's results. The sensitivity of a technology to a parameter that may change, such as the unit price of electricity, may help the user determine with more certainty what technology to choose to treat PRB CBM waters.

The factors or variables that were examined included the following common variables for all technologies examined: unit cost of electricity, facility life, brine disposal cost, influent flow rate (Q_i) and sodium removed. Technology specific factors included operating and maintenance replacement costs for IX resin, RO membranes, EDR membranes, and HEEPM membranes. Acid cost was the final factor included in analysis.

The sodium removed factor analysis was performed by holding the influent water constituent concentrations constant for all analyses with the sodium and total dissolved solids concentrations equal to 600 mg/L and 1074 mg/L, respectively. The effluent concentration for sodium was then

set at 100 mg/L for 500 mg/L of sodium removed, and 500 mg/L for 100 mg/L of sodium removed. Performing the analysis in this manner held all influent concentrations constant, and forced sodium to be the limiting constituent.

After performing the simulation experiments by running the toolbox 64 times for all 2^{7-1} factorial designs and 32 times for 2^{6-1} factorial designs the responses (total treatment cost, \$/bbl) were entered into Design Expert software (Stat-Ease 2007) to perform an analysis of variance (ANOVA). The first results output were the sum of squares and the relative percent contribution of each factor to the total sum of squares. The factor with the largest percent contribution to the total sum of squares has the largest effect on the toolbox's response and vice versa (Montgomery 1997).

RO treatment cost is most sensitive to the amount of sodium removed with brine disposal cost the second most sensitive variable. Similarly, the IX treatment cost is most sensitive to the amount of sodium removed with acid cost the second most significant factor and brine disposal cost the third most significant factor. HEEPM treatment cost is also most sensitive to sodium removed. The next most significant factor for HEEPM is the cost of electricity, followed by facility life and influent flow rate.

Electrodialysis reversal treatment cost is most sensitive to facility life. This is due to capital costs accounting for most of the costs associated with EDR. The effect of the variable is also negative which means that if EDR is utilized the facility life should be maximized to minimize overall treatment cost. The second most sensitive variable for EDR is influent flow rate (Q_i). This factor also has a negative effect which means that the influent flow rate for an EDR facility should be maximized to minimize treatment costs. Other factors that EDR treatment costs are sensitive to include brine disposal cost, electrical cost and sodium removed.

Predicting Cost-Effective Technologies

To determine the impact of key variables on the total treatment cost (\$/bbl) for treating PRB CBM waters optional user inputs were changed one at a time for a total of seven scenarios (Table 5-6). The toolbox was then run with six different sodium removals (Table 5-7) per scenario. Sodium removed was selected as the performance parameter. Treatment cost (\$/bbl) versus sodium removed was then plotted for selected treatment technologies to determine to compare technologies. Selected results from these analyses are reported below. For the full results, see Sajtar (2008).

Scenario 2 provides a baseline for Scenarios 3-7 and the results are shown in Figure 5-1. IX H_2SO_4 is the most cost effective treatment technology for sodium removed < 540 mg/L. Above that, EDR becomes the most cost effective treatment technology. At sodium removals below 240 mg/L IX HCl is the next most cost effective technology (just above IX H_2SO_4). The contributions of the key variables to the total treatment cost for a specified sodium removal are summarized in Table 5-8.

Brine disposal cost has been shown to be significant with respect to the total treatment cost for all technologies. To determine how brine management/disposal cost affects crossover points, two brine disposal costs were examined ($1/bbl and $5/bbl of brine).

The Scenario 2 results (Figure 5-1) illustrate the treatment cost associated with a brine disposal cost of $5/bbl of brine (the default value). Figure 5-2 illustrates treatment costs when the brine disposal cost is reduced to $1 /bbl of brine. Most notably, the cross over point where EDR

Table 5-6: Scenarios Used to Evaluate Technology Costs and Cost Effectiveness. "x" and "y" equal the same value used in scenario 1 and 2, respectively.

Parameter	Units	Scenario						
		1	2	3	4	5	6	7
Treatment Facility Life	yrs	5	10	y	y	y	y	y
Influent Flow Rate	bbl/day	100,000	x	10,000	x	x	x	x
Brine Disposal	$/bbl brine	5	x	x	1	x	x	x
Electric Cost	$/kW-hr	0.07	x	x	x	0.21	x	x
HCl Cost	$/ton	225	x	x	x	x	135	x
H_2SO_4 Cost	$/ton	135	x	x	x	x	x	225

Table 5-7: Water Parameters Used to Evaluate Technology Costs and Cost Effectiveness. All units are mg/L.

User FTDS [a]	Calculated FTDS [b]	Feed Na [b]	Effluent Na [a]	Na Removed [c]
2500	2774	858	100	758
2000	2219	687	100	587
1500	1665	515	100	415
1000	1110	343	100	243
750	832	257	100	157
500	555	172	100	72

[a] Selected Input
[b] Determined by toolbox
[c] Feed Na – Effluent Na

becomes the most cost effective technology increased from approximately 540 mg/L of sodium removed to over 760 mg/L. This increase is because EDR generates much less brine than the other technologies making EDR less cost effective at lower brine disposal costs.

Also, RO is no longer the most costly treatment technology. This is because RO generates the most brine of all the technologies which makes RO treatment costs very sensitive to brine disposal cost. Brine disposal costs clearly influence what technology is the most cost effective.

The total treatment costs for all selected technologies, except IX, showed sensitivity to the cost of electricity. Two different electrical costs were examined, $0.07/kW-hr (Scenario 2, Figure 5-1) and $0.21/kW-hr (Scenario 5, Figure 5-3).

Increasing the cost of electricity increased all cross over points. Most notably, EDR does not become the most cost effective until the sodium removed is above 280 mg/L (versus IX HCl) and over 760 mg/L (versus IX H_2SO_4). Also, the RO, HEEPM and IX HCl lines have become nearly parallel as a result of increasing the cost of electricity.
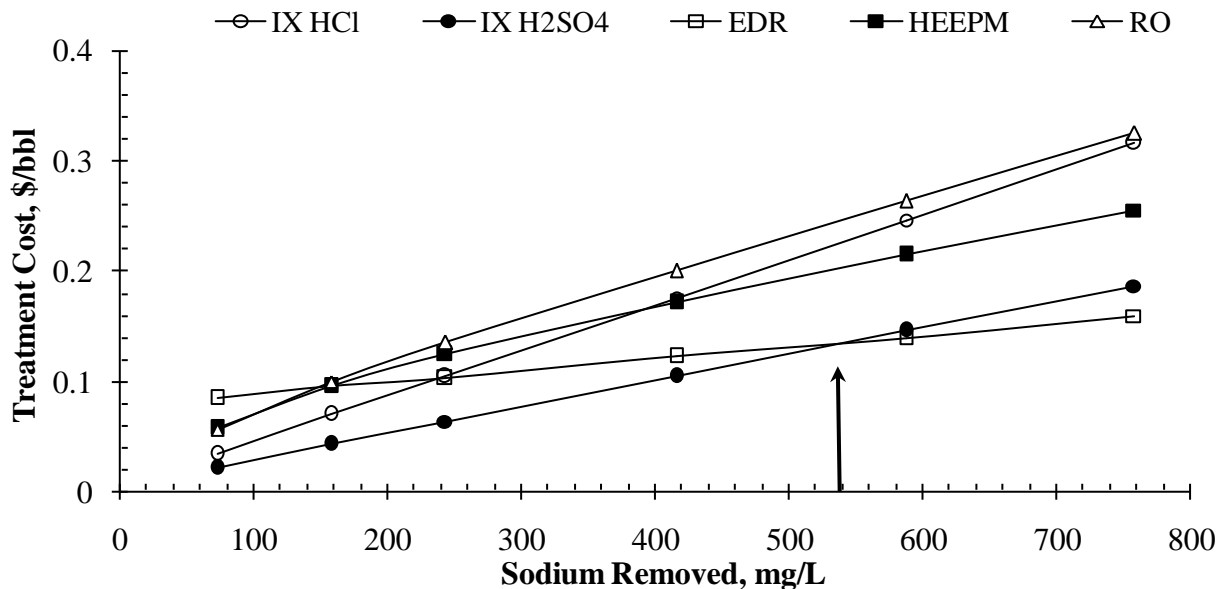
Figure 5-1: Scenario 2, facility life equal to 10 years, treatment cost vs. sodium removed (Refer to Table 5-6 for full Scenario description). Arrows represent crossover points discussed in the text.

Table 5-8: Scenario 2 Economic Parameter Percent Contribution to Total Treatment Cost for 243 mg/L Sodium Removed. (Refer to Table 5-6 for full Scenario description)

Parameter	IX HCl	IX H2SO4	EDR	HEEPM	RO
Capital	6%	11%	47%	20%	9%
Brine	32%	54%	20%	16%	46%
Electric	0.1%	0.1%	6.4%	27.0%	7.0%
Labor	1%	2%	17%	9%	7%
Chemical	56%	27%	1%	18%	16%
Parts	4%	6%	4%	7%	12%
Iron Pretreatment	0%	0%	5%	3%	3%
Total	100%	100%	100%	100%	100%
Total Cost ($/bbl)	0.104	0.063	0.102	0.124	0.135

Table 5-9 illustrates the percent contribution of each cost component to the overall treatment cost, respectively, for sodium removed equal to 243 mg/L. The increase in electrical cost caused

the electrical cost component (and percent contribution) to increase for all technologies. Most notably, the electrical component for HEEPM and RO increased from $0.035 to $0.10/bbl and $0.01 to $0.03/bbl, respectively. However, electrical cost does not appear to have a large influence on overall technology cost effectiveness because IX is not an energy intensive process.
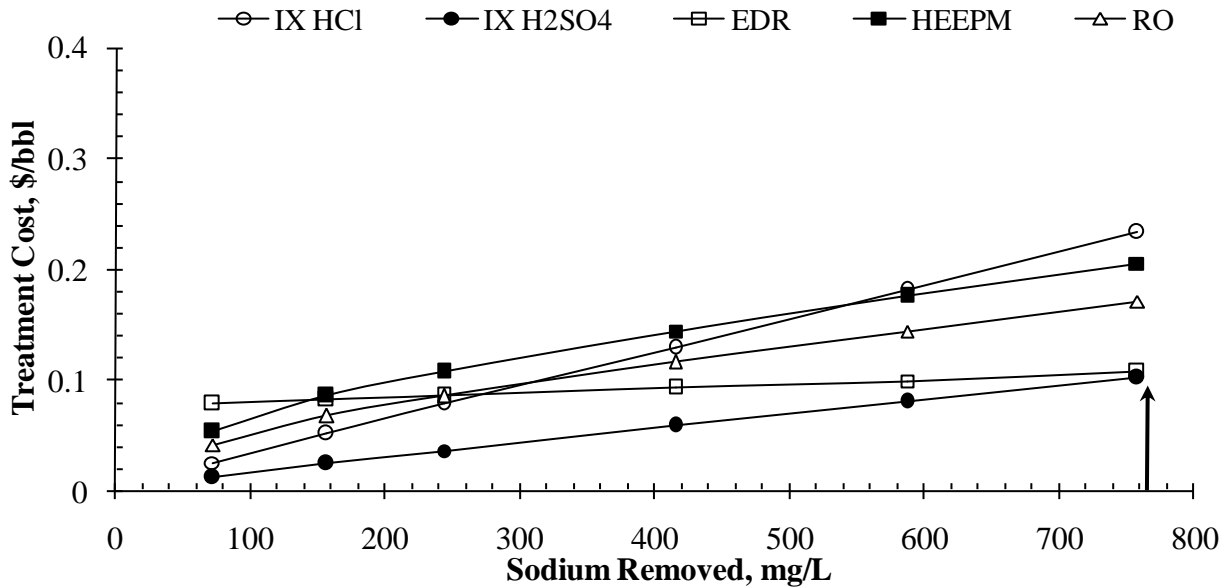
Figure 5-2: Scenario 4, brine disposal cost equal to $1/bbl of brine, treatment cost vs. sodium removed (Refer to Table 5-6 for full Scenario description). Arrows represent crossover points discussed in the text.
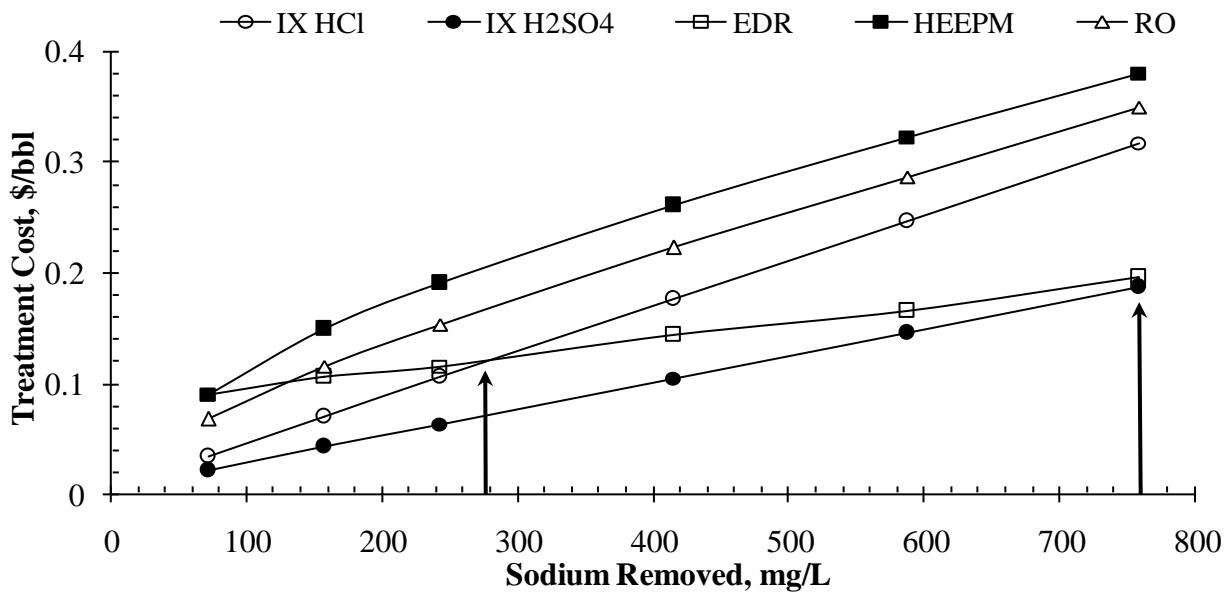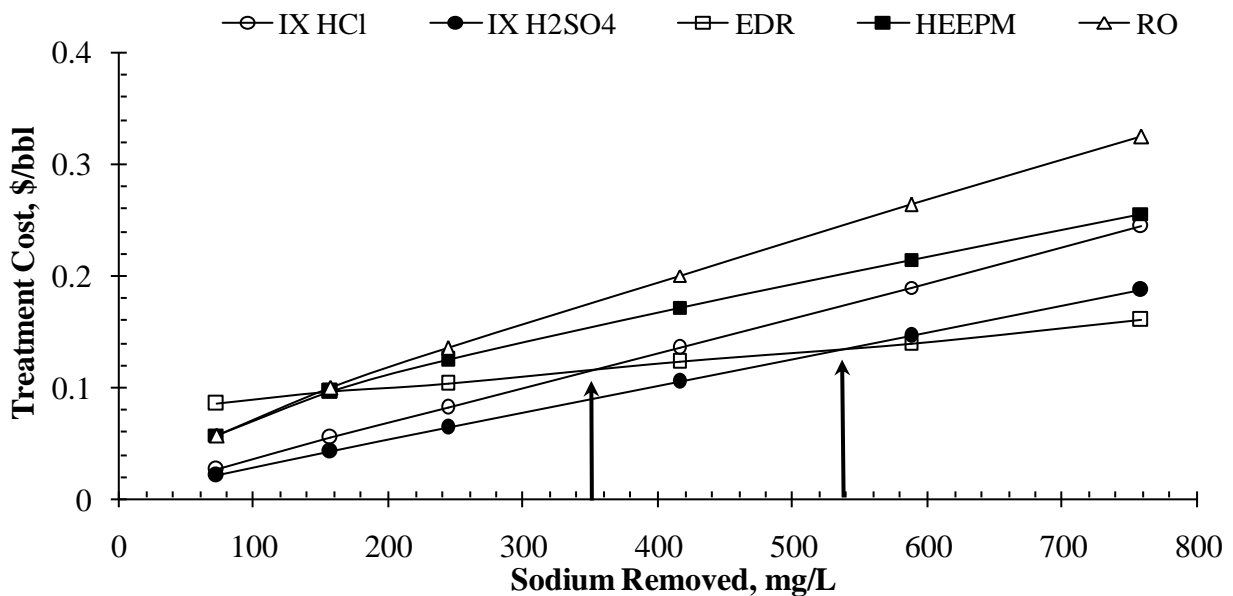
Figure 5-3: Scenario 5, electrical cost equal to $0.21/kW-hr, treatment cost vs. sodium removed (Refer to Table 5-6 for full Scenario description). Arrows represent crossover points discussed in the text.

Table 5-9: Scenario 5 Economic Parameter Percent Contribution to Total Treatment Cost for 243 mg/L Sodium Removed. (Refer to Table 5-6 for full Scenario description)

Parameter	IX HCl	IX H2SO4	EDR	HEEPM	RO
Capital	6%	11%	41%	13%	8%
Brine	32%	54%	18%	11%	40%
Electric	0.3%	0.4%	17%	52.6%	18.4%
Labor	1%	2%	15%	6%	6%
Chemical	56%	27%	1%	11%	14%
Parts	4%	6%	4%	5%	11%
Iron Pretreatment	0%	0%	4%	2%	2%
Total	100%	100%	100%	100%	100%
Total Cost ($/bbl)	0.105	0.063	0.106	0.190	0.153

Acid cost was the final factor examined. Two acid costs were selected for this analysis $135/ton and $225/ton (default values for hydrochloric acid and sulfuric acid). The results are illustrated in Figures 5-4 and 5-5.

When comparing results from Figures 5-4 and 5-5 crossover points change as a result of acid cost. The crossover points at the lower acid cost of $135/ton (Figure 5-4) shows EDR being the most cost effective when sodium removals are greater than 350 mg/L (IX HCl) and 540 mg/L (IX H$_2$SO$_4$). The higher acid cost of $225/ton illustrated in Figure 5-5 makes EDR the most cost effective treatment technology when greater than 235 mg/L (IX HCl) and 410 mg/L (IX H$_2$SO$_4$) of sodium are removed. Therefore the cost of acid does influence technology cost effectiveness.

As a result of increasing acid cost, the percent contribution of chemical cost increased for all technologies except EDR. EDR does not change because chemical/acid requirements are considered constant for this process.

The total treatment costs for all technologies from all scenarios at 243 mg/L of sodium removed are summarized in Table 5-10. Based on toolbox results, when treating PRB CBM waters the cost effectiveness of treatment technologies are influenced by optional user inputs. However, IX H_2SO_4 is the most cost effective technology up to the crossover point where EDR becomes the most cost effective (approximately 410 to 760 mg/L of sodium removed depending on the conditions). There are, however, possible safety concerns associated with IX H_2SO_4 which may make it necessary to select the next most cost effective technology when removing lower amounts of sodium, IX HCl or EDR.

Also, extra costs such as, pipelines to get the water to and from the facility, roads, equalization storage, water degassing, and profit to a consulting firm or treatment technology provider have not been accounted for. These costs have not been included due to their variability and the lack of data resulting from their proprietary nature. Therefore, it is strongly recommended that the producer get detailed treatment cost estimates prior to deciding what technology to utilize.

Figure 5-4: Scenario 6, acid cost equal to $135/ton, treatment cost vs. sodium removed (Refer to Table 5-6 for full Scenario description). Arrows represent crossover points discussed in the text.
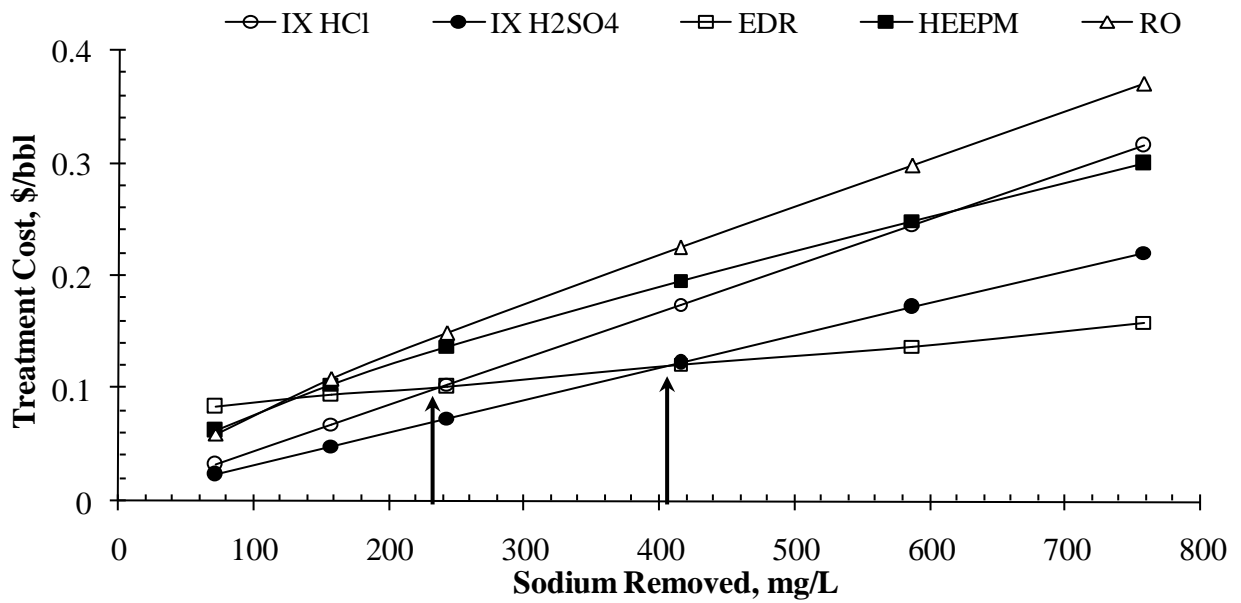
Figure 5-5: Scenario 7, acid cost equal to $225/ton, treatment cost vs. sodium removed (Refer to Table 5-6 for full Scenario description). Arrows represent crossover points discussed in the text.

Table 5-10: Total Treatment Costs for all scenarios at 243 mg/L of Sodium Removed. Refer to Table 5-6 for full scenario descriptions. Units are $/bbl of influent water.

Technology	Scenario						
	1	2	3	4	5	6	7
IX HCl	0.111	0.104	0.113	0.078	0.105	0.081	0.104
IX H2SO4	0.069	0.063	0.071	0.036	0.063	0.063	0.074
EDR	0.149	0.102	0.132	0.085	0.115	0.102	0.102
HEEPM	0.148	0.124	0.145	0.107	0.190	0.124	0.138
RO	0.147	0.135	0.143	0.085	0.153	0.135	0.149

Conclusions:

The CBM-DTC Toolbox makes it possible to compare five different demineralization technologies on an equal platform to determine preliminary treatment cost approximations, and facilitate initial technology selection. Results show that PRB CBM water treatment costs may range from $0.036/bbl to $0.190/bbl depending on the technology selected and the conditions (Table 5-10).

Sensitivity analyses have shown that treatment cost is directly impacted by the amount of sodium removed from the water (as the amount of sodium removed increases the treatment cost increases regardless of the technology selected). Also, if the limiting constituent for the process is not sodium the most cost effective technology may change. For example, if chloride or sulfate must be removed from the water to meet a discharge requirement, then cation exchange will not be able to treat the water to meet the requirement because chloride or sulfate cannot be removed from water via cation exchange. Sensitivity analyses also indicated that a treatment facility's flow rate and operational life should be maximized to decrease overall treatment cost.

Toolbox results have indicated that cation exchange is the most cost effective technology for treating PRB CBM waters when low amounts of sodium must be removed from the water. However, this result is attributed solely to the major anion in PRB CBM waters being bicarbonate (HCO_3^-). If sulfate or chloride, for example, were the major anion(s) in PRB CBM waters another technology, such as EDR, may become the most cost effective. This is attributed to both anion and cation exchange being required which will increase the treatment cost for ion exchange.

Based on the CBM-DTC Toolbox results a feasibility study of electrodialysis reversal treatment should be performed in the PRB through the use of a pilot scale EDR treatment plant. This may become more necessary in the future if brine disposal costs increase, which will make EDR treatment even more competitive versus ion exchange treatment technologies.

PRB CBM producers and vendors should also work toward decreasing brine management costs through all possible means including volume reduction and by-product generation/ utilization. Technologies that will aid in this task may include bipolar electrodialysis, membrane distillation, and evaporation with crystallization. Most notably, sodium sulfate or sodium chloride brines

generated in ion exchange processes may be converted into viable products such as sulfuric acid or hydrochloric acid through the use of bipolar ED.

The final recommendation is for PRB producers and treatment vendors to consider using renewable resources such as, solar, wind, and water (energy recovery turbines) to aid in powering water treatment operations. In theory after the initial capital investment these technologies may reduce overall treatment costs considerably, especially for energy intensive processes like reverse osmosis or electrodialysis reversal.

References:

Ayers, R.S. Westcot, D.W. 1994. Water Quality for Agriculture. Food and Agriculture Organization of the United Nations Rome, 1985 © Food and Agriculture Organization of the United Nations.

Beagle, D. 2007. EMIT Water Discharge Technology LLC. Personal Contact via email. LastCorrespondence: June 13, 2007.

Bueker, B. 1997. Power Plant Water Chemistry: A Practical Guide. PennWell Publishing Company.

Dow Chemical Company. Dow Liquid Separations: FILMTEC Reverse Osmosis Membranes Technical Manual July 2005.

Drake, R. 2007. Drake Water Technology, LLC. Personal Communication by email. Last Correspondence: February 22, 2007.

EET. 2006. EET Corporation, 3106 Roane State Hwy, Harriman, TN 37748. www.eetcorp.com.

Jackson, R.E. and Reddy, K.J. 2007. Geochemistry of CBNG produced water in Powder RiverBasin: Salinity and Sodicity. *Water, Air, and Soil Pollution* 184:49-61.

Jackson, R.E. and Reddy, K.J. 2007. Trace Element Chemistry of Coal Bed Natural Gas Produced Water in the Powder River Basin, Wyoming. *Environmental Science and Technology* 41:5953-5959.

Keith, K. Bauder, J. Wheaton, J. 2003. Coal Bed Methane: Frequently Asked Questions.

Lamb, D. 2006. Wyoming Department of Environmental Quality. Personal communication. Last Meeting: August 22, 2006.

McBeth, I.H. Reddy, K.J. Skinner, Q.D. 2003. Chemistry of trace elements in coalbed methane product water. *Water Research*. 37:884-890.

McBeth, I.H., K.J. Reddy, and Q.D. Skinner. 2003. Water chemistry of coalbed methane product water in three Wyoming watersheds. *Journal of American Water Resources Association*.39:575-585.

Metcalf & Eddy, Inc. 2003. Wastewater Engineering: Treatment and Reuse, 4th Edition. McGraw-Hill, Inc.

Mickley, M.C. 2001 Membrane Concentrate Disposal: Practices and Regulations, US Dept. of the Interior, Bureau of Reclamation, Agreement No. 98-FC-81-0054, Program report No. 69, September 2001.

Miller, J. E. 2003. Review of Water Resources and Desalination Technologies, Materials Chemistry Department Sandia National Laboratories, SAND 2003-0800.
Montgomery, D.C. 1997. Design and Analysis of Experiments 4th edition. John Wiley and Sons, Inc.

Montgomery, D.C. 1997. Design and Analysis of Experiments 4th edition. John Wiley and Sons, Inc.

Patz, M.J., K.J. Reddy, and Q.D. Skinner. 2004. Chemistry of coalbed methane discharge water interacting with semi-arid ephemeral stream channels. *Journal of American Water Resources Association*. 40:1247-1255.

Patz, M.J., K.J. Reddy, and Q.D. Skinner. 2006. Trace elements in coalbed methane discharge water interacting with semi-arid ephemeral stream channels. *Water, Air, and Soil Pollution*. 17:55-67.

Reahl, E.R. 2006. Half a Century of Desalination with Electrodialysis. General Electric Company, Technical Paper. TP1038EN 0603.

Reynolds, T.D. 1982. Unit Operations and Processes in Environmental Engineering. Brooks/Cole Engineering Division, Wadsworth, Inc.

Rice, C.A., Ellis, M.S., and Bullock, J.H., Jr., 2000 Water Produced with coalbed methane in the Powder River Basin, Wyoming: preliminary compositional data, USGS Open File-Report 00-372.

Royce, B., Kaplan, E., Garrell, M., and Geffen, T.M. 1984. Enhanced Oil Recovery Water Requirements, *Environmental Geochemistry and Health*, 6:44-53.

Ruckelshaus Institute of Environment and Natural Resources. 2005. Water Production from Coalbed Methane Development in Wyoming: A Summary of Quantity, Quality, and Management Options. December, 2005.

Sajtar, E.T. 2008. *Toolbox to Evaluate Treatment Technologies for PRB CBM Water*, M.S. Thesis, Department of Civil and Architectural Engineering, University of Wyoming.

Schoeman, J. J. Thompson, M.A. 1996. Chapter 12: Electrodialysis. Water Treatment Membrane Processes. Edited by: Mallevialle, J. Odendaal, P. E. Wiesner, M. R. American Water Works Association, American Water Works Association Research Foundation, Lyonnaise des Eaux, and Water Research Commission of South Africa.

Sferrazza, L. 2006. President EET Corporation. Personal contact via email. Last contact: October 10, 2006.

Stat-Ease, Inc. 2007. Design Expert Version 7.1.2
USEPA. 2006. United States Environmental Protection Agency.
http://www.epa.gov/safewater/mcl.html, Last visited: April 23, 2007.

Stearns, M. Tindall, J.A. Cronin, G. M. Friedel, M.J. and Bergquist, E. 2005 Effects of Coal-Bed Methane Discharge Waters on the Vegetation and Soil Ecosystem in Powder River Basin,

Soltanpour, P.N. and Follett, R.H. 1999. Soil Test Explanation, Colorado State Cooperative Extension Publication No. 0.502Wyoming, *Water Air and Soil Pollution*., 168:33-57.

Wachinski, A.M. 2006. Ion exchange Treatment for Water. American Water Works Association.

Weber, W.J. and DiGiano, F.A. 1996. Process Dynamics in Environmental Systems. John Wiley & Sons Inc.

Western Resources Project Final Report. 2005. Produced Groundwater Associated with Coalbed Natural Gas Production in the Powder River Basin. Wyoming State Geological Survey Report of Investigations No. 55.

WHO. 2006. World Health Organization.
http://www.who.int/water_sanitation_health/dwq/gdwq0506.pdf, Last visited: October 19, 2006.

WYDEQ. 2007. Wyoming Department of Environmental Quality.
http://deq.state.wy.us/wqd/index.asp, Last visited: April 21, 2007.

WYPDES. 2006. Wyoming Pollutant Discharge Elimination System website.
http://deq.state.wy.us/wqd/WYPDES_Permitting/WYPDES_PNs_and_appr_permits/Pages/issuedpermits.asp. Last visited: October 10, 2006.

Xie, X. 2007. Personal Contact via email. Last Correspondence: May 18, 2007

Yoon, Y. and Lueptow, R.M. 2005. Reverse Osmosis Membrane Rejection for Ersatz Space Mission Wastewaters, *Water Research*, 39:3298-3308.

Task 6 – Application of CBM Water to Improved Oil Recovery by Low Salinity Waterflooding in Wyoming

N. R. Morrow[6], X. Xie, and H. Pu

This task was to evaluate the potential of injecting water that is co-produced with coalbed methane (CBM) for improved oil recovery in Wyoming. Two subtasks were performed for this work: 1) survey of CBM water and oil reservoirs; 2) Laboratory tests of CBM water injection for improved oil recovery.

Coalbed methane (CBM) has become increasingly important due to rising energy prices. In order to produce CBM, large amounts of water must be produced to decrease the pressure of the coal seams and release the adsorbed methane. CBM water disposal has been a critical issue that impacts CBM development in Wyoming. Production of CBM water across all Wyoming coal fields could reach about 54.3 billion barrels if all of the recoverable CBM gas (31.7 tcf) from the projected reserves were produced over the coming decades (Ruckelshaus Institute, 2005). Table 6-1 lists the water production and injection for the past 3 years. The salinity of most of the CBM water in Wyoming ranges from 300 to 2500 ppm, the sodium adsorption ratio (SAR) is high, ranging from 5.6 to 69 with the mean SAR of 11.7 (Veil et al., 2004). Rice et al. (2000) also reported that 40% of water samples tested from the PRB showed SAR > 10. Usually it is desired that the water for irrigation and other agriculture uses has a SAR value of 8 or lower. Therefore the produced water has limited suitability for domestic and animal consumption or for agriculture. Currently the only economic way of disposal is by surface discharge, which has been contested due to environmental damage. Other problems involved with the extraction of such large volumes of groundwater include impacts on domestic water wells and natural springs, water rights, lowering of water tables, and groundwater recharge issues. Environmentally friendly and economically sound management of CBM water production is essential to all those issues.

Table 6-1: Water production and injection in PRB, Wyoming

Year	PRB CBM water production, MMBbl	State total CBM water production, MMBbl	State total water production, MMBbl	PRB water injection, MMBbl	State total water injection, MMBbl
2005	531	578.9	2130	0.619	856
2006	680	707.3	2280	0.977	2040
2007	519	581	1980	2.15	845

Data source: http://wogcc.state.wy.us

Subsurface disposal of CBM water has to be categorized under the restrictive Class V injection. The application of the water injection to improve oil recovery was proposed and investigated. Such application can be permitted as Class II injection which is more advantageous economically than Class V injection. Use of CBM water for oil recovery will also reduce the

---

[6] Department of Chemical and Petroleum Engineering. University of Wyoming, Laramie, WY. email: morrownr@uwyo.edu

depletion of fresh water aquifers currently used in Wyoming as sources of injection water and can provide value-added disposal.

Numerous studies indicate that injection of water with salinity lower than 4000 ppm can increase oil production by 6 to 12% of original oil in place, both at the outset of development of a reservoir and at the mature stage of waterflooding. These studies include laboratory waterflooding tests, full reservoir conditions testing, pilot tests and observations on field-wide performance. Based on these studies, the Tensleep sandstone cores from Teapot Dome field have been tested for response to low salinity CBM waterflooding to determine the potential of use of CBM water for improved oil recovery. Crude oil from the Minnelusa formation (an Aeolian sandstone comparable to Tensleep) was used as the test oil. A synthetic CBM brine based on the CBM water composition from a field (Operator WyoDak) which represents the average salinity of PRB CBM water was used in the waterflood tests. The results of this study are of practical interest for the following reasons: (1) The uniqueness of the Tensleep rock mineralogy; (2) The significant oil production from Tensleep formation in Wyoming; and (3) The abundance of low salinity CBM water that needs to be disposed.

Preliminary laboratory test indicated that low salinity CBM water injection can improve oil recovery of the Tensleep rock by 4 to 10%, providing an encouraging possibility for value added disposal of CBM water. Another advantage is that oil wells and CBM wells/CBM water outfalls in the PRB are close to each other, making the transportation of CBM water economically viable. The low salinity CBM water can be a valuable resource for improved oil recovery. If applicable, it can help the CBM industry tremendously in Wyoming.

Methods:

The CBM water and oil reservoir survey was to evaluate the potential of low salinity water injection to specific oil fields for improved recovery. Data mining sources included the US Geological Survey (USGS), the Wyoming Oil and Gas Conservation Commission (WOGCC), the Wyoming Department of Environmental Quality (WYDEQ), and other related sources. The following data have been collected and entered into a Microsoft Access database:

- Map of oil fields in Wyoming (Fig. 6-1)
- Oil and gas pipeline distribution in Wyoming (Fig. 6-2)
- Location of oil and gas wells, CBM wells and CBM water outfalls (Figs. 6-3a and 6-3b)
- Oil and gas and water production history data
- Oil reservoir petrophysical properties, crude oil properties, and drive mechanisms
- Water ion composition and salinity from each CBM water outfall

The database provides a useful tool for evaluation of using CBM water from a particular outfall for a potential oil field. Specific oil reservoir information from the PRB, including lithology, porosity, permeability, formation water salinity, and oil production data, has been collected and is listed in a Excel file. Both database and the Excel file are available from the report authors.

The most important step was to test for improved oil recovery by CBM water injection. Laboratory core flood tests using Wyoming Tensleep rock/crude oil and CBM water were performed to validate the technique.
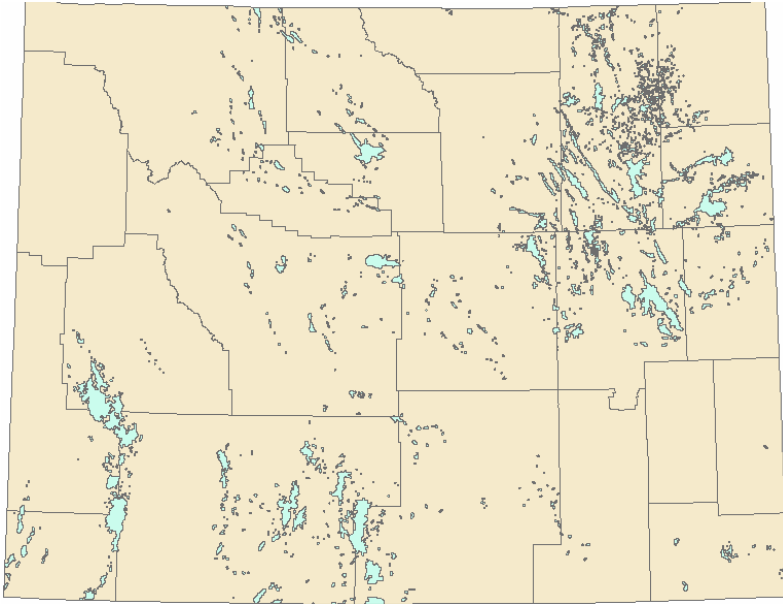
Figure 6-1: Oil fields in Wyoming (up to December 2006).
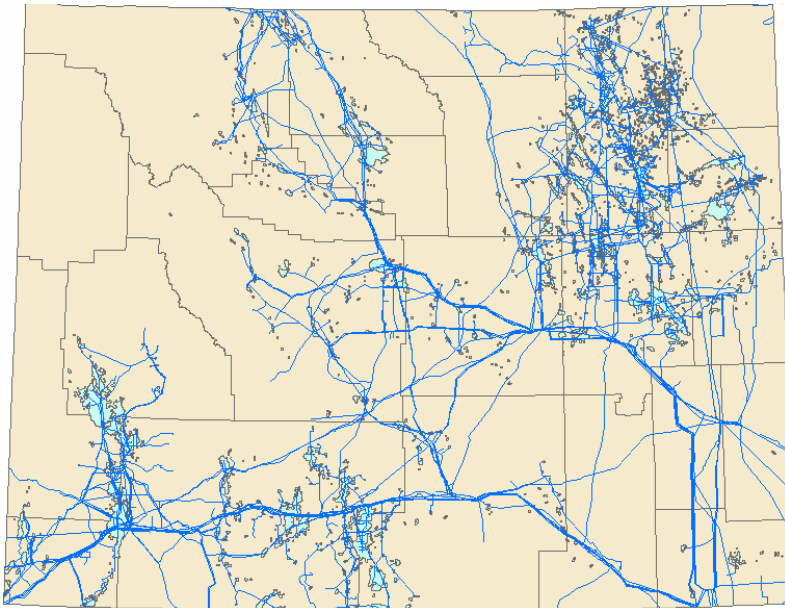
Figure 6-2: Oil and gas pipeline distribution along with oil fields (up to December 2006).
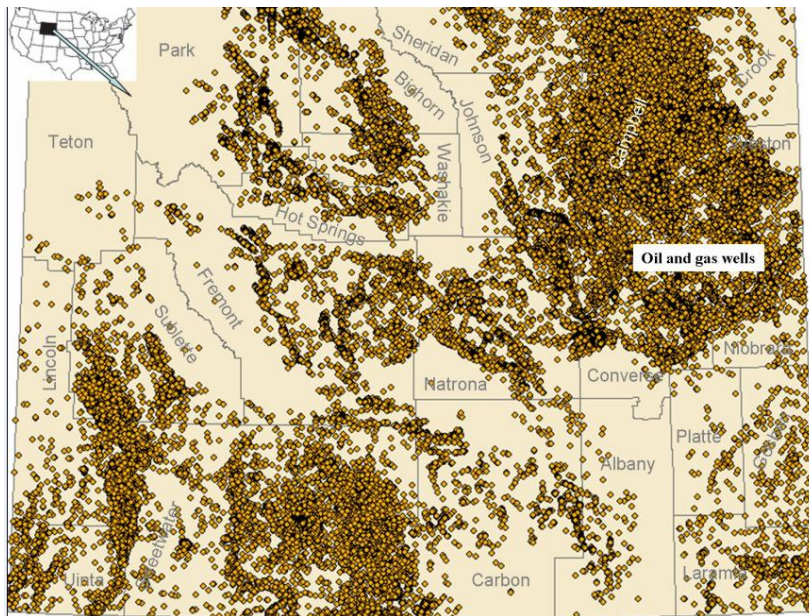

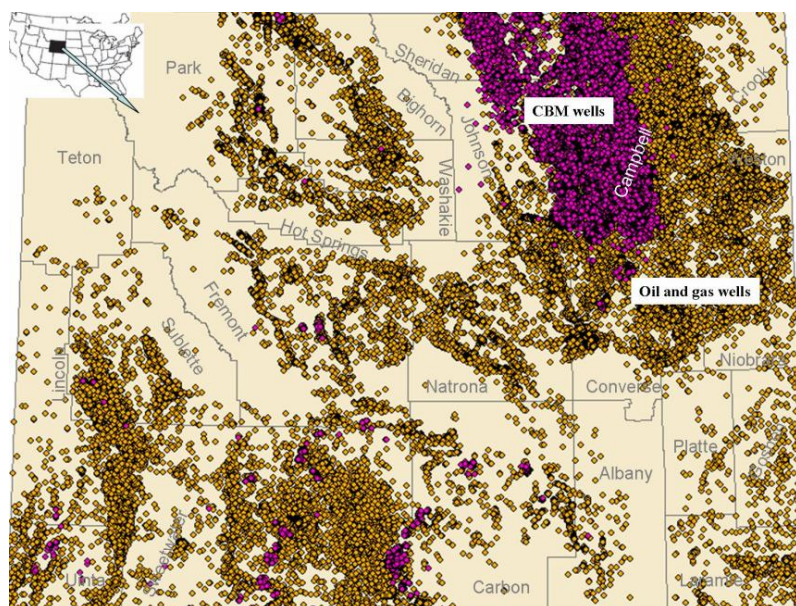**Figure 6-3a: Oil and gas wells in Wyoming (up to December 2006).**

Figure 6-3b: CBNG wells along with oil and gas wells (up to December 2006).

Laboratory tests of waterflooding with CBM water to improve oil recovery from Ten Sleep
Sandstones

Numerous laboratory tests and field tests show that oil recovery by injection of low salinity brine
(up to 4000 ppm) can be increased in both secondary mode (at the outset of development of a
reservoir) and tertiary mode (extension of field life at a mature stage of waterflooding) (Tang and
Morrow 1997, Webb et al. 2004, Zhang and Morrow 2006, Zhang et al. 2007). Webb et al.
(2005) reported increased oil recovery ranging from 2 to 18% in tertiary mode. Laboratory tests
of secondary mode flooding show oil recovery increases of up to 60% compared to high salinity
flooding (Tang and Morrow 2002). Results of pilot tests on watered out fields in Alaska were in
good agreement with laboratory observations. Furthermore, unexpectedly high field wide
recoveries have been ascribed to injection of low salinity water. British Petroleum (BP) has
reported that the low salinity process has the potential to add about 1 billion barrels to BP's
reserves worldwide over the next 20 years.

Almost all of the low salinity waterflooding tests have been performed on sandstones so far. The
successful cases for improved oil recovery appeared to be sandstones containing kaolinite. The
possible mechanisms include the effect of rock surface wettability alteration, fines migration, ion
exchange, osmotic pressure, interfacial phenomena induced by snap-off emulsion, etc. However,
the mechanisms of increased oil recovery by low salinity flooding are not yet understood,
particularly with respect to why the response of some reservoir cores is much better than for
others. The potential for application of low salinity flooding to a specific reservoir requires tests
on cores/crude oil/brine obtained from that reservoir.

Materials

To test the effect of CBM water injection on improved oil recovery, three reservoir rock samples
from Tensleep formation, Teapot Dome Field of Natrona County, Wyoming were obtained. Thin

section analysis and SEM pictures indicated that the reservoir sandstone rock was composed of quartz, feldspar, cement, with very small amounts of clay and small dolomite crystals of about 10 mm in size and had good sorting. The dolomite crystals are in the pores and on the quartz surfaces (Figs. 6-4a, b, c). Micro-CT scanning also showed the abundance of dolomite particles. The permeability and porosity of the core samples were about 40 md and 14% respectively (Table 6-2). Crude oil from the Tensleep formation was used as the test oil, the properties are shown in Table 6-3. Synthetic brine based on the analysis of a water sample from the Minnelusa formation was used as the reservoir brine, designated as MRB. The composition is listed in Table 6-4. Synthetic CBM water used in the laboratory was based on the water composition of CBM well Echo 15-19 (Operator WyoDak) which represented the average salinity of CBM water in the PRB (Table 6-4). The bicarbonate component was excluded.
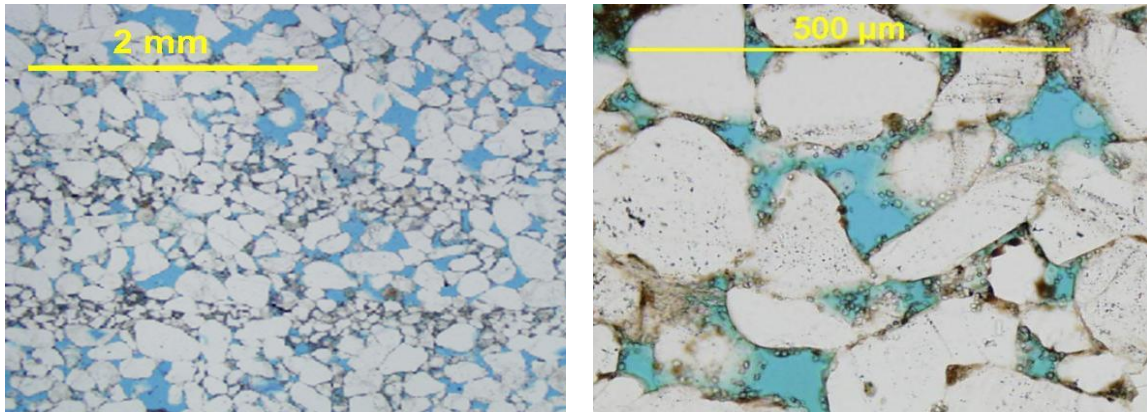
Figure 6-4a: Thin sections of Tensleep cores from Teapot Dome Field.
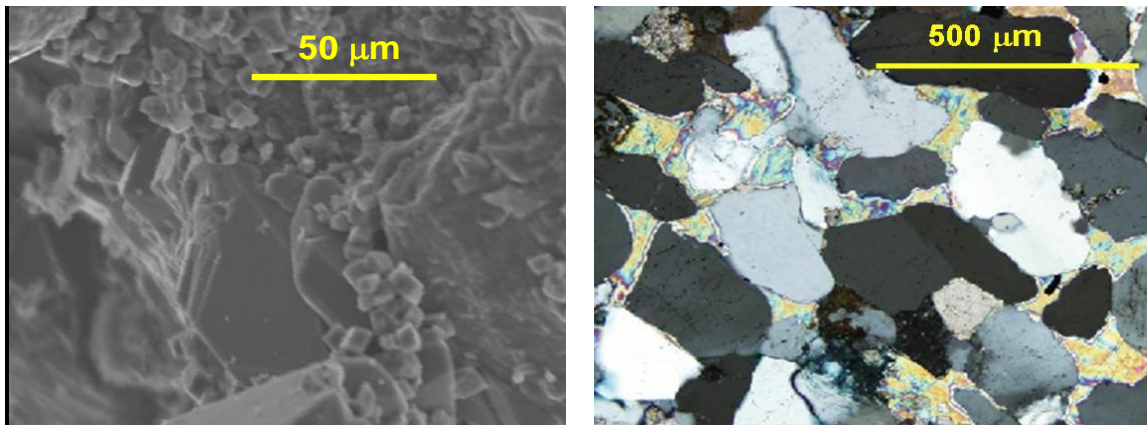
Figure 6-4b: SEM pictures of Tensleep rock.
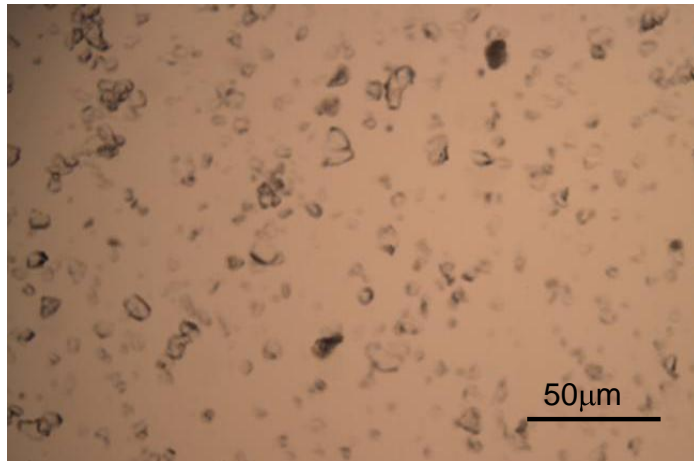
Figure 6-4c: Suspension of dolomite crystals.

Table 6-2: Tensleep Core Properties

Core No.	L (cm)	D (cm)	ϕ (%)	K_g (md)
T1	6.24	3.80	14.11	33.18
T2	8.10	3.80	13.35	36.40
T3	6.91	3.80	13.98	40.07

Table 6-3: Crude Oil Properties (20°C)

Oil sample	ρ, g/ml	μ,cp	n-C_7 Asph, wt%	Acid # mg KOH/g oil	Base # mg KOH/g oil
Tensleep	0.8692	19	3.2	0.16	0.96

Table 6-4: Compositions of Reservoir Brine and CBM Water

Components	Minnelusa reservoir water (MRB), mg/L	CBM Water (CBM), mg/L
NaCl	29,803	915.7
KCl	-	28.7
$CaCl_2$	2,104	191.5
$MgCl_2$	-	180.4
Na_2SO_4	5,903	-
$MgSO_4$	841	-
TDS	38,651	1,316.3

The reservoir cores were first cleaned with toluene – methanol – toluene displacement to remove the oil residue and deposited salts, and dried by evaporation at room temperature and then heated at 105°C. The cores were then saturated with Minnelusa brine. Tensleep crude oil was used to establish initial water saturation S_{wi} which was all around 22%. After aging for 10 days at 75°, the cores were either flooded first with Minnelusa brine, then with CBM brine (tertiary mode), or directly flooded with CBM brine (secondary mode). Waterfloods were performed at a constant

flow rate of 0.25 ml/min at 75°C. Each core was waterflooded multiple times due to the limited availability of reservoir cores. The cumulative oil recovery, effluent brine pH, and pressure drop were recorded against the injected pore volume. Spontaneous imbibition tests were performed on two cores at 75° after multiple cycles of waterflooding to evaluate the wettability of the cores.

After four cycles of waterflooding, one core was cleaned and then flushed with 450 cc of 15% hydrochloric acid. The core was then flushed with the Minnelusa formation brine until the effluent pH was neutral. The objective of this treatment was to investigate the effect of dissolving the fine interstitial dolomite crystals on oil recovery by low salinity waterflooding.

Results and Discussion:

Core 5501B

The preliminary test performed on Core 5501B for tertiary response to CBM water indicated that waterflood recovery was stable at 62% after injection of 10 PV of MRB brine (Fig. 6-5a). Injection of 10 PV of CBM water resulted in additional recovery of 9.5% OOIP (original oil in place). This is the first example of significant increase in oil recovery by injection of low salinity brine from essentially clay-free sandstone.
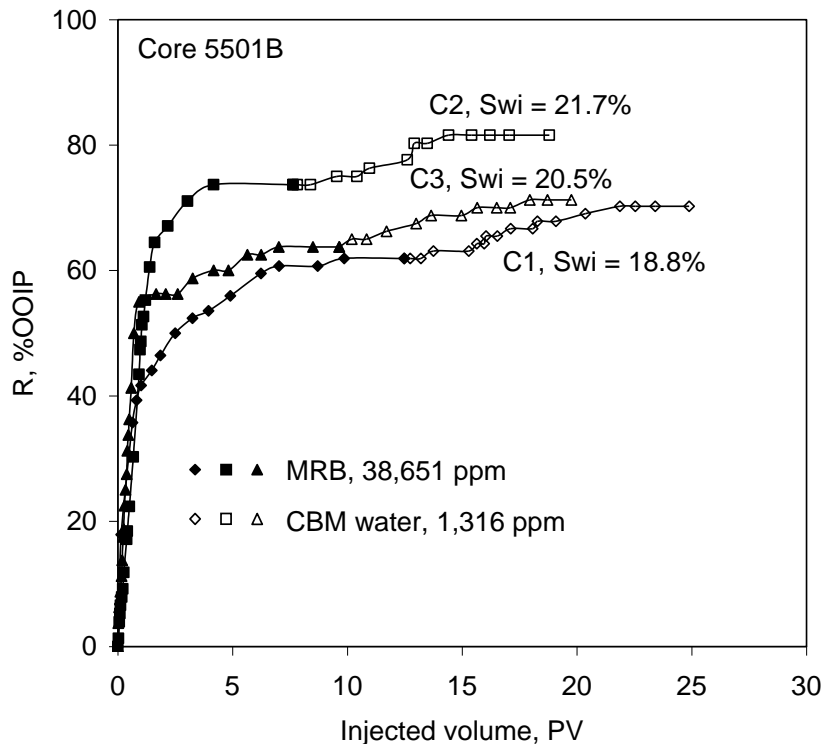
Figure 6-5a: Tertiary oil recovery by CBM water injection.

The core was then cleaned and re-aged at $S_{wi} = 21.7\%$. The second cycle secondary recovery was 73% compared to 62% for the first flooding cycle. During injection of MRB the pressure drop passed through a maximum of 18 psi, then fell to 14 psi followed by continuous slow rise to 18

psi after injection of 7.5 PV of MRB brine. Injection of 7 PV of CBM water resulted in additional recovery of 7.9% OOIP. The pressure response was unusual with respect to previous low salinity tertiary floods on sandstones (Zhang et al. 2007). Instead of passing through a maximum, the pressure rose continuously from 18 psi to almost 30 psi with injection of 11 PV of CBM water even though the remaining oil saturation was decreased and then stayed constant (Fig. 6-5b).
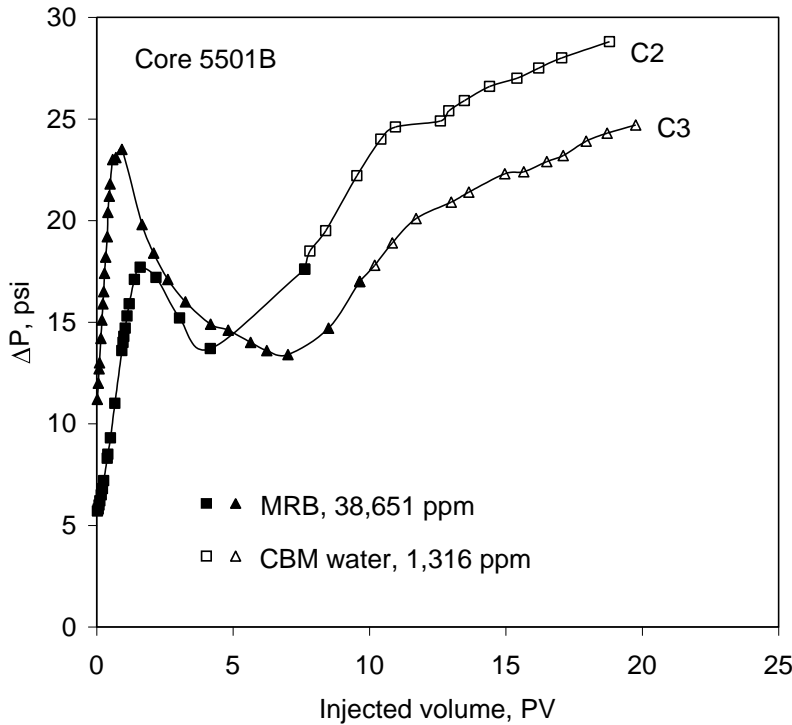
Figure 6-5b: Injection pressure profile for Core 5501B.

For the third cycle, the core was re-aged at $S_{wi} = 20.5\%$. Injection of MRB caused the pressure to pass through a maximum of 23 psi. After a period of decline, as for the second cycle, the pressure started to rise even though a stable oil recovery of 63.8% had been reached. After switching to injection of CBM water, the pressure continued to rise smoothly and was close in form to that for the second cycle (see Fig. 6-5b); the additional oil recovery was 7.5 % OOIP (see Fig. 6-5a).

For all floods, the pH of the effluent brine showed no response to injection of CBM water and only small overall change between 6 and 7.

A spontaneous imbibition test was performed after the third cycle. The core was cleaned and re-aged at $S_{wi} = 25.7\%$. Oil recovery by spontaneous imbibition of MRB was less than 10% OOIP with the rate being about 4 orders of magnitude slower than imbibition at very strongly water-wet conditions (see Fig. 6-6). The core wettability falls within the category of weakly water-wet to neutral-wet.

83
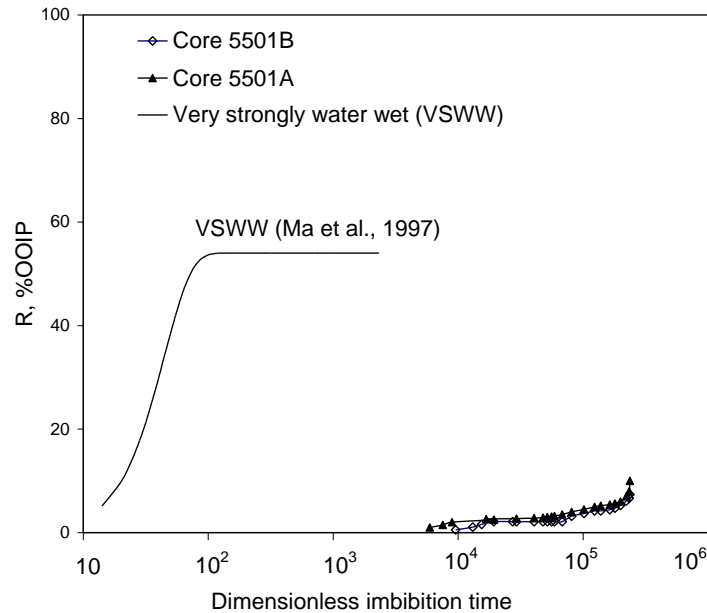
Figure 6-6: Spontaneous imbibition oil recovery for Cores 5501B and 5501A.

Core 5501A

For the first cycle, Core 5501A was first flooded with 11 PV of MRB. After injection of 7 PV, oil recovery became stable at 60% OOIP (Fig. 7a). Initially, the pressure drop increased to a maximum of 27 psi after injection of 2.5 PV followed by decay to a minimum of 24 psi at 5 PV. The pressure then showed steady rise, as for Core 5501B, even though oil saturation did not change during the period of 7 to 12 PV injection. Injection of CBM water caused further rise in pressure to a stable value of 42 psi (Fig.7b). In spite of the large pressure drop, only 3% additional oil recovery was given by injection of CBM water.

For Cycle 2, after re-cleaning, the core was re-aged at $S_{wi} = 21\%$. Upon injection of MRB, the pressure drop increased to a maximum of 13 psi after injection of 2.5 PV followed by decay to a minimum of 8 psi at 4 PV. Waterflood recovery for MRB stabilized at 70% OOIP recovery (Fig. 7a). Again, the pressure drop continued to increase even though the residual oil saturation was stable. Overall, the pressure response to injection of CBM water was significantly less than for the first cycle. After injection of 6 PV of CBM water, an additional 6% OOIP of oil was recovered. Continued injection gave no further oil recovery but slight overall decline in pressure drop.

For the third cycle, the core was cleaned and re-aged at $S_{wi} = 17.4\%$. The pressure drop increased to a maximum of 27 psi after injection of 1.0 PV, followed by decay to a minimum of 10 psi at 5 PV (Fig. 6-7b). The pressure drop again showed overall increase even after attaining a stable residual oil saturation to MRB flooding. During injection of 7.2 PV of CBM water, the pressure drop increased slowly first and then stabilized. Oil recovery increased by 5.9% OOIP. Even though the pressure drops for the second and third cycles were less than half that for the first cycle, the tertiary recoveries were both higher.

The pH of the effluent brine was close to neutral during MRB waterflooding and subsequent injection of CBM water for all the cycles.
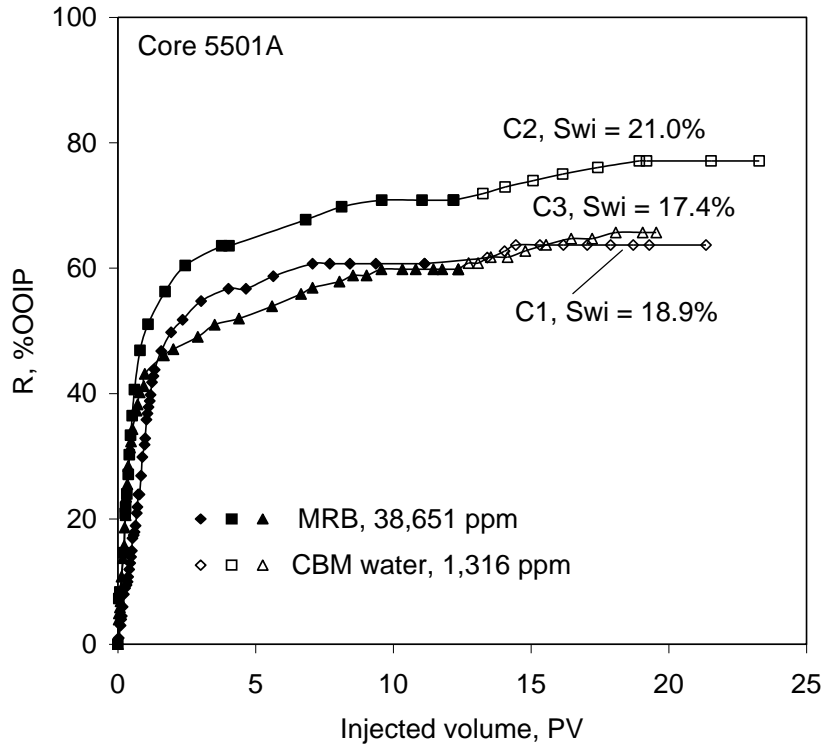
Figure 6-7a: Waterflooding oil recovery for Core 5501A.
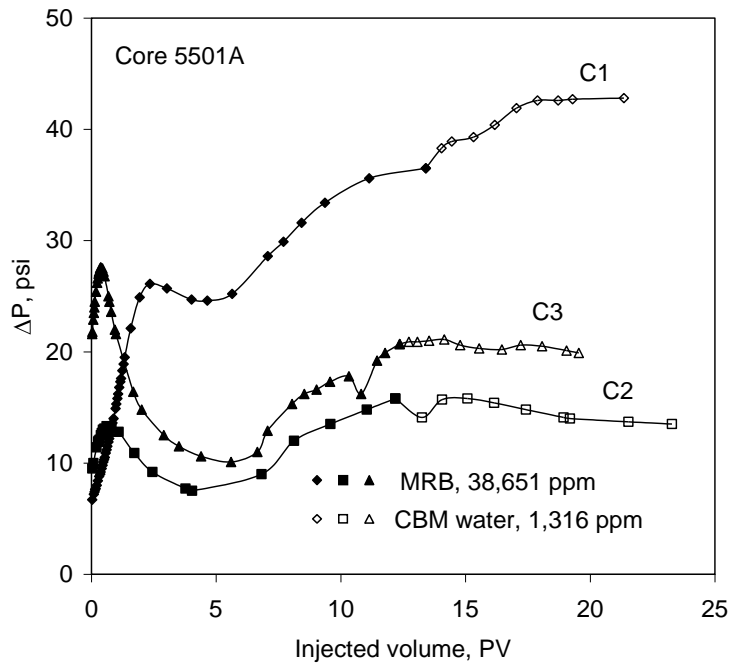
Figure 6-7b: Injection pressure change for Core 5501A.

After the third cycle, the core was cleaned and re-aged at $S_{wi} = 23.5\%$. The oil recovery by spontaneous imbibition of MRB was recorded versus imbibition time. Oil production versus time was similar to that obtained for Core 5501B (see Fig. 6-6).

The core was cleaned by solvents again and saturated with MRB brine. The core was flooded first with MRB brine for 12 PV and then flooded with CBM water for another 12 PV. The water permeability to MRB brine held steady at close to 14 md during the injection. When the injected brine was switched to CBM water the permeability dropped to 8 md and then rose to a steady value of about 9.5 after 7 PV of injection (Fig. 6-8). The reduction in permeability by about one third suggests that the dolomite particles are more readily dispersed by the low salinity brine because of reduced Van der Waals' attraction forces that result from double layer expansion. Therefore, the particle dispersion may contribute to the observed pressure increase during waterflooding.
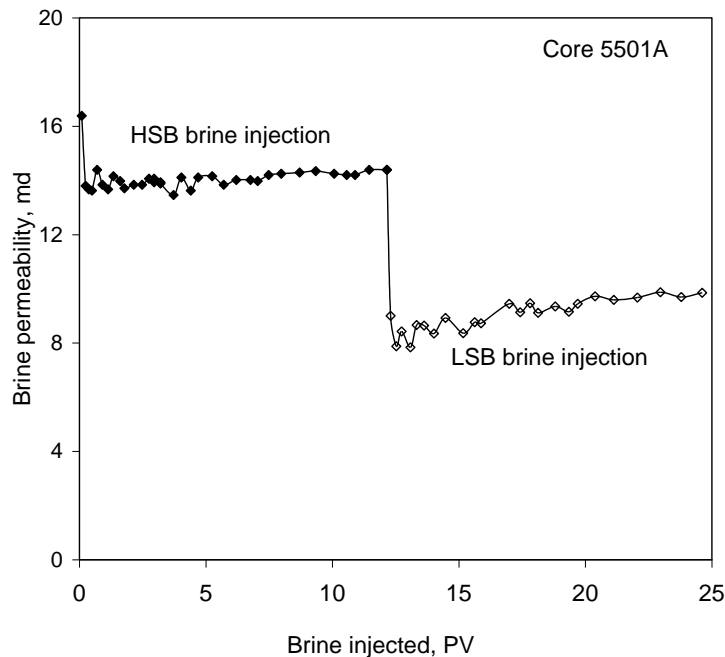
Figure 6-8: The effect of brine salinity on water permeability.

Core 5479B

The first cycle of core cleaning and waterflooding was nullified due to the equipment failure. The core was re-cleaned and re-aged at $S_{wi} = 21.8\%$. After early breakthrough at 23 % OOIP oil recovery, the recovery became stable at only 34.2 % OOIP (C1 in Fig. 9a). The maximum pressure during MRB flooding was 28 psi. Recovery reached a stable value and the pressure had declined to a minimum of 23 psi after injection of about 4 PV of MRB. The injection pressure then slowly increased to 24.1 psi at 7 PV injection (Fig. 6-9b).

CBM water was then injected. The pressure across the core rose to 47 psi after injection of 4 PV. Subsequent decay in pressure was accompanied by tertiary response with most of the additional oil recovery of 8.3% OOIP being produced during the 2 PV of CBM water injection after

reaching the maximum pressure. The pressure profile for CBM water injection is comparable to previously reported behavior (Zhang et al. 2007). The pH increased from 6 to 6.7 while flooding with LSB.
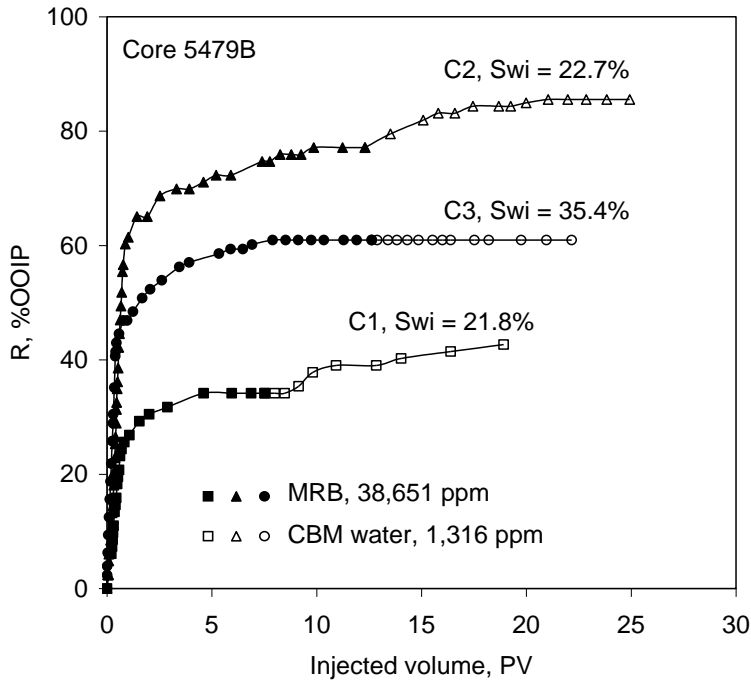

Figure 6-9a: Oil recovery by waterflooding for Core 5479B.
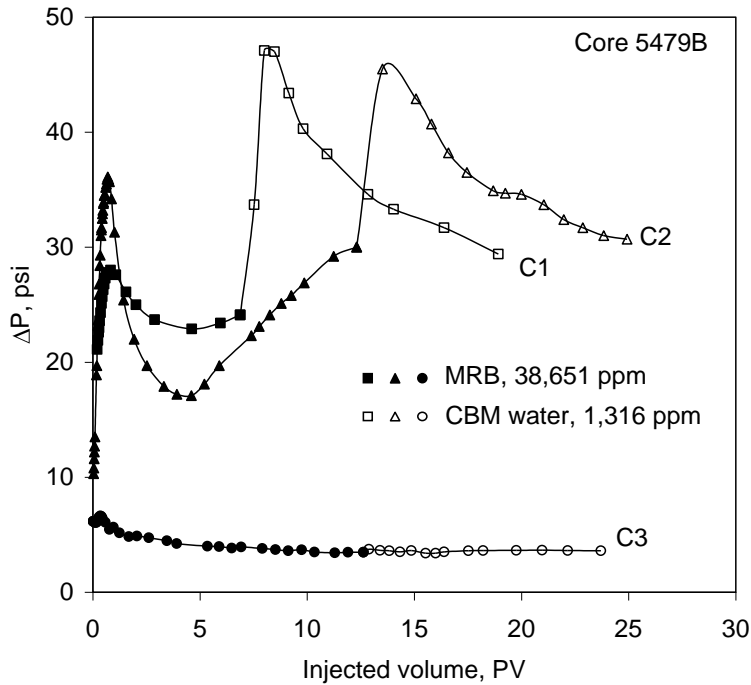

Figure 6-9b: Injection pressure profile for Core 5479B.

For Cycle 2, the core was cleaned and re-aged at 22.7% initial water saturation. Early oil production before obvious water breakthrough of MRB brine was over 60%, more than double that for the first cycle (Fig. 6-9a). The pressure rose to a maximum of 36 psi, fell to a minimum of 17 psi and then increased steadily even though, as in several of the previous tests, oil recovery was stable at 77.1% OOIP. Injection of CBM water caused a comparable pressure response to that for the first cycle. Even though the secondary recovery for this cycle had already yielded 77.1%, tertiary mode recovery reached 8.3% OOIP after injection of 12 PV of CBM water. The pH of the effluent brine was close to 6 during MRB injection and rose to about 7 during the course of CBM water injection.

As a test of the effect of the presence of dolomite, Core 5479B was cleaned and then flushed with 450 cc of 15% hydrochloric acid. The core was then flushed with copious MRB until the effluent pH was neutral. The objective of this treatment was to investigate the effect of dissolving the fine interstitial dolomite crystals on oil recovery. Acidization caused the dry weight of the core to decrease by 5.09% (8.83g). The porosity increased from 13.6% to 18.7%. The liquid permeability increased from 18.2 to 28.1 md which was less than expected from the increase in porosity, possibly because of the effects of acidization on cements and pore geometry.

The acidized core was re-aged after establishing an S_{wi} of 35.4% at the same flow rate that gave initial water saturations of about 20% in all previous cycles. The reduced pressure drop to flow of crude oil and significant change in character of the pore space probably contributed to the high initial water saturation compared to values obtained prior to acidization. Injection of MRB resulted in breakthrough recovery of 46% OOIP and a maximum pressure of only 8 psi. The pressure decayed to 5 psi after 5 PV and then, rather than continuing to rise as in previous tests, dropped slightly during subsequent injection. Recovery stabilized at 60.9% OOIP (Fig. 6-9a).

Upon injection of CBM water, in contrast to results for the non-acidized cores, the pressure remained close to constant at about 3.6 psi and there was no detectable response in recovery even after injection of 12 PV of CBM water. The pH of the effluent brine remained close to 6 throughout the test.

Reproducibility

Variation in secondary recovery for consecutive floods after cleaning and re-aging between floods occurred for all the tested cores, which is similar to that observed for clay bearing reservoir rock (Loahardjo et al. 2007). Each cycle of core preparation and flooding affects the subsequent test. Variation in secondary recovery for consecutive floods on individual cores also indicates that subtle changes in crude oil-brine-rock interactions can have large effects on oil recovery from mixed-wet rocks. As a consequence, establishing baseline secondary recoveries for crude oil/brine/reservoir core combinations is problematic when duplicate core plugs are not available. In contrast, investigation of low salinity flooding in tertiary mode can demonstrate a clear connection between reduction in salinity and increase in oil recovery through both laboratory tests and pilot tests for wells producing at very high water cut.

Conclusions:

A survey was performed for the CBM well location, water composition, the distribution of oil fields, reservoir formation, petrophysical properties and water/oil & gas production history. The data provide important information with respect to the availability of low salinity CBM water for improved oil recovery.

The injection of CBM water for the Tensleep cores resulted in significant improved oil recovery. Up to 10% OOIP can be produced by injection of CBM water after injection of high salinity formation water.

Another important formation in the PRB, the Minnelusa formation, has the similar rock mineralogy to that of the Tensleep formation. CBM water injection may be applied to both formations for higher oil recovery.

Other factors that impact the viability of using CBM water to improve oil recovery are the relative locations of CBM wells and targeted reservoirs, the compatibility of the rock and fluid properties, and transportation costs. This cost can be minimized since the oil reservoirs and CBM reservoirs often overlay each other in the Powder River Basin.

References:

Lohardjo, N., Xie, X. and Morrow, N.R. 2007. paper SCA 2007-82 presented at the International Symposium of the Society of Core Analysts, Calgary, Alberta, Canada, September 2007.

Rice, C.A., Ellis, M.S. and Bullock, J.H., Jr. 2000. USGS: Water co-produced with coalbed methane in the Powder River Basin, Wyoming: preliminary compositional data. Open File Report OF00-372, 2000.

Ruckelshaus Institute of Environmental and Natural Resources. 2005. Water production from coalbed methane development in Wyoming: A summary of quantity, quality and management options. Report prepared for the Office of the Governor, State of Wyoming.

Tang, G.Q. and Morrow, N.R. 1997. SPE Reservoir Engineering, November 1997.

Tang, G. and Morrow, N.R. 2002. Geophysical Monograph 129, 171-179.

Veil, J.A., Puder, M.G., Elcock, D. and Redweik, R.J. 2004. U.S. DOE, NETL Contract W-31-109-Eng-38. Argonne National Laboratory, January 2004.

Webb, K.J., Black, C.J.J. and Al-Ajeel, H. 2004. paper SPE 89379 presented at the 2004 SPE/DOE Fourteenth Symposium on Improved Oil Recovery held in Tulsa, Oklahoma, U.S.A., April 17-21, 2004.

Webb, K.J., Black, C.J.J. and Edmonds, I. J. 2005. 13th European Symposium on Improved Oil Recovery. Budapest, Hungary, 25 - 27 April 2005.

Zhang, Y.S. and Morrow, N.R. 2006. paper SPE 99757 presented at the 2006 SPE/DOE Symposium on Improved Oil Recovery, Tulsa, Oklahoma, U.S.A., 22 – 26 April 2006

Zhang, Y.S., Xie, X. and Morrow, N.R. 2007. paper SPE 109849 to be presented at the SPE Annual Technical Conference and Exhibition, Nov. 11-14, 2007, Anaheim, California, USA.

Task 7 – Enhancing the Beneficial use of CBNG Waters

George F. Vance[7] and Mike A. Urynowicz

One of the primary concerns associated with CBNG waters is their potentially high SARs and the influence Na^+ has on soils, vegetation, wildlife and livestock in different environments, e.g., streams, agricultural lands, rangelands, and other PRB ecosystems. Some CBNG producers are treating poor-quality CBNG water using ion exchange, reverse osmosis, and other similar types of treatment to improve its quality for release into streams and other waterways, or for beneficial purposes such as livestock watering and irrigation. Unfortunately, current CBNG-water treatment technologies are often expensive or ineffective for their intended purpose (Ganjegunte et al., 2005, 2008; Vance et al., 2004, 2006, 2008).

The objective of this project was to evaluate the use of zeolites and ZrP for CBNG water treatment. Using naturally occurring materials such as zeolites has several benefits. The advantages of utilizing material from natural zeolite deposits as a cation exchanger in the treatment of PRB CBNG produced water are as follows: 1) zeolite deposits are at or near the surface and are easy to mine; 2) deposits are generally of large volume; 3) deposits commonly are flat-lying; and 4) deposits are often characterized by high mineral purity (>75%). Therefore the mining costs of the zeolite deposits are generally low (Mumpton 1978, 2000). Typically the cost of mining and preparation (i.e., crushing and sizings) of zeolite for the end use application is minor with respect to transportation costs.

Commercial zeolite deposits in the U.S. are associated with the alteration of volcanic tuffs in alkaline lake deposits and open hydrologic systems. Commercial deposits in the United States are in Arizona, California, Idaho, Nevada, New Mexico, Oregon, Texas, Utah, and Wyoming. Total domestic production of zeolites was estimated to be 46,000 tonne compared with an estimated 36,400 tonne in 2001. Zeolites in these deposits are chabazite, clinoptilolite, erionite, mordenite, and phillipsite. Other components, such as orthoclase and plagioclase feldspars, montmorillonite, opal, quartz, and volcanic glass, are present in some deposits. Different zeolites have cation preferences that result in cation selectivity. Clinoptilolite and chabazite zeolites have a preference for larger cations. For example, clinoptilolite cation selectivity follows the order of: $Cs > Rb > K > NH_4 > Ba > Sr > Na > Ca > Fe > Al > Mg > Li$ (Mumpton, 1999). The slightly higher preference of Na^+ over Ca^{2+} of clinoptilolite zeolites, plus high Na^+ concentration in the solution, indicates clinoptilolite is a good choice for removing Na^+ from CBNG waters.

Methods:

Zeolites used in this study included several obtained from locations around the western U.S. that had different amounts of exchange ions and total cation exchange capacities (CEC) (Table 1). Zeolite exchangeable cation concentrations and CEC were determined by a modified method of Cerri et al. (2002) that involved zeolite sample reacted for 2 h with 1 M NH_4OAc at room temperature followed by centrifugation and filtration (Whatman filter #42) of the supernatant.

---

[7] Department of Renewable Resources. University of Wyoming, Laramie, WY. email: GFV@uwyo.edu

This process was repeated two more times with the three extracts combined in a 100 ml volumetric flask that was brought to volume using 1 M NH_4OAc. Following the displacement of exchangeable cations from the sample with NH_4^+ acetate, Na^+, K^+, Ca^{2+} and Mg^{2+} were analyzed using inductively coupled plasma spectrometry (Suarez, 1996). The sum of major exchangeable cation concentrations was used to determine the effective cation exchange capacity (ECEC). The zirconium phosphate ($ZrP = Zr(HPO_4)_2 \cdot nH_2O$) used in this study was obtained from Magnesium Elektron Inc. (MEI) (New Jersey) and used as received. The CEC of ZrP was 667 $cmol_{(+)}$ kg^{-1}, which is greater than three times that of the zeolite clinoptilolite samples.

Table 7-1: Effective CEC and exchangeable cations ($cmol_{(+)}$ kg^{-1}) of the different zeolite samples.

	Sample	Location	Na	Ca	Mg	K	Effective CEC
AM1	Ash Meadows (AM)	Nevada	114	20	2	95	230
FC1	Fossil Canyon (FC1)	California	86	13	2	27	128
FC2A	Fossil Canyon (FC2a)	California	149	13	1	35	198
FC2B	Fossil Canyon (FC2b)	California	142	19	2	30	193
SC1	St. Cloud (SC)	New Mexico	4	77	18	13	112
MH1	Mud Hills (MH)	California	92	41	3	25	162
BRZ	Bear River (BR)	Idaho	10	67	3	56	136
FL1	Fort LaClede (FL)	Wyoming	140	50	2	26	218
AZ-C	Bowie (BW-Chabazite)	Arizona	-	-	-	-	250

Upon consideration and comparison of the cost, availability, and potential performance we selected and focused on the use of commercially available natural clinoptilolite samples obtained from the St. Cloud zeolite (ST-Zeolite) mine in Winslow, NM (Austin and Bowman 2002) and the Bear River zeolite (BR-Zeolite) mine in Preston, ID, and initially we evaluated a commercial pre-activated Ca-rich chabazite from Arizona (AZ-Zeolite) [Cabsorb® Chabazite Products (Cabsorb ZS500RW)], provided by GSA Resources Inc. (http://www.gsaresources.com). In addition, a locally available natural zeolite (clinoptilolite) was also selected for this study due to its accessibility, low cost, and high CEC. The WY-zeolite samples were collected from a zeolite deposit in Sweetwater County, WY. Zirconium phosphate (ZrP) was also examined for its ability to retain Na^+. ZrP are layered materials that are inorganic ion-exchangers as well as hosts to numerous compounds used in intercalation chemistry and have application as molecular sieves, catalysts, ion and proton conductors, and matrices for chemical modification.

X-ray analysis was conducted on the different zeolite and ZrP samples after drying at approximately 80°C for several hours to remove water, which ranged from <1-6%. Pulverized samples were scanned using 2-60° 2θ using CuKα radiation at 1.54 Å.

The water chemistry of the CBNG water (Table 7-2) was chosen by compiling published data from various sources (BLM 2003, King et al. 2004ab, Jackson and Reddy 2007) and prepared

using appropriate amounts of inorganic chemicals and tetraethyl orthosilicate as the silicon (Si) source. World Health Organization (WHO) hard water (http://www.who.int) standards were prepared by dissolving 0.304 g of anhydrous $CaCl_2$ and 0.139 g of $MgCl_2 \bullet 6H_2O$ in 1 L distilled water. This produced water with a hardness of 342 mg L^{-1} calculated as $CaCO_3$. According to drinking water hardness category, this water would be classified as very hard water.

Table 7-2: Water chemistry of CBNG waters (mg L^{-1}) studied.

	Na	Ca	Mg	K	Cl	SO$_4$	HCO$_3$	SiO$_2$	SAR	pH
CBNG Water I	205	10	2.5	1.25	45.4	5	505	5	15.5	8.20
CBNG Water II	411	10	2.5	2.5	65.8	10	1010	10	30.1	8.90
CBNG Water III	822	10	2.5	2.5	65.8	10	1010	10	60.2	8.90

Batch Adsorption Kinetic and Equilibrium Studies

Adsorption kinetic studies were carried out using 20.0 g zeolite samples diluted with 1,000 ml of CBNG water at ambient temperature. Aliquots of these samples (~5 ml) were collected at various times using a syringe with a GHP Acrodisc 0.2 μm filter attached. The samples were then acidified using a few drops of concentrated HNO_3 and stored until analyzed.

Adsorption studies were conducted using the batch equilibration technique. A 5.0 g zeolite sample was weighed into 50 ml polyethylene bottles containing varying concentrations of NaCl and/or spiked using stock solutions containing both $CaCl_2$ and $MgCl_2$ with the final volume adjusted to 45 mL using DI water. The initial Na^+ concentrations in the tubes ranged from 0 to 5,000 mg/L. Initial Ca^{2+} and Mg^{2+} concentrations in the tubes ranged from 100 to 4,000 mg L^{-1} and 20 to 700 mg L^{-1}, respectively. The tubes were shaken on a reciprocal shaker for 48 h, centrifuged and the supernatant solution filtered and acidified using a few drops of concentrated nitric acid and stored until analyzed.

Packed Column and Regeneration Studies

Packed column studies were carried out using a continuous flow-through column apparatus or Spectra/Chrom™ LC glass columns. Different zeolite sizes (4x6, 6x8, 6x14, and 14x40, 40x100, 100x140, –140, and –325 mesh), flow rates (3.0, 6.0 or 16 ml/min) and water qualities were evaluated. Effluent was collected using an automated fraction collector. Regeneration studies on the spent media were conducted using 0.1M $CaCl_2$ at a flow rate that was half of that used for the CBNG water. Columns were extensively rinsed with 3–4 L of DI water to remove pore residual $CaCl_2$ (checked by $AgNO_3$ solution).

For the WY-zeolite, two different treatment approaches were used. The first approach used 45 g of 14×40 mesh WY-zeolite packed into columns that were then pretreated with 2 L 0.1 M $CaCl_2$ at a flow rate of 3 mL min^{-1} followed by extensive rinsing with ~2–3 L DI water to remove residual $CaCl_2$ (checked by $AgNO_3$ solution). Columns were used for studying CBNG water treatment at different flow rates. Upon completion of CBNG water treatment study, columns were subjected to regeneration using 0.1 M $CaCl_2$ solution followed by DI water rinsing. The regenerated zeolite columns were used again for CBNG water treatment. Leachates were

collected using an automatic fraction collector. A second approach utilized a Na-WY-zeolite that was first used for WHO hard water treatment, followed by treatment of CBNG water and then hard water treatment again. The collected solutions were filtered and acidified as described above.

Additional column studies were performed using 6 soil columns operated as constant head permeameters with a hydraulic head change of 198 cm. The soil columns were 5 x 50cm and each contained 15 cm of soil. The soil was a composite sample collected from the UW Sheridan Research and Extension (R&E) Center during a reconnaissance trip and from borehole installation (sees next section for a more detailed description). Three of the 6 columns also contained a 2 inch layer of Zeolite placed on top of the soil.   Water was pumped into a 114 liter gravity feed tank with a Masterflex® L/S Standard Drive Pump and size 24 Masterflex® tubing (Cole-Parmer Instrument Company, Vernon Hills, IL). To minimize air entrainment effects, columns were backflow saturated with de-aired water that was used for the duration of the study. Water was de-aired by bubbling helium gas into the water supply tank. Tap water was initially used in the column study to establish baseline hydraulic conductivities. Once established, a synthetic CBNG Water II (Table 2) was introduced into the columns to evaluate the permeability effects of Na^+, with infiltration rates measured gravimetrically. Flow rate was recorded for a period of two weeks following the introduction of simulated CBNG water.

For the ZrP studies, we also used Spectra/Chrom^{TM} LC glass columns (10 x 300 mm) that contained 220 mm of ZrP. Flow rate was set at 3.0 ml min^{-1}. Upon completion of CBNG water treatment, the column was subjected to regeneration using 1 M HCl solution, followed by DI water rinsing and was then used again for CBNG water treatment.

Field Studies

A field study was conducted adjacent to the Sheridan R&E Center, which is located in northwest PRB and is in close proximity to several active CBNG wells and reservoirs. Before initiating the field study, we observed many of the current practices used to manage CBNG produced waters, consulted with local stakeholders, collected soil and water samples, and evaluated potential field-site locations. The location of our field site included a recently excavated evaporation pond not yet in operation that allowed for collection of soil samples, with CBNG water samples collected from an evaporation pond outfall located nearby the R&E Center.

The field study was performed using a total of 12 falling head permeameters installed in separate boreholes; each located a distance of approximately 8 m from each other in three rows of four. The permeameters were constructed with 3 m lengths of 15 cm diameter Schedule 40 polyvinylchloride (PVC) conduit and installed to a depth of approximately 2 m below ground surface (bgs) and instrumented with data logging pressure transducers (In-Situ Level TROLL 500) to measure temperature, pressure, and depth of water. A separate pressure transducer was used as a control to record the ambient temperature and barometric pressure at the site. Each of the permeameters was operated in an open borehole configuration. Approximately 300 grams of BR-zeolite was added to 6 of the 12 permeameters to form a 5 cm permeable reactive barrier on top of the subsoil. The remaining 6 permeameters contained no zeolite and served as controls. The permeameters were filled with either CBNG produced water collected from a nearby CBNG

well outfall or tap water (control). Each of the four experimental conditions (control/control, control/CBNG, Zeolite/control and Zeolite/CBNG) were triplicated. The permeameters were filled with water on June 12, 2008 and again on July 9, 2008 and operated until August 20, 2008 when the site was decommissioned. Following the completion of the field studies, intact cores were collected from the bottom of each borehole (2–3 m bgs). The cores were composited into samples representing the 0-5, 5-15, 15-30, 55-65, and 95-105 cm soil intervals.

Analyses

The concentrations of cations (Na^+, Ca^{2+}, Mg^{2+}) in solution were analyzed using inductively coupled plasma (ICP) spectroscopy (Thermo Jarrell Ash, model P300) with K analyzed using Atomic Absorption (AA) spectroscopy (Perkin Elmer, model 2380). The solutions were also analyzed for pH and electrical conductivity (EC) using pH and conductivity meters, respectively.

Results and Discussion:

Material Characterization

X-ray diffraction (XRD) analysis indicated a significant occurrence of clinoptilolite in ST-zeolite samples (80% and 85% clinoptilolite, which was similar to the manufacturer's specifications). For ST-zeolite, other minerals identified by XRD analysis included smectite, quartz, cristobalite, feldspar and illite. For BR-zeolite, XRD analysis also confirmed a dominant presence of clinoptilolite (85–92%) with no apparent impurities, with the balance of materials comprised of chalcedony. The WY-zeolite sample consisted of approximately 90% clinoptilolite with a minor amount of heulandite. A previous scanning electron microscopy (SEM) study by Hulbert (1987) found that our WY-zeolite deposit sample consisted of clinoptilolite crystals typically smaller than 10 μm in diameter, grading into sub-micrometer size grains.

The measured CECs were 112 and 136 $cmol_{(+)}$ kg^{-1} for ST-zeolite and BR-zeolite, respectively. Both ST-zeolite and BR-zeolite samples are naturally enriched with exchangeable Ca^{2+}. In addition, BR-zeolite also contained considerable exchangeable K (56 $cmol_{(+)}$ kg^{-1}) as compared to that of ST-zeolite (13 $cmol_{(+)}$ kg^{-1}) (Table 1). The Ca-rich Arizona zeolite was used as received from the company. According to the manufacturer this product originated from a natural high Na^+ chabazite that was thermally treated at low to high temperatures. The upgrading process resulted in partial recrystallization with the exchangeable cations in the final product dominated by Ca^{2+}. Whole rock chemical analysis of the WY-zeolite suggests the material is high in sodium content (Na_2O) at 4.4%, as compared to that of CaO (1.50%), MgO (0.30%) and K_2O (1.53%), respectively. Major exchangeable cations on the WY-zeolite were 140, 26, 50 and 2 $cmol_{(+)}$ kg^{-1} for Na^+, K^+, Ca^{2+} and Mg^{2+}, respectively. The sample has a high effective CEC value of 218 $cmol_{(+)}$ kg^{-1}.

Despite the high effective CEC of the natural WY-zeolite sample, its high exchangeable Na^+ content lowers its utility for direct use for the purpose of CBNG water treatment. Modified zeolite samples were therefore developed by converting the exchangeable Na^+ to Ca^{2+} before use for CBNG water treatment.

Adsorption Kinetics

Results indicated that Na^+ adsorption rates were faster for BR-zeolite compared to ST-zeolite (Fig. 7-1). In addition, BR-zeolite removed more Na^+ and released greater amounts of Ca^{2+} than ST-zeolite. Other major exchangeable cations (i.e., K^+ and/or Mg^{2+}) were also replaced by Na^+ and released into the solution. More Ca^{2+} and K^+ were released by BR-zeolite than from ST-zeolite. Since K is an important plant nutrient, increased levels in the treated water would be beneficial for agricultural irrigation purposes.
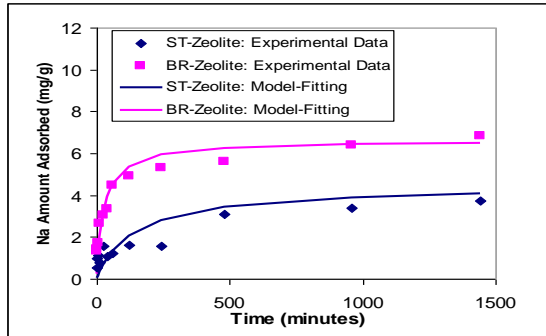
Figure 7-1: Modeling Na^+ adsorption kinetics by ST-zeolite (14x40) and BR-zeolite (14x40).

Adsorption kinetics is related to many factors that included particle size, pore structure and solute diffusion. Generally, two kinetic models of adsorption have been frequently used: (1) active available site model and (2) chemical reaction rate model, which is based upon the mass law concept. For many adsorption processes occurring on heterogeneous materials, it has been found that the pseudo-second-order kinetic equation agrees well with chemisorption as the rate controlling step. The pseudo-second-order kinetic rate equation can be expressed as (Ho and McKay 1999, 2000):

$$\frac{dQ_t}{dt} = k*(Q_{eq} - Q_t)^2 \quad (2)$$

where Q_{eq} is the sorption capacity at equilibrium, Q_t is the solid-phase loading of Na^+ at time t (min) and k (g mmol^{-1} min^{-1}) is the pseudo-second order rate constant. Considering the boundary conditions of $Q_t = 0$ (at $t = 0$) and $Q_t = Q_t$ (at $t = t$), the following linear equation can be obtained:

$$\frac{t}{Q_t} = \frac{1}{v_o} + \frac{1}{Q_{eq}} t \quad (3)$$

$$v_o = k*Q_{eq}^2 \quad (4)$$

where v_0 (mmol/g*min) is the initial adsorption rate. Therefore, by plotting t versus t/Q_t, values for v_0 and Q_{eq} can be determined.

Adsorption results show that a 24-h equilibration period (1,440 min) was sufficient to establish steady state or equilibrium for future sorption experiments using similar particle sizes and initial Na^+ concentrations. The results also suggest that equilibrium may not be obtained in the pilot tests where empty bed contact times (EBCT) are on the order of 3–5 min.

Adsorption data were used to estimate rate constants, initial sorption rates, and zeolite adsorption capacities for Na^+ (Table 3). High coefficient of determination values ($R^2 \sim 0.97$–0.99) indicated that the adsorption of Na^+ on the tested media were well described using the pseudo-second-order kinetic model. Approximately 22% to 32% of the initial Na^+ in solution (about 411 mg L^{-1}) was removed by the end of the 24-h equilibration period. Rate constants and initial adsorption rates decrease in the order of BR-Zeolite > ST-Zeolite with BR-Zeolite having the highest equilibrium sorption capacity in the kinetic tests.

Table 7-3: Kinetic parameters for Na^+ adsorption by zeolites in CBNG Water II using pseudo-second-order model

Media	R^2	K	v_o	Q_{eq} (mmol g^{-1})	Q_{eq} (mg g^{-1})
ST-Zeolite (14x40)	0.972	0.036	1.36×10^{-3}	0.195	4.47
BR-Zeolite (14x40)	0.999	0.127	1.05×10^{-2}	0.287	6.60

R^2 = Model-fitting coefficient;
K = The pseudo-second-order rate constant for the kinetic model (g/mmol∗min);
v_o = Initial adsorption rate (mmol/g∗min);
Q_{eq} = The sorption capacity at equilibrium ($mmol_{As}$/g) or mg/g.

Differences in adsorption by the two zeolites can be attributed to variations in the physical and chemical properties of the media (i.e., composition, pore size, surface area, surface charge, Na^+ affinity). Adsorption kinetic parameters are informative in predicting Na^+ removal from CBNG waters. Diffusion coefficients are also important parameters for predicting the diffusion rate of adsorbate molecules in porous media. In order to determine the effective diffusivity of Na^+ in the macropores of adsorbent media, a diffusion equation for a macropore-controlled system on a spherical shell element of the adsorbent particle, proposed by Ruthven (1984), was used:

$$(1-\varepsilon_p)\frac{\partial q}{\partial t} + \varepsilon_p \frac{\partial c}{\partial t} = \varepsilon_p D_p \left(\frac{\partial^2 c}{\partial R^2} + \frac{2}{R}\frac{\partial c}{\partial R} \right)$$
(5)

where ε_p is adsorbent particle porosity, $q(R,t)$ is the adsorbed phase concentration (µg L^{-1} of adsorbate), t (s) is time, c (µg L^{-1}) is the adsorbate concentration in the supernatant solution, D_p ($cm^2 s^{-1}$) is the macropore diffusivity of adsorbate in the adsorbent, and R (cm) is the radial distance from the center of the adsorbent particle. The macropore diffusivity (D_p) is assumed to be independent of concentration in the above equation. For fractional adsorption uptake (M_t/M_{max}), the solution for the equation with a 2% error is given by:

$$\frac{M_t}{M_{max}} \cong 1 - \frac{6}{\pi^2} \exp\left(\frac{\pi^2 D_e t}{R_p^2} \right)$$
(6)

where M_t (µg L^{-1}) is the mass gain of adsorbent at time t, M_{max} (µg L^{-1}) is the mass gain of adsorbent at infinite time, and D_e ($cm_2 s^{-1}$) is the effective diffusivity defined by:

$$D_e = \frac{\varepsilon_p D_p}{\varepsilon_p + (1-\varepsilon_p)K}$$
(7)

A plot of Ln(1-(M_t/M_{max})) vs. time should generate a straight line with a slope of $\left(\dfrac{-\pi^2 D_e}{R_p^2}\right)$ and an intercept of $Ln\left(\dfrac{6}{\pi^2}\right)$, from which the effective diffusivity, D_e, for Na^+ diffusion in the macropores of the media can be calculated.

The values for effective diffusivity De (cm^2/s) calculated based on data points with M_t/M_{max} above 40% and assuming an average particle size of 0.315 mm, are 2.01×10^{-9} ($R^2 = 0.939$) for ST-zeolite (14×40) and 7.03×10^{-9} ($R^2 = 0.948$) for BR-zeolite (14×40), respectively. BR-zeolite has a higher D_e value than that of ST-zeolite.

Adsorption Equilibrium Studies

The Na^+ adsorption curves showed L-type adsorption on ST-zeolite and BR-zeolite. The L-type adsorption curves are described well using the Langmuir equation:

$$q = \frac{q_{max}KC}{1+KC} \quad (8)$$

where q is the amount adsorbed (mg g^{-1}), q_{max} is the maximum adsorption capacity of the solid phase, K is the Langmuir constant and C is the solution Na^+ concentration at equilibrium. Rearranging to a linear form, Eq. (8) becomes:

$$\frac{C}{q} = \frac{1}{Kq_{max}} + \frac{C}{q_{max}} \quad (9)$$

Plotting C/q vs. C results in a slope of $1/(q_{max})$ and intercept of $1/(Kq_{max})$.

The BR-zeolite had a greater adsorption affinity for Na^+ than did the ST-zeolite at the same equilibrium solution Na^+ concentrations. The maximum Na^+ adsorption capacities from the adsorption curves for ST-zeolite and BR-zeolite were 9.6 and 12.3 (mg g^{-1}) or 0.42 and 0.54 (meq/g), which accounts for approximately 38% and 39% of their measured effective CEC values, respectively. The previously reported cation selectivity order indicated Na^+ is only slightly preferred over Ca^{2+} on clinoptilolite, while K is more strongly adsorbed. The binding strength constant of BR-zeolite is higher than that of ST-zeolite, indicating that Na^+ could be more strongly adsorbed by BR-zeolite. The adsorption results are consistent with the findings observed in the kinetic studies.

Cation adsorption behavior (i.e., adsorption capacity and selectivity) by zeolites are related to a variety of factors such as mineral purity, crystallinity, media purity, cation valence/hydration degree and pre-existing cations, ion concentration and multiple adsorption sites with varying degree of accessibility as well as rate-limiting steps (mass transfer and diffusion). Although ST-zeolite contains slightly higher exchangeable Ca^{2+} concentrations than that of BR-zeolite, the ease of which Ca^{2+} exchanged from ST-zeolite is lower than that of the BR-zeolite, suggesting that the Ca^{2+} in ST-zeolite may occupy stronger adsorption sites. The higher K in BR-zeolite suggests the preference for K on stronger adsorption sites. This could result in Ca^{2+} bound to relatively weak adsorption sites, making the Ca^{2+} in BR-zeolite more easily replaced by Na^+ then that in ST-Zeolite.

Considering charge balance, the amount of Ca^{2+}, Mg^{2+} and K^+ released accounted for more than 85% of the adsorbed Na^+ on both ST-zeolite and BR-zeolite, which suggests that the difference is probably due to the release of other cations. Overall, the adsorption results of this study suggest that both zeolites can be used to reduce Na^+ level in CBNG waters by releasing Ca^{2+}, Mg^{2+}, and K^+, with the BR-zeolite having a higher Na^+ adsorption capability than ST-zeolite.

The Ca^{2+} and Mg^{2+} adsorption isotherm curves for Na-WY-zeolite also showed L-type adsorption that was well described using the Langmuir equation. The maximum Ca^{2+} and Mg^{2+} amount of adsorption by WY-zeolite was calculated to be 10.3 and 1.2 mg g^{-1}, respectively, accounting for about 30% of the measured effective CEC value. Results for modification of the WY-zeolite sample indicated exchangeable Na^+ in the natural WY-zeolite was easily replaced using a 0.1 M $CaCl_2$ solution (Ca^{2+}=4,000 mg L^{-1}); 1 L of 0.1 M $CaCl_2$ solution removed a majority of the exchangeable Na. The amount of Na^+ removed in the first leaching of 1 L 0.1 M $CaCl_2$ solution was 23.7 mg g^{-1}, accounting for approximately 75% of the total exchangeable Na^+ of the natural occurring Na-WY-zeolite sample. The remaining exchangeable Na^+ in the WY-zeolite was strongly adsorbed and hard to replace with Ca^{2+}. These findings were comparable with a previous study reported by Hulbert (1987) who investigated Na^+, Ca^{2+}, and NH_4^+ exchange on zeolite materials collected from an outcrop of blue-green tuff in the Fort LaClede deposit, Sweetwater County, WY and found that Ca^{2+} replaces Na^+ with decreasing selectivity as Ca^{2+} loading increases to about 80% at 30°C and that the Fort LaClede clinoptilolite at 30°C has a moderate selectivity for Ca^{2+} over Na^+ at ~80% Ca^{2+} loading. Above this loading, WY-zeolite is slightly selective for Na. Our batch study results suggested the maximum amount of Ca^{2+} that could be adsorbed was about 10.3 mg g^{-1}. This is slightly lower than that obtained in the packed column study, which was 16.0 mg g^{-1}. This suggests that in a dynamic column system, more Na^+ can be replaced by Ca^{2+} as compared to that in a batch study, presumably due to the constantly high Ca^{2+} concentration in the leaching solution.

Effect of Water Chemistry and Particle Size

The effects of water chemistry and zeolite particle size on the CBNG water quality were also studied. BR-zeolite samples with varying particle sizes and different CBNG waters were used to describe adsorption reactions. Results indicate the finer particle size materials had a greater reduction in SAR of the three CBNG waters, i.e., 14×40 < 40×100 ≈ 100×140 ≈ –140 ≈ –325. In porous materials such as zeolites, the majority of reactive sites are on internal surfaces. For example, ST-zeolite (14×40) has been characterized to have an average pore diameter of 4 Å, an internal CEC of 0.8 meq g^{-1}, and an external CEC of 0.1 meq g^{-1}. Therefore, diffusional resistance to mass transport within larger particle-sized zeolites is generally higher than that of smaller particle-sized zeolites, with some internal surfaces of the larger particles not utilized for adsorption. As a result, smaller particle-sized zeolite materials would generally give rise to higher adsorption rates and capacities due to shorter paths within and between particles.

Packed Column Studies and Data Analysis

Column performance depended upon a variety of factors that included adsorbent type, particle size, adsorption capacity, column diameter, water flow rate, adsorbent bed depth, and weight of adsorbent. Column breakthrough curves for ST-zeolite (14×40 mesh) in CBNG water II and corresponding change in effluent SAR values (flow rate = 3.0 ml min^{-1}) column and contact time, and water chemistry were examined. Column performance results were consistent with the trends observed in the batch adsorption kinetic and equilibrium studies. Monitoring of the effluent solution pH indicated that, as compared to influent solution (pH 8.90±0.10), there was no significant change in pH values of the leachates for ST-zeolite (pH 9.00±0.30) and for BR-zeolite (pH 8.90±0.10). BR-zeolite was found to remove more Na$^+$ from the CBNG waters and there was a longer breakthrough period as compared to the ST-zeolite. In addition, BR-zeolite released significant K, which is an important plant nutrient. Interestingly there was almost no removal of Na$^+$ or Ca^{2+} released in the column study for the AZ-chabazite, though it has Ca^{2+} as the dominant exchangeable cation and high CEC, suggesting that the Ca^{2+} in the pre-activated Ca-rich chabazite is strongly adsorbed. This may be attributed to the upgrading treatment process of the raw materials, which, according to the manufacturer, involves heating and recrystallization.
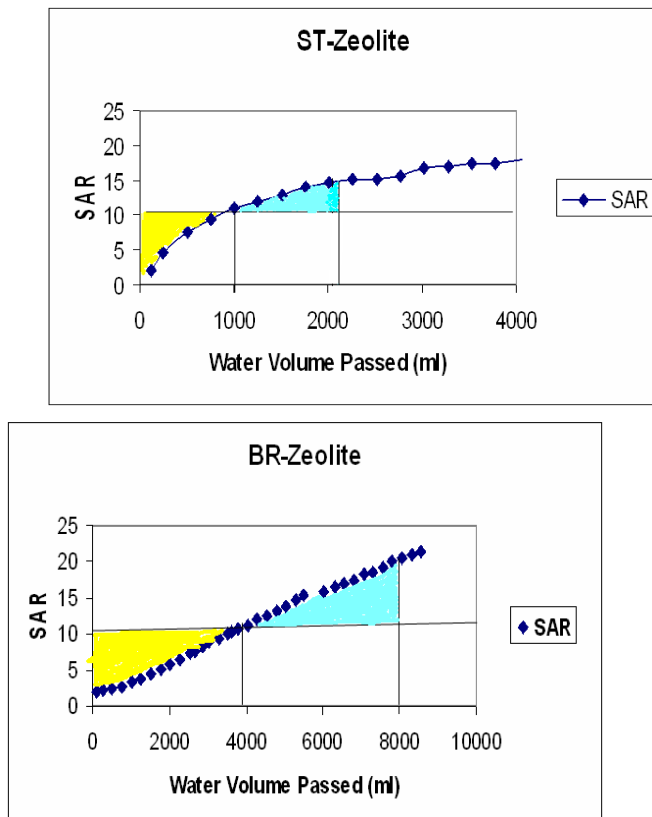
Figure 7-2: SAR breakthrough curves for ST-Zeolite and Br-Zeolite columns.

If one considers CBNG water with SAR values equal to or less than 10 to be suitable for land application, the SAR breakthrough curves shown in Figure 7-2 can be used to estimate flow-through treatment system processes that result in effluent SAR of 10 (Vance et al., 2007). This

would allow for prediction of the amount of CBNG water (SAR = 30) that can be treated per metric tonne of ST-zeolite and BR-zeolite. Results of our studies indicate about 8,000 and 30,000 L of CBNG water (SAR = 30) could be treated by a tonne of ST-zeolite (14×40) and BR-zeolite (14×40), respectively.

In the PRB, WY, CBNG water is generally pumped into reservoirs or ponds. Therefore, if CBNG water were treated in a column and continuously collected in a large containment reservoir, CBNG waters processed initially would have very low SAR values (<<10) with progressive treatment resulting in water with higher SAR values (>10). Thus, if treated waters with high SAR (>10) were mixed with the initially treated waters with low SAR (<<10), then the overall SAR would be less. In order to estimate the overall water volume that can be treated to a mean SAR value of 10, the area between the SAR curve and SAR = 10 cutoff line was integrated. The total amount of additional CBNG waters that could be treated and combined with the initially processed waters to reach a final SAR value of 10 would therefore be estimated using an equivalent area above SAR 10 (upper shaded area). This concept of accumulative treatable water volume is important in defining reduction in CBNG SARs. Extrapolating the results suggests that one tonne of ST-zeolite (14×40) or BR-zeolite (14×40) can treat approximately 16,000 or 60,000 L of the synthetic CBNG Water II (SAR = 30), respectively, to a final SAR around 10, which is considered safe for land application for agricultural use. Therefore, BR-zeolite can treat nearly four times more water than ST-zeolite. However, the maximum adsorption capacities obtained from the adsorption curves were 12.3 and 9.6 (mg g^{-1}) for BR-Zeolite and ST-Zeolite, respectively, suggesting BR-zeolite can treat 1.3 times more than that of ST-zeolite. This discrepancy could presumably be attributed to the lower effective diffusivity (D_e) for Na$^+$ diffusion in the macropores of the ST-zeolite than BR-zeolite as observed in our kinetic studies.

Ca^{2+} Adsorption by WY-Zeolite

Despite a large effective CEC value for the natural WY-zeolite sample, its high exchangeable Na$^+$ content lowers its direct usefulness for the purpose of CBNG water treatment. Modified zeolite samples were therefore developed by converting the exchangeable Na$^+$ to Ca^{2+} before use for CBNG water treatment. The Ca^{2+} and Mg^{2+} adsorption isotherm curves by Na-WY-zeolite showed L-type adsorption that was well described using the Langmuir equation. The maximum Ca^{2+} and Mg^{2+} amount of adsorption by WY-zeolite was 10.3 and 1.2 mg g^{-1}, respectively, accounting for about 30% of the measured effective CEC value.

Results of the Ca-WY-zeolite studies indicated exchangeable Na$^+$ in the natural WY-zeolite was easily replaced using a 0.1 M CaCl$_2$ solution (Ca^{2+} = 4,000 mg L^{-1}); 1 L of 0.1 M CaCl$_2$ solution removed a majority of the exchangeable Na. The amount of Na$^+$ removed in the first leaching of 1 L 0.1 M CaCl$_2$ solution was 23.7 mg g^{-1}, accounting for approximately 75% of the total exchangeable Na$^+$ of the natural occurring Na-WY-zeolite sample. The remaining exchangeable Na$^+$ in the WY-zeolite is strongly adsorbed and hard to replace with Ca^{2+}. These findings were comparable with a previous study reported by Hulbert (1987). Hulbert (1987) investigated Na$^+$, Ca^{2+}, and NH$_4^+$ exchange on zeolite materials collected from an outcrop of blue-green tuff in the Fort LaClede deposit, Sweetwater County, WY and found that Ca^{2+} replaces Na$^+$ with decreasing selectivity as Ca^{2+} loading increases to about 80% at 30ºC and that the Fort LaClede

clinoptilolite at 30°C has a moderate selectivity for Ca^{2+} over Na^+ at < 80% Ca^{2+} loading. Above this loading, the zeolite is slightly selective for Na.

Our batch study results indicated the maximum amount of Ca^{2+} that could be adsorbed was about 10.3 mg g^{-1}. This is slightly lower than that obtained in the packed column study, which was 16.0 mg g^{-1}. This suggests that in a dynamic column system, more Na^+ can be replaced by Ca^{2+} as compared to that in a batch study, presumably due to the constantly high Ca^{2+} concentration in the leaching solution.

Ca^{2+}-Premodified WY-Zeolite

Upon pretreatment with $CaCl_2$, the Na-rich WY-zeolite was converted to a Ca-rich zeolite, which was used for column studies evaluating CBNG water treatment. Results indicate that, as the CBNG water was passed through the Ca-WY-zeolite column, Na^+ was gradually removed with Ca^{2+} and Mg^{2+} being released into the eluting solution, resulting in a lower SAR of the water. This suggests that the Ca^{2+} on the zeolite can be readily exchanged by Na, even though divalent Ca^{2+} has been generally reported to be more competitive than monovalent cations in ion exchange on zeolites.

Defining acceptable SAR values of the CBNG water for irrigation is difficult because soils differ throughout the western U.S. Based upon previous studies and reports (Rice et al. 2000, King et al. 2004ab, Vance et al. 2004), an SAR value of 10 is an acceptable value. With zeolite treatment and breakthrough point set at an acceptable SAR value of 10, one tonne of Ca-WY-zeolite can treat ~60,000 L. However, if CBNG water were treated in a column and continuously collected in a large containment reservoir or in ponds, which occurs in the PRB then CBNG waters processed initially would have very low SAR values (<10) with progressive treatment resulting in higher SAR values (>10). Thus, if leachate with high SAR (>10) were mixed with the initial water with low SAR (<10), the overall SAR would be less (Vance et al. 2007). The area between the SAR curve and SAR=10 cutoff line (lower shaded area in Fig. 7-2) can be integrated in order to estimate the overall water volume that can be treated to a mean SAR value of 10. The total amount of additional CBNG waters that could be treated and combined with the initially processed waters to reach a final SAR value of 10 would thus be estimated using an equivalent area above SAR 10 (upper shaded area in Fig. 7-2). Extrapolating the results suggests that one metric tonne of the pretreated WY-zeolite can treat ~120,000 L CBNG water to reduce its SAR from 30 to an acceptable level of 10, which is nearly twice as much as that when SAR 10 is set as the breakthrough point. Following this method, the treatable water volume using a known amount of zeolite can be estimated to maintain any given SAR value to meet irrigation water quality requirements. However, in this study, the treatable water volume was calculated based upon the breakthrough point at SAR 10.

Effect of Flow Rate, Particle Size and Water Chemistry

Results show that when flow rates were increased from 3.0 to 6.0 ml min^{-1}, the treatable water volume by one tonne of ST-zeolite (14×40) and BR-zeolite (14×40) was reduced from 16,000 or 60,000 L to 11,000 and 50,000 L per tonne, respectively. This would imply that the exchange

reactions are controlled by an external diffusion process. Reduction in contact time results in less Na^+ removed and lower concentrations of Ca^{2+} and Mg^{2+} released.

Column studies using 40×100 BR-zeolite at a flow rate of 16 ml min^{-1} indicated a volume of treatable water of approximately 60,000 L per tonne, which is similar to that observed for 14×40 BR-zeolite at a flow rate of 3.0 ml min^{-1}. This suggests that the finer zeolite particle size and higher flow rate are capable of producing a similar treatment as that using larger particle size and a lower flow rate. Finer particle size zeolites could result in a greater reduction in SAR; however, higher flow rates could result in less Na^+ adsorption and Ca^{2+} release due to the limit of diffusion process depending on zeolite particle size.

Breakthrough curves of CBNG waters in BR-zeolite (14×40) column indicated that because SAR and Na^+ concentration in CBNG Water III was twice as high as that of CBNG Water II less water could be treated. Thus an increase in the initial Na^+ concentration in the CBNG Water resulted in a lower treatable water volume, which was approximately 21,000 L per tonne compared to 60,000 L per tonne for CBNG Water II. Based upon our results, it is reasonable to assume that more water can be treated if the CBNG water contains less Na. However, for practical CBNG water treatment, the actual treatable water volume will be dependent upon its composition chemistry and other factors.

Regeneration of Spent Zeolite Media and Reuse

In order to evaluate the potential for recycling the zeolite media to minimize treatment cost, regeneration of the spent column was carried out using 0.1 M CaCl$_2$ before reuse. Results of the regeneration and reuse studies indicated that a majority (90%) of the adsorbed Na^+ can be replaced by Ca^{2+} after passing 2 L 0.1 M CaCl$_2$ solution through the column. An equivalent amount of Ca^{2+} was adsorbed during the regeneration process, suggesting the spent zeolite media can be recycled. It is anticipated that increasing the concentration of the regeneration CaCl$_2$ solution could result in less CaCl$_2$ solution used as well as a lower volume of spent brine generated, thus lowering treatment costs.

Regeneration of BR-zeolite (14×40) indicated that a majority (90%) of the adsorbed Na^+ can be replaced by Ca^{2+} after leaching 2 L 0.1 M CaCl$_2$ solution (Ca^{2+} = 4,000 mg L^{-1}), suggesting the spent media can be recycled. In addition, the BR-zeolite (40x100) (flow rate = 16 ml min^{-1}) columns can also be regenerated using a 0.1 M CaCl$_2$ solution. Results of the regeneration effluent solution composition indicated that ~2 L 0.1 M CaCl$_2$ solution should be sufficient to remove a majority of the adsorbed Na, which is consistent with regeneration results obtained on 14×40 BR-zeolite at a flow rate of 6.0 ml min^{-1}. Increasing the concentration of the regeneration CaCl$_2$ solution could result in less CaCl$_2$ solution used as well as a lower volume of spent brine generated, thus reducing treatment cost.

Regenerated BR-Zeolite (40×100) was subjected to further CBNG Water II treatment. As compared to the first treatment more CBNG water was treated upon regeneration (76,000 L). This can be attributed to a higher concentration of Ca^{2+} (4,000 mg L^{-1}) in CaCl$_2$ regeneration solutions resulting in further replacement of un-exchanged cations (i.e., Na^+, K^+, Mg^{2+}) upon

treatment in CBNG water, thus making more Ca^{2+} available for replacement and greater treatable water volumes.

The regenerated WY-zeolite column was subjected to further CBNG water treatment. As compared to the first treatment using the WY-zeolite, an equivalent amount of CBNG water could be treated with the regenerated Ca-WY-zeolite (120,000 L). Using natural Ca-rich zeolites, it was found that the treatable water volume at SAR 10 was ~16,000 and 60,000 L per tonne, respectively, for the natural Ca-rich St-zeolite and BR-zeolite. Therefore, the pretreated WY-zeolite resulted in a nearly 700 and 200% more water treated compared to natural Ca-rich zeolite from New Mexico and Idaho, respectively.

Bench-Scale Tank Study

Based upon the kinetic, adsorption isotherm, and column studies discussed above, 250 g of ~325 mesh BR-Zeolite was premixed and added to a bench-scale tank (72 L volume) that contained CBNG water. After allowing the solutions to equilibrate for 24 hr, solution was sampled at two sampling points (-10 and -25 cm). Water chemistry of the bench-scale study simulated CNBG Water I (Table 2). The tank was not disturbed during the experiments.

The results of the bench-scale tank study are presented in Figure 7-3. Observed trend of the change in SAR with amount BR-zeolite added can be extrapolated from the data. It was determined
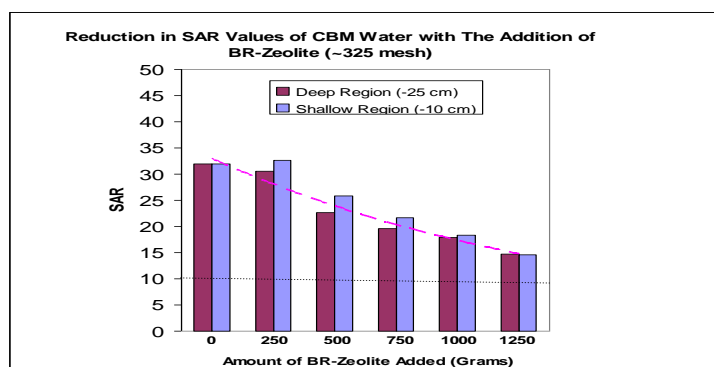
Figure 7-3: Change in SAR versus additions of BR-zeolite.

that about 2 kg of sample would be needed in order to lower the initial SAR value of the water in the 72 L tank from ~ 32 to the level of ~10, which would be equivalent to approximately 4 kg per barrel water. This is consistent with results predicted from the kinetic and adsorption isotherm studies. If the cost for BR-zeolite is ~\$100 per tonne, then the cost for treatment would be around \$0.40 per barrel. This is relatively high because it is a one-time treatment.

Zirconium Phosphate

The potential use of synthetic zirconium phosphate (Zr-P) for treating CBNG waters was also examined. Packed column studies were conducted by using surrogate CBNG waters. Regeneration of the media was also studied. Results of column breakthrough studies using ZrP

indicated a majority (~99%) of the cations could be removed upon passing CBNG water through the columns (Fig. 7-4), with a significant reduction in the pH value of the treated water due to the release of H^+ as a result of cation exchange process.
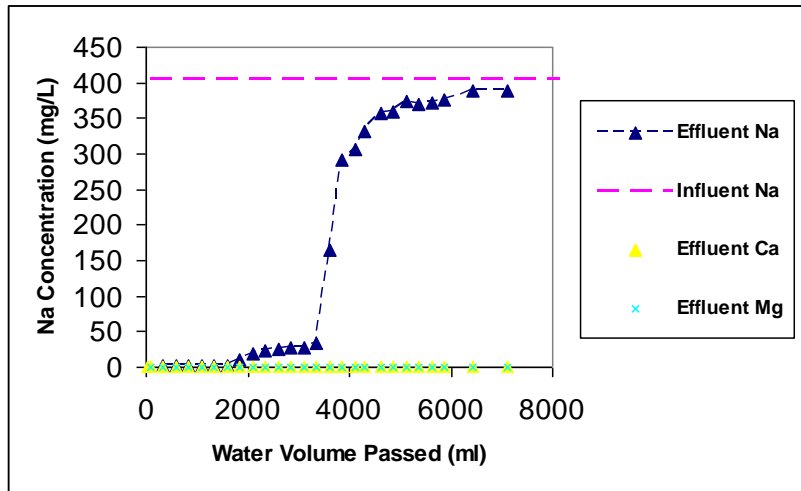
Figure 7-4: Breakthrough cation curves for CBNG water (SAR=30) in ZrP columns.

An estimated 220,000 L of CBNG water ($Na^+ = 411$ ppm, SAR=30) per tonne of ZrP could remove Na^+, Ca^{2+}, Mg^{2+} and K^+. The capacity of a tonne of ZrP was much higher than observed in our natural Ca-rich zeolites for treating CBNG water. We found that the treatable water volume at SAR 10 was only 16,000, 60,000 and 120,000 L per tonne, respectively, for ST-zeolite, BR-zeolite, and the Ca-WY-zeolite. The higher capacity was contributed to the higher CEC value of ZrP.

Results on the column regeneration and reuse of the column for CBNG water treatment indicated a majority (~99%) of the adsorbed cations can be released by passing only 168 ml of 1N HCl, (87% in the first 84 ml leachate), suggesting that the column media could be easily regenerated. It has been well-documented that ZrP is very stable within a pH ranging from 3-10 (Bortun 2006). XRD results also confirmed the high stability of ZrP after CBNG water treatment and regeneration. It can be concluded that the spent media can be easily regenerated using HCl solution for reuse without degradation of treatment performance.

In order to model the column performance, the two-parameter model proposed by Lin and Huang (2000) was used to describe the change in Na^+ concentrations in the ZrP packed column. During the flow-through of the influent aqueous solution flows through the stationary bed of media, some fractions of the Na^+ in aqueous solution is adsorbed by the media while the others pass through the bed. The rate of decrease in the Na^+ concentration can be described by:

$$\left(-\frac{dA}{dt}\right) = kAP \quad (10)$$

where A is the fraction of Na^+ being adsorbed by the column media, and P is the fraction of Na^+ remaining in the aqueous solution and passing through the stationary bed; k is the proportionality constant; and $P = 1 - A$. This equation can be further integrated assuming initial condition of $A = A_a$ at $t = t_a$,

$$ln\left(\frac{A(1-Aa)}{Aa(1-A)}\right)=k(t_a\text{-}t) \qquad (11)$$

or

$$ln\left(\frac{Pa(1-P)}{P(1-Pa)}\right)= k(t_a\text{-}t) \qquad (12)$$

When 50% Na^+ is adsorbed at $P_a = 0.5$, the adsorption time, t_a is designated as τ and the above equation becomes:

$$P = \left(\frac{1}{1+\exp[k(\tau-t)}\right) \qquad (13)$$

or

$$t = \tau + 1/k\,ln\left(\frac{P}{1-P}\right) \qquad (14)$$

or

$$ln\left(\frac{Co}{C}-1\right) = k\tau - kt \qquad (15)$$

The Na^+ fraction (P) that passes through the column is equal to C/C_o in which C is the Na^+ concentration in the aqueous solution at time t and C_o is the original influent Na^+ concentration. Plotting column running time, t, versus $ln[C/(C_o - C)]$ would yield a straight line with intercept and slope of the straight line equal to τ and $1/k$, respectively. Alternatively, τ can also be obtained at the adsorption time when $ln[C/(C_o - C)]$ is zero. The obtained τ and $1/k$ values can be used to establish the entire breakthrough curve.

Lin and Huang's model assumes that 50% breakthrough occurs at τ, thus the media should be completely saturated at 2τ. Due to the symmetrical nature of the breakthrough curve, the amount of Na^+ being adsorbed by the media is half of the total Na^+ entering the column within the 2τ period. Hence, the following equation can be derived:

$$W_e = \tfrac{1}{2}\,C_o\,F(2\tau) = C_oF\tau \qquad (16)$$

Using the above equation, the adsorption capacity of the column (W_e) as a function of the influent Na^+ concentration (C_0), flow rate (F) and the 50% breakthrough time τ can be determined.

The model recently proposed by Lin and Huang (2000) was used here to predict breakthrough time of experimental data. The data for the column running time (t) versus $ln[C/(C_o - C)]$ were linear, though with relatively low correlation coefficient, presumably due to the running interruption of column arising from the pressure buildup. Based on model parameters, both the predicted Na^+ breakthrough curve and data predictions versus experimental breakthrough curves were highly correlated ($R^2 = 0.935$).

CBNG water in the PRB is dominated by Na^+ and bicarbonate (HCO_3^-) ions. In our previous studies using zeolites for treating CBNG waters, we found that zeolite does not remove HCO_3^-

ions in CBNG waters. It is anticipated that post-treatment precipitation of $CaCO_3$ ($K_{sp} = 8.48$), $MgCO_3$ ($K_{sp} = 5.17$) and/or $MgCa(CO_3)_2$ ($K_{sp} = 17.09$), or other solids might occur due to evaporation and thereby leading to an increase in SAR values as suggested from our bench meso-scale studies. Therefore, in order to avoid possible post-precipitation of Ca^{2+} and Mg^{2+}, the use of ZrP would be beneficial if the CBNG water contains high amount of HCO_3^- and CO_3^{2-}. Treatment of CBNG water using ZrP would be able to reduce the water pH value and alkalinity as ZrP releases H^+ and neutralizes the alkalinity during cation exchange process. The treated CBNG water could either be mixed with untreated CBNG water or be further adjusted with other chemicals and technologies to reach desired SAR values for discharge or beneficial use. Overall, results of the ZrP studies indicate Na^+, Ca^{2+}, Mg^{2+} and K^+ could be almost completely removed from CBNG water by ZrP due to its high cation exchange capacity (667 $cmol_{(+)}$ kg^{-1}) with the pH of the treated CBNG reduced due to the release of H^+ from ZrP, resulting in the simultaneous removal of HCO_3^- and/or CO_3^{2-} in water. Adsorption was described using a two-parameter model. Majority (~99%) of the adsorbed Na^+ and other cations were easily removed by using ~ 9.3 ml 1 M HCl g^{-1} ZrP; higher HCl concentrations would result in less brine solution. The regenerated ZrP was not altered and was easily reused without affecting its performance for further CBNG water treatment. Integrating ZrP with other water treatment processes (i.e., post-addition of Ca/Mg/K-bearing materials and/or mixing with untreated CBNG waters) would allow the water quality to be adjusted for discharge or for different beneficial uses.

Field Study - Soil and Water
Results from the CBNG produced water samples collected from nearby the R&E Center included an SAR value of 29.4, which is significantly higher than the acceptable limit of 10 (Zhao et al. 2008ab), but within the range of values reported for PRB CBNG produced waters (5-70). Both EC (2.02 dS m^{-1}) and pH (7.93) of the CBNG water also falls within the range of reported values (0.4-4.9 dS m^{-1} and 6.8-8.0). Figure 7-5 shows the averaged SAR results from composite samples representing the 0-5, 5-15, 15-30, 55-65, and 95-105 cm soil intervals below each borehole. A comparison of the average SAR values for the boreholes that received CBM water suggests that the presence of zeolite resulted in a reduction in SAR for each of the intervals except 5-15cm.
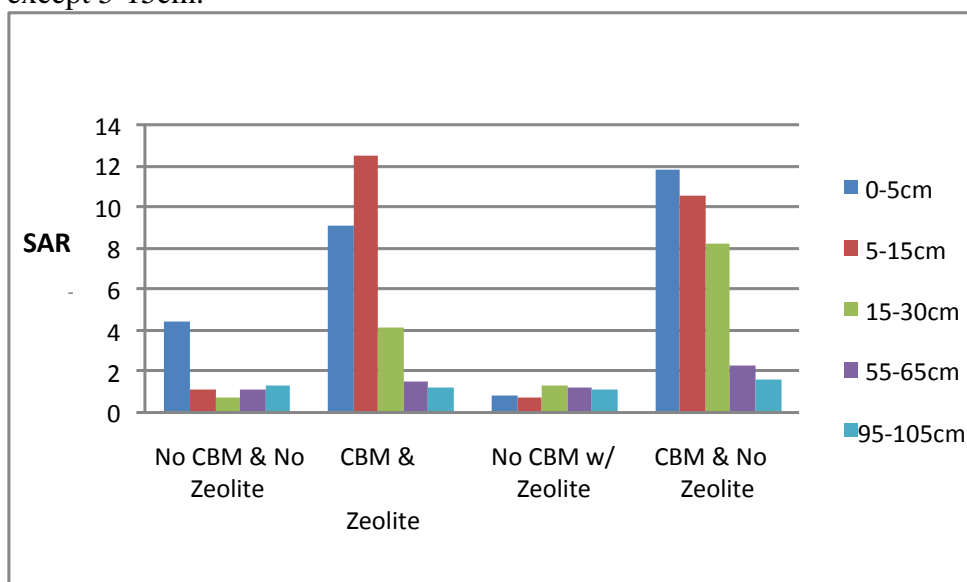
Figure 7-5: Average SAR versus soil interval.

Economic Feasibility

Prices for natural zeolite vary with zeolite content, processing, and world markets. Unit values for the 2005 zeolite market, obtained through a U.S. Geological Survey of domestic zeolite producers, ranged from $50 to $140 per tonne. The bulk of the tonnage sold ranged from $80 and $140 per tonne. The prices for industrial or agricultural applications ranged from $30 to $70 per tonne for granular products down to 40 mesh and from $50 to $120 per tonne for finer (-40 to +325 mesh) ground material. Therefore, not considering other expenses and the potentials of regeneration and reuse of the media, the cost of treating CBNG water with ST-zeolite is about $0.80–1.00 per barrel (159 L), for BR-zeolite approximately $0.20–0.40 per barrel. If repeated use of the column is considered, the cost would be reduced. It is well known that zeolites have many applications as adsorbents in agriculture, water treatment, aquaculture, household products, industry and air/gas treatment. For example, zeolites are used for products such as pet litter, fish tank media, or odor control applications with prices ranging from $0.50 to $4.50 kg^{-1}. Therefore, by exploring applications of the spent zeolite media for other local, regional and/or nationwide uses, there could be a significant reduction in the treatment cost, making the use of zeolite treatment a more feasible, cost-effective technology for CBNG water treatment.

An Integrated Treatment Process

The Na-rich WY-zeolite required Ca-modification before use. Regeneration of Na-WY-zeolite is generally accomplished by leaching with a concentrated Ca^{2+} solution, causing the Na^+ adsorption reaction to be reversed. However, one of the major drawbacks of this process is that most of the salt employed in the regeneration process is flushed out of the system and must be disposed. Many authorities prohibit spent brine solution discharge, requiring users to dispose of the spent brine at an approved site or for use as a commercial alternative water softening method, which generally incurs additional treatment expenses.

In addition to the large quantity of CBNG water generated, Wyoming and other western U.S. states also face serious water quality problems associated with water hardness (http://water.usgs.gov). Water hardness varies throughout the U.S., but water hardness problems are generally found in Arizona, Florida, Indiana, Iowa, Nebraska, New Mexico, South Dakota, Utah, Wisconsin and Wyoming. Water hardness refers to the level of unwanted minerals, principally Ca^{2+} and Mg^{2+}, found in drinking water supplies. Hard water is an aesthetic issue (poor lathering, spots on dishes) and a mechanical issue (clogged pipes, expensive repairs, poor washing machine performance), but it is not a health concern. Municipal water is required by federal law to be treated and tested for sanitation, hardness, corrosivity, and other features.

To address both CBNG water as well as water quality/hardness issues facing Wyoming and other western U.S. states, an integrated study was conducted to develop a cost-effective treatment technology by maximizing the utilization of zeolite materials for treatment of problematic waters. Contrary to the CBNG water treatment process, hard water treatment requires a reduction in the amount of Ca^{2+} and other hard water cations (Fig. 7-6).
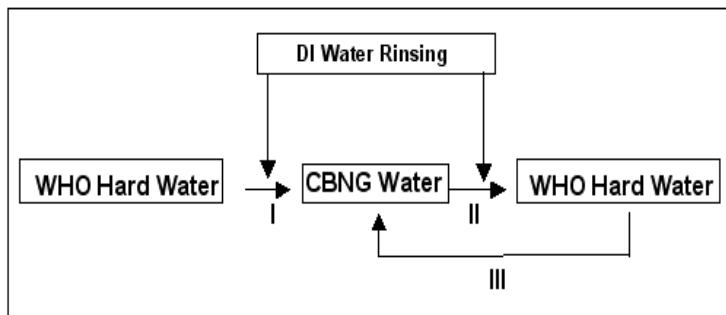
Fig. 7-6: Experimental flowchart of integrated treatment process for hard water (Ca-rich) and CBNG water (Na-Rich) using WY-zeolite.

Results of using the natural WY-zeolite, which is Na-dominant, for hard water treatment indicated that Na-WY-zeolite can effectively remove both Ca^{2+} and Mg^{2+} from hard water and release Na. It was estimated that one tonne of Na-WY-zeolite can treat 125,000 L (~33,000 gallons or ~790 barrels) of hard water to soft water standards by reducing its hardness from 342 mg L^{-1} $CaCO_3$ equivalent to an acceptable hardness of 34.2 mg L^{-1} $CaCO_3$ equivalent. Though WY-zeolite also contains 26 $cmol_{(+)}$ kg^{-1} K, during hard water treatment, little K was released, presumably due to the relatively high cation selectivity for K by clinoptilolite.

After treatment of hard water, spent zeolite media becomes Ca/Mg-rich and can be used for CBNG water treatment. Results of the treatment of CBNG water using Ca/Mg-rich zeolite indicated a tonne of this Ca/Mg-rich zeolite can treat ~120,000 L (~32000 gallons or ~750 barrels) to reduce its SAR from 30 to an acceptable level of 10. Upon rinsing with deionized water, the spent column can then be reused for hard water treatment.

One precaution in this process involves the rinsing step using DI water to remove residual Na^+ in the column. Fine particles may become resuspended and leach from the column as a result of a reduction in ionic strength. This was also observed while rinsing raw WY-zeolite material with DI water, which suggests a loss of some of the most reactive particles and potential blocking of adsorption sites, thereby lowering treatment capacity. However, effluent solutions were clear without suspended solid particles in both hard water and CBNG water treatment processes. For practical applications, the DI water rinsing process is not necessary, and presumably the zeolite capacity would remain higher. Previous studies (Liu and Lo, 2001) also reported the diminishing usable capacity of a zeolite over time for the removal of NH_4, which might be due to incomplete regeneration and/or disintegration of the zeolite.

Conclusions:

Rapid development of the CBNG industry in many parts of the western U.S. has resulted in the co-production of potentially saline-sodic waters. In this study, the potential utilization of Ca-rich and Ca-modified natural zeolites, as well as a ZrP sorbent was examined for removal of Na^+ from CBNG waters in order to lower the water SAR. Column studies indicated that a metric tonne of Ca-modified WY- zeolite can be used to effectively treat ~60,000 (or accumulatively ~120,000) L of CBNG water in order to lower the SAR of the simulated CBNG water from 30 to an

acceptable level of 10. The spent media can be easily regenerated using concentrated CaCl2 solution for reuse.

As compared with previous studies using natural zeolites, the pretreated WY-zeolite had a much higher CBNG water treatment potential than natural Ca-rich zeolites from New Mexico and Idaho. The price of zeolite used for industrial or agricultural applications ranges from \$30–70 tonne for granular products down to 40 mesh (Virta, 2005). Not considering other expenses and the potentials of regeneration and reuse of the media, the material cost of the locally available WY-zeolite used for accumulatively treating CBNG water is much lower, about \$0.05-0.10 per barrel (159 L), as compared to \$0.20-0.40 per barrel for the Ca-rich BR-zeolite (Zhao et al., 2008a) and ~\$1.00-2.00 per barrel for the ST-zeolite (Huang and Natrajan, 2006; Zhao et al., 2008a). Thus, the use of a locally available WY-zeolite in CBNG water treatment appears to be more promising and cost-effective. An integrated treatment process using Na-rich WY-zeolite to alternately treat hard water and CNBG water would also be a potentially promising cost-effective technology, especially in the western United States. One advantage of using zeolite in treating CBNG water and/or hard waters is that it is relatively inexpensive in comparison with traditional methods used for treating waters and addresses regional water problems by using local mineral resources. It would not only reduce the cost of water treatment, but also the burden of generation of wastes, such as spent saline solutions by maximizing the use of adsorbent media by integrating two water treatment processes. The integrated system will also help stimulate the local mining industry as well as improve regional water quality management.

It is well known that zeolites have many applications as adsorbents in agriculture, water treatment, aquaculture, household products, industry and air/gas treatment (Mumpton, 1999; Virta, 2005). Therefore, by exploring other applications of the spent zeolite media for other consumers, there could be a further reduction in treatment costs, making the use of zeolite treatment a more feasible, and cost competitive technology in CBNG water treatment.

CBNG water treatment using ZrP appears to be an efficient and affordable means of improving the quality of saline-sodic CBNG irrigation water since a tonne of ZrP can be used to treat 220,000 L (~58,000 gallons or 1,400 barrels) by removing the Na^+ and other cations in CBNG water. This is due to its high CEC value which is much higher than Ca-rich zeolites for treating CBNG water. Use of ZrP resulted in a significant reduction of water pH due to the release of H^+, which also leads to the removal of aqueous HCO_3^- and/or CO_3^{2-}. This would be beneficial for preventing the possible post-precipitation of solids and subsequent increase in SAR values. The spent ZrP media can be easily regenerated using HCl solution for reuse without degradation of treatment performance. Integrated with other water treatment technologies (i.e., water mixing and/or post-addition of Ca/Mg/K-bearing materials), the water quality can be further adjusted for discharge for various purposes. The spent media can be easily regenerated using HCl solution for reuse without degradation of the treatment performance.

References:

Austin G.S. and R.S. Bowman. 2002. St. Cloud Mining Company's Stone House Zeolite Mine and new uses for clinoptilolite, Proc. Soc. for Mining, Metallurgy and Exploration (SME) National Meeting, SME, Littleton, CO, USA.

Bureau of Land Management (BLM). 2003. Final Environmental Impact Statement and Proposed Plan Amendment for the Powder River Basin Oil and Gas Project. Volumes 1 to 4, US Department of Interior, BLM, Casper, WY.

Cerri, G., Langella, A., Pansini, M. and Cappelletti, P. 2002. Methods of determining cation exchange capacities for clinotilolite-rich rocks of the Logudoro region in Northern Sardinia, Italy. Clays and Clay Minerals 50:127-135.

Ganjegunte, G.K. and G.F. Vance. 2005. Evaluation of changes in soil chemistry from leaching saline-sodic waters through Powder River Basin soils: A column study approach. Presented at the American Society of Agronomy/Soil Science Society of America Annual Meetings, Salt Lake City, UT. Agronomy Abstracts CD p. 212

Ganjegunte, G.K., L.A. King and G.F. Vance. 2008. Cumulative soil chemistry changes from application of saline-sodic waters. Special Issue: Environmental impacts and sustainable reuse of degraded water reuse. Journal of Environmental Quality 37:S-128-S138 (Invited Special Issue)

Ho Y.S. and G. McKay. 1999. Pseudo-second order model for sorption processes, Process. Biochem., 34:451–465.

Ho Y.S. and G. McKay. 2000. The kinetics of sorption of divalent metal ions onto sphagnum moss peat. Water Res. 34:735–742.

Hulbert, M.H. 1987. Sodium, calcium, and ammonium exchange on clinoptilolite from the Fort Laclede Deposit, Sweetwater County, Wyoming. Clays and Clay Minerals Vol. 35 (6):458-462.

Jackson R.E. and K.J. Reddy. 2007. Geochemistry of CBNG produced water in the Powder River Basin: Salinity and sodicity. Water, Air, Soil Poll.
Kabata-Pendias, A. 2001. Trace elements in soils and plants. CRC press, Boca Raton, FL, 413 pp.

King, L.A., J. Wheaton, G.F. Vance and G.K. Ganjegunte. 2004a. Water issues associated with coalbed methane [natural gas] in the Powder River Basin of Wyoming and Montana. Reclamation Matters. 2:7-12.

King, L.A., Vance, G.F. Ganjegunte and G.K. and Carroll, B.K. 2004b. Vegetation responses to saline-sodic coalbed methane waters in the Powder River Basin. Living with Coalbed Methane. Montana Soil and Water Conservation Society Proceedings, Billings, MT.

Lin, S.H. and C.Y. Huang. 2000. Modelling of aqueous BTEX adsorption in column and multistage adsorbers. Journal of Environmental Engineering 126:802-806.

Mumpton, F.A. 1999. La roca magica: Uses of natural zeolites in agriculture and industry. Proc. Natl. Acad. Sci. USA. Vol. 96, pp. 3463–3470. Colloquium Paper.

Ruthven, D.M. 1984. Principles of Adsorption and Adsorption Processes, Wiley-Interscience, New York.

Ruthven, D.M. 1984. Principles of Adsorption and Adsorption Processes, Wiley-Interscience, New York.

Vance, G.F., L.A. King and G.K. Ganjegunte. 2004. Coalbed methane co-produced water: Management options, Reflections, June 31–34.

Vance, G.F. L.A. King and G.K. Ganjegunte. 2008. Soil and plant responses from land application of saline-sodic waters: Implication of management. Special Issue: Environmental impacts and sustainable reuse of degraded water reuse. Journal of Environmental Quality 37:S-139-S148.

Vance, G.F., H. Zhao, M.A. Urynowicz, G.K. Ganjegunte and G.W. Gregory. 2007. Potential utilization of natural zeolites for treating coalbed natural gas (CBNG) produced waters: Batch and column studies. Presented at the 2007 National Meeting of the American Society of Mining and Reclamation, Gillette, WY, June 2-7, 2007. R.I. Barnhisel (Ed.) Published by ASMR, 2134 Montavesta Rd., Lexington, KY 40502.

Virta, R.L. 2004. U.S. Geological Survey Minerals Yearbook.

Zhao, H., G.F. Vance, G.K. Ganjegunte, and M.A. Urynowicz. 2008a. Use of zeolites for treating natural gas co-produced waters in Wyoming, USA. Desalinization Journal 228:263-276.

Zhao, H., G.F. Vance, M.A. Urynowicz and R.W. Gregory. 2008b. Integrated treatment process using a natural Wyoming clinoptilolite for remediating produced waters from coalbed natural gas operations. Applied Clay Science (Available online doi:10.1016/j.clay.2008.03.007)

Task 8 – Longitudinal Changes in Toxicity of CBNG Produced Water along Beaver Creek in the Powder River Basin, Wyoming

Laurie Heath and Joseph S. Meyer[8]

By-products of coal formation include methane (CH_4), carbon dioxide (CO_2), nitrogen-containing compounds (e.g., ammonia -- NH_3) and water (De Bruin et al. 2004). Along with the relatively high concentrations of CO_2, groundwater in coal beds in the Powder River Basin (PRB) of northeast Wyoming can contain elevated concentrations of total dissolved solids [TDS, often dominated by sodium (Na^+) and bicarbonate (HCO_3^-) ions in those coal beds] compared to many surface waters (Meyer et al. 2007: pp. 10-16). Because elevated concentrations of Na^+, HCO_3^- and ammonia can be toxic to fish and other aquatic life, disposal of CBNG produced water is a concern (Clearwater et al. 2002).

Often, produced water from multiple CBNG wells is piped into an ephemeral drainage via a central discharge point or outfall, resulting in year-round, effluent-dominated flow. Although water quality of some CBNG effluents might be predicted to adversely affect aquatic life in these drainages (Clearwater et al. 2002), fish have been observed swimming in CBNG effluent-dominated streams, such as Beaver Creek, many km upstream from their confluences with the Powder River (personal communication, Todd Adams, CBM Associates, Inc., Laramie, Wyoming, USA; February 2006).

Ammonia is one of the most important pollutants in the aquatic environment because it is widely distributed and relatively toxic to aquatic organisms (Russo 1985). Ammonia assumes two chemical forms: (1) the positively charged (ionized) ammonium (NH_4^+) ion, which is less toxic; and (2) the neutral (un-ionized) ammonia molecule (NH_3, also referred to herein as UIA), which is more toxic. The TA-N concentration is the sum of those two forms. The relative amounts of NH_4^+ and NH_3 are a function of pH, temperature and ionic strength (Russo 1985).

Rice et al. (2000) reported the pH of produced water analyzed from wellheads in the PRB ranged from 6.8 to 7.7. Although these CBNG produced waters contain high concentrations of HCO_3^- and thus usually would have higher pH, the CO_2-supersaturated water from deep wells has approximately circumneutral pH. As CO_2 degasses from the supersaturated waters when they contact the atmosphere, the H^+ concentration of the produced water decreases. Therefore, the pH of CBNG effluents generally increases as the effluents flow downstream and CO_2 degasses.

Produced waters tend be dominated by Na^+, Ca^{2+}, Mg^{2+} and HCO_3^- (Table 5 in Clearwater et al. 2002). When those waters contact stream beds containing gypsum ($CaSO_4$) soils, Ca^{2+} and SO_4^{2-} can be mobilized. In addition to the Ca^{2+} already in the produced water, the increased Ca^{2+} concentrations should cause calcium carbonate ($CaCO_3$) to precipitate, with a concomitant buffering of the pH at ~8.0 to ~8.5. Therefore, the pH of the produced water should increase as it flows downstream, but at a slower rate than if the produced water did not dissolve gypsum – due to the increased amount of $CaCO_3$ buffering that is possible because of the increased amount

---

[8] Department of Zoology and Physiology. University of Wyoming, Laramie, WY. email: meyerj@mywdo.com

of Ca^{2+} in the water. If the pH remains circumneutral at or near the outfall, the ammonia would be dominated by the less toxic form (NH_4^+).

Since 2004, Wyoming Pollution Discharge Elimination System (WYPDES) permits have required monitoring of some CBNG effluents with acute and chronic, static-renewal whole effluent toxicity (WET) tests (USEPA 2002a, 2002b). Standard static-renewal WET tests expose organisms in beakers of effluent, which are placed in a water bath and are exposed to the ambient atmosphere. The pH of the effluent in those beakers is partly controlled at equilibrium by the partial pressure of CO_2 (pCO_2) in the atmosphere over the solution. The higher the pCO_2, the more protons are produced and the lower the pH (Mount and Mount 1992). In this report, we refer to beakers of fish exposed to ambient atmosphere in the laboratory as ambient-pH because the pH depends in part on the ambient atmosphere in the room.

If CO_2 degasses from the open containers (ambient-pH beakers), the pH increases. These pH increases can be very important for ammonia toxicity. For example, increasing the pH from 7.8 to 9.0 increases the percentage of unionized ammonia by approximately an order of magnitude. Therefore, use of ambient-pH toxicity test methods could arte-factually increase the pH and the ammonia toxicity of CBNG effluent. For that reason, USEPA (2002b) approved CO_2 pH-controlled WET test methods to maintain the pH of the effluent at stream conditions. The CO_2 pH-controlled method is similar to the ambient-pH method, but the toxicity tests are conducted inside sealed glass chambers blanketed with an air mixture into which 2 to 3% CO_2 is injected. In this study, we compared the ambient-pH and CO_2 pH-controlled toxicity methods.

Before this study, limited data were available about the toxicity of CBNG produced waters to aquatic organisms. Three other studies within the past few years evaluated streams influenced by CBNG produced water in the Tongue River and Powder River watersheds of Wyoming. Forbes (2003) tested several CBNG wellhead produced waters and nearby stream waters to determine if they were acutely or chronically toxic to two aquatic invertebrates (*Ceriodaphnia dubia* and *Daphnia magna*) and the fathead minnow (FHM; *Pimephales promelas*). She concluded that only 2 of the 30 waters were acutely toxic to FHM, of which both waters were collected from streams that had unknown CBNG effluent contribution.

WDEQ (2003) implemented a study to examine the potential toxicity of CBNG produced waters by collecting water samples for acute and chronic WET tests from 10 sites in the PRB. Based on results of that study, WDEQ (2004) concluded that any toxicity issues related to CBNG produced water are limited to areas of the Big George coal seam. Acute and chronic WET tests using *Daphnia magna* and FHM were incorporated into WYPDES permits that discharge from the Big George coal seam beginning in 2004.

Finally, since 2003 the United States Geological Survey (USGS) has been evaluating the potential toxicity of $NaHCO_3$ in streams influenced by CBNG produced water. Those researchers have conducted laboratory toxicity tests with $NaHCO_3$ added to simulated Tongue River and Powder River waters and have conducted in-situ seasonal caged-fish studies similar to the approach used in this study (USGS 2006, Farag et al. 2007). Although the research is on-going, they concluded that 96-h LC50s (median lethal concentrations) for early life stage fish exposed to $NaHCO_3$ in simulated Tongue River and Powder River waters were 1,100 to 1,600

mg NaHCO$_3$/L (USGS 2006). Farag et al. (2007) reported significant in-situ mortality of caged FHM larvae <24 h old, in summer 2006.

We hypothesized that in-stream biogeochemical changes in CBNG produced water alter its toxicity and thus allow aquatic organisms to inhabit ephemeral drainages at predictable distances downstream from produced-water discharge points. Additionally, we hypothesized that ambient-pH laboratory toxicity test methods arte-factually increase ammonia toxicity. To test these hypotheses, we conducted a four-tiered study in Beaver Creek, a tributary to the Powder River, Wyoming. In 2006 and 2007, we conducted three seasonal field bouts that included (1) in-stream toxicity tests using caged FHM larvae placed along a longitudinal gradient downstream from a CBNG discharge point, (2) concurrent laboratory toxicity tests in ambient-pH and CO$_2$ pH-controlled conditions with the same batch of FHM larvae exposed to water collected at the same in-stream locations as the caged-fish tests, (3) geochemical analyses of the effluent-dominated water, and (4) complementary studies that sampled fish, amphibian, and reptile populations during summer 2006. We also evaluated the potential for changes in ammonia concentrations while CBNG-related waters are transported from the field to the laboratory.

Herein we predominantly discuss the potential toxicity of ammonia in CBNG effluents because ammonia is labile; therefore, its fate and effects can be altered considerably by interactions with a stream ecosystem. However, in this report we also discuss the potential toxicity of NaHCO$_3$, which will be less influenced by in-stream biogeochemistry.

Methods:

This project had two components: (1) field and laboratory toxicity tests, with associated water-chemistry analyses and stream-community surveys, and (2) an ammonia-lability study. For the first component, we conducted field bouts in July/August and October 2006, and January 2007. For the second component, we conducted ammonia-lability experiments in October 2006 and March 2007. Because the October 2006 ammonia-lability results were inconclusive, we herein only include March 2007 results. Johnson (2007) reported the October 2006 results.

Study Site

We conducted this study on Beaver Creek in Campbell County, northeast Wyoming. This region receives an average annual precipitation of 40 cm (http://www.wrcc), with warm summers (average 29 °C) and cold winters (average 12 °C) (http://www.weather.com). Vegetation along Beaver Creek includes small shrubs, sagebrush, and short prairie grasses. Land uses include livestock grazing, wildlife habitat, oil and gas development, and recreation.

Historically, Beaver Creek was ephemeral before CBNG development. It flows ~65 km from the headwaters to the Powder River (Fig. 8-1). The CBNG effluent we studied (WYPDES WY0046922-001) is discharged by Williams Production RMT Company into Beaver Creek, 25 km upstream from the Powder River. The study reach was 14 stream km long.
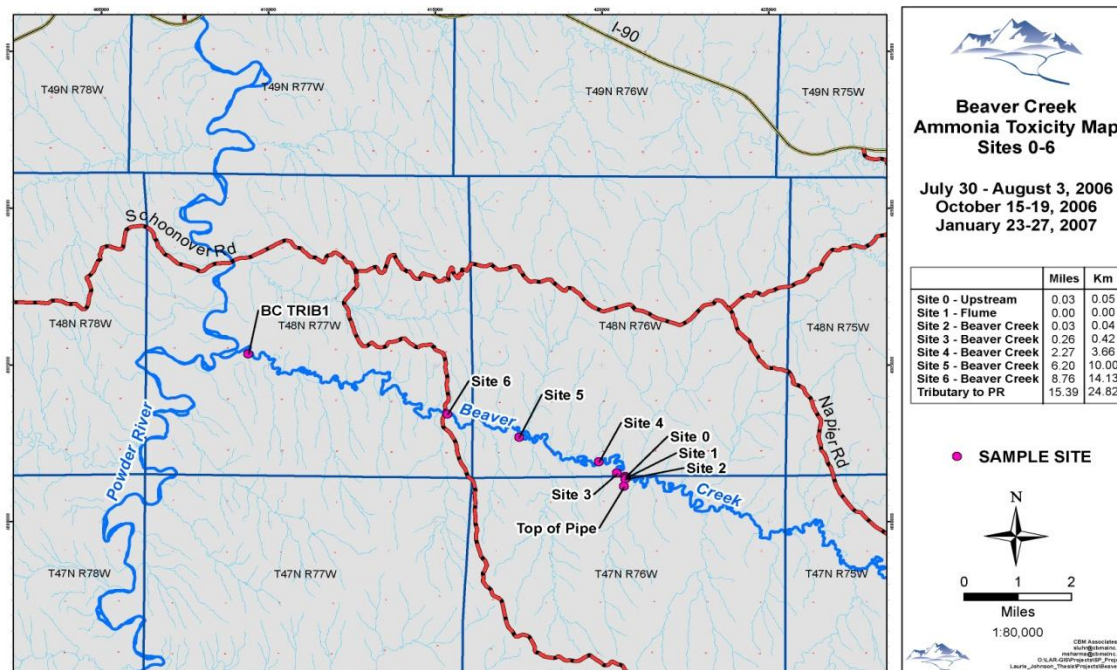
Figure 8-1: Beaver Creek is a tributary to the Powder River in northeast Wyoming. In-stream toxicity tests were conducted at Sites 1 to 6, which were 24.8, 24.8, 24.4, 21.1, 14.8 and 10.7 km, respectively, upstream from the confluence with the Powder River.

Approximately 150 to 180 CBNG wells piped produced water to an initial surface-discharge point (top-of-pipe) 300 m from Beaver Creek. From there the water flowed into two retention ponds (15 m × 15 m wide, 2.5-3 m deep) and then entered an underground collection system, from which it was piped to a concrete flume that discharged into Beaver Creek.

In this study, the top of the concrete flume was Site 1, 24.8 km from the confluence with the Powder River. Sites 2 to 6 were 0.04, 0.4, 3.7, 10.0 and 14.1 km, respectively, downstream from the end of the concrete flume. In-stream toxicity tests using caged fathead minnow (FHM) larvae were conducted at Sites 1 to 6, and water was collected for laboratory toxicity tests and chemical analyses at the same sites. We sampled water at Site 0 directly upstream from the flume only during the July/August 2006 field bout, but no in-stream or laboratory toxicity tests were conducted with that water.

Effluent flow into Beaver Creek was measured using a flume meter. Beaver Creek dimensions (~0.3 m deep × ~4 m wide) varied with the flow and seasonal vegetation. The stream bed consisted of fine sediment at Site 1 to fine gravel at Site 6. In July/August, the vegetation changed from algae near the outfall, to short wetland grasses near Site 3, to taller wetland grasses at Site 5. At Site 6, Beaver Creek opened into a meadow that cows grazed.

Toxicity Tests

We conducted in-stream and laboratory toxicity tests with FHM larvae. The in-stream tests were conducted according to Burton (2005). Concurrent toxicity tests were conducted at the

University of Wyoming's Red Buttes Environmental Biology Laboratory, following standard 96-h static-renewal methods (EPA 2002a). In Table 2-1 in Johnson (2007), test conditions used in the in-stream and laboratory toxicity tests are compared to the test conditions specified by EPA (2002a). The in-stream and the laboratory toxicity tests used the same batch of taxonomically verified FHM that were hatched at ENSR Analytical Laboratory, Fort Collins, Colorado, on 18 July and 2 October 2006, and on a combination of 9 and 12 January 2007. The ages of the fish at initiation of the in-stream toxicity tests were 12 and 13 d old in July/August and October, respectively, and a combination of 11 and 14 d old in January. The ages of the fish at initiation of the laboratory tests were 14, 15, and a combination of 12 and 15 d old in July/August, October and January, respectively. For in-stream tests, Burton (2005) recommended using 7- to 14-d-old FHM larvae because 1- to 7-d-old larvae have decreased survival using this in-situ test design. Because younger larvae tend to be more sensitive to toxins, the optimal age of fish would have been closer to 7 d, but difficulties coordinating the hatch dates and the field weeks precluded our using younger fish. We used FHM because they have a sufficient toxicity database (Burton 2005) and inhabit ephemeral drainages of the PRB (Davis 2008).

The larvae were transported from ENSR Lab to Red Buttes Lab in culture water. At Red Buttes Lab, the fish were acclimated to water with a hardness of ~155 mg/L as $CaCO_3$, whereas the average hardness at Site 1 during a pilot study was ~160 mg/L as $CaCO_3$. Each batch of hardness-acclimated fish was split at Red Buttes Lab, with one-third transported to the PRB in oxygenated, temperature-monitored coolers. The remaining two-thirds were held at Red Buttes Lab for use in the ambient-pH and CO_2 pH-controlled WET tests.

At each site during each field bout, we acclimated the fish to the temperature of the site water before pipetting 10 FHM into an in-situ cage in a tub of site water. The in-situ cages were constructed of cellulose acetate/butyrate transparent core tubing (12.7 cm long × 6.7 cm diameter, 448 ml capacity; Fig. 8-2). Removable polyethylene closures capped each end; and two rectangular windows (4 cm × 8 cm) cut on opposite sides were covered with 250-μm nylon mesh, allowing water to flow through. The cages were submerged below the water surface with the mesh windows perpendicular to the stream current and then were emptied of air by gently tapping the sides. At each site, 6 replicate cages were secured in a plastic-covered-wire basket according to a randomization grid. The end of the basket was weighted with bricks, secured by plastic zip ties. A tarp-covered diversion was placed directly upstream from the basket to control flow and prevent debris from clogging the cages.
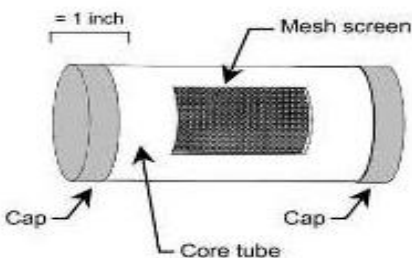
Figure 8-2: Cages (12.7 cm long × 6.7 cm diameter; 448 ml capacity) used in in-stream toxicity tests. Removable caps on both ends allowed easy access, and rectangular mesh side windows allowed water to flow through.

Before each deployment, we measured stream pH, temperature and dissolved oxygen concentration in the creek. Cages were deployed at Sites 1 to 6 in July/August and October. In January, cages of FHM were deployed only at Sites 1 to 4, because Sites 5 and 6 were frozen. Cage 3 was not deployed at Site 3 during January because we did not have enough fish. Because water-temperature fluctuations seemed to adversely affect the fish during October, we attached temperature probes to the baskets at Sites 2, 3 and 4 during January.

At each site, cages 1 to 5 were not opened and were left primarily undisturbed for 96 h, as suggested by Burton (2005). The only exception was that we cleaned the nylon mesh daily to ensure adequate water flow through the cages. Cage 6 was opened at 48 h, and survival was recorded; however, this was not used to calculate 96-h survival. At 96 h, we recorded final pH, temperature and dissolved oxygen concentration and recorded live and dead fish in each cage.

We included a field control and a handling control in each field bout. The field control, a plastic tub filled with Red Buttes well water, had 4 to 5 replicate cages of FHM. The tub of well water was placed in the creek between Sites 1 and 2 to maintain in-stream temperature and lighting. The field-control water was renewed at 48 h with Red Buttes well water at the in-stream temperature. The handling control determined if the transport and handling of the fish adversely impacted survival. After the last site deployment, we pipetted 10 FHM into at least three cages and had them transported to Red Buttes Lab in a cooler of aerated well water, within 24 h of deployment. At Red Buttes Lab, these handling-control cages of fish were acclimated in ~3 L of well water before being placed into the same water bath as the laboratory toxicity-test beakers. Survival was recorded at time of receipt and at 96 h.

On either the day of deployment (in January) or the next day (in July/August and October), two 4-L cubitainers of unfiltered, unpreserved water were collected from each test site and transported on ice the same day to Red Buttes Lab. After they arrived at the laboratory, the cubitainers were refrigerated overnight, and static-renewal 96-h whole effluent toxicity (WET) tests (USEPA 2002a) were initiated with one cubitainer from each site, within 36 h of collection. The second cubitainer of site water was used to renew the exposure solutions in the WET tests at 48 h.

The FHM at Red Buttes Lab were held in well water in flow-through plastic tubs and fed twice daily with 24-h-old brine shrimp (*Artemia* sp.) until test initiation. In July/August and January, 10 fish were added to each beaker in the ambient-pH test and 10 fish were added to each beaker in the CO_2 pH-controlled test. In October, only 8 fish were used in the laboratory WET-test beakers because not enough fish were available. In July/August and October, the WET tests were conducted at 20 °C; in January, the tests were inadvertently conducted at 25 °C.

To prepare the ambient-pH WET tests, 5 randomly placed replicate beakers of each undiluted site water and 5 replicate beakers of well water (lab control), all with fish added, were incubated in 20 or 25 °C water baths open to room air. For the CO_2 pH-controlled tests, each site had 5 randomly placed replicate beakers of undiluted site water and 2 replicate beakers of well water (lab control), all with fish, placed in a CO_2 chamber. During October and January, one beaker of

each water (well and site) in each treatment (ambient-pH and CO_2 pH-controlled) was incubated without fish to determine the effect the fish had on ammonia concentrations.

All beakers used in the CO_2 pH-controlled studies were placed in sealed glass chambers (41 cm long × 20 cm wide × 14 cm deep). A separate glass chamber was used for each site. An air mixture containing 2 to 3% CO_2 was injected into each chamber at ~0.3 psi for ~5 seconds, and then the chamber was immediately sealed. Daily, pH of water in each chamber was recorded; and additional CO_2 gas was added if the pH increased more than 0.3 units from the initial pH. Additional CO_2 gas was not added after the initial 96 h.

In the laboratory, water temperature, dissolved oxygen and pH were recorded daily from one replicate of each treatment. Additionally, fish survival was recorded daily for at least 96 h; and survival was recorded daily for 144 h during October and January. To monitor pH drifts, the 5 remaining beakers in both treatments were incubated an additional 48 h after the end of each 96 h test (i.e., 144 h total). Because the second 4-L cubitainer was used to renew all beakers at the original 48 h, this additional time resulted in a 96-h un-renewed extended exposure time.

Field Observations of Biota

We recorded observations of fish, frogs and snakes during each field bout. The Wyoming Game and Fish Department (WGFD) conducted an amphibian-and-reptile survey on 28 June 2006 (Turner 2007). Davis (2008) seined four 300-m reaches along Beaver Creek on 26 and 27 July 2006, and calculated richness and diversity of the fish assemblages. Davis's Site A was downstream near the mouth of the Powder River, Site B was our Site 6, Site C was our Site 5, and Site D was between our Sites 2 and 3.

Ammonia Lability

After an initial, inconclusive ammonia-lability study in October 2006 (see Johnson 2007), we conducted a second study in March 2007. In that study, we compared results among several laboratories and among several shipment and handling methods, and tested if ammonification occurs between time of sampling at the stream and receipt of samples at a lab a few hours to days later. Total ammonia nitrogen concentrations at various subsampling times were analyzed in samples sent to Energy Labs Inc. in Gillette, Wyoming and Billings, Montana (ELI-G and ELI-B, respectively), Parametrix Environmental Research Laboratory in Albany, Oregon (PERL), Columbia Analytical Services, Inc. in Kelso, Washington (CAS) and Red Buttes Lab in Laramie, Wyoming (RB). Total nitrogen, NO_3^- and NO_2^- were analyzed in samples sent to ELI.

In the laboratory, we filled a 20-L cubitainer with deionized water to monitor contamination during collection and transport. In the field, we also filled 20-L cubitainers with water collected from the top-of-pipe and from ~ 40 m downstream in Beaver Creek (in-stream). These cubitainers were subsampled at 6 time intervals (0, 1, 2, 8, 24 and 48 h) in such a way as to minimize air input and to maintain their original pH. In addition to sub-sampling for TA-N analyses, we froze unfiltered, unpreserved samples to be analyzed for NO_3^- and NO_2^- at ELI. Details of the sampling procedure are presented in Johnson (2007).

The role a given laboratory plays in PRB CBNG water chemistry analyses and toxicity testing determined what collection and shipping methods were to be used for that laboratory. For example, PERL conducts WET tests on effluent discharged from CBNG outfalls in the PRB, using unfiltered, unpreserved samples that are shipped to it via air. They analyze TA-N by ion-selective electrode (ISE) and ship acid-preserved subsamples to CAS for TA-N analysis by colorimetry. Therefore, we daily shipped by air to PERL, two refrigerated sets of bottles (one bottle in each set was unfiltered and unpreserved, and the other bottle was filtered and unpreserved) to be analyzed at PERL by ISE on one set, and the other set was to be acid-preserved by PERL and then shipped overnight to CAS for colorimetric TA-N analysis. These subsamples were designated as PERL/CAS. Similarly, acid-preserved samples are sometimes collected at the same time as water for a WET test and shipped by ground to ELI for colorimetric TA-N analysis. In this study, we shipped refrigerated acid-preserved filtered and acid-preserved unfiltered samples for TA-N and TN analyses along with frozen unpreserved, unfiltered samples for NO_3^- and NO_2^- to ELI via ground transportation. Also, with the original intent to check if transportation choice (ground versus air) affected TA-N concentration, we packaged 48-h refrigerated acid-preserved filtered and acid-preserved unfiltered samples to be shipped overnight by air to CAS; however, due to a shipping error by the University of Wyoming, those samples were sent via ground transportation. Finally, subsamples taken directly from the unpreserved ELI bottle at each collection time were fixed with colorimetric reagent and stored on ice in a dark cooler, for same-day TA-N analysis at Red Buttes Lab. Deionized water containing known concentrations of TN, TA-N, nitrate (NO_3^-) and nitrite (NO_2^-) were sent as blind samples to ELI, and blind samples of TA-N were sent to CAS and PERL to check analytical accuracy.

Chemical Analyses

In the field, temperature, pH, conductivity, turbidity and dissolved oxygen were recorded once or twice daily at all sampling locations. Along with the toxicity test water, water samples were collected and transported to Red Buttes Lab for chemical analysis. Water samples for anions, cations, and dissolved organic carbon were filtered on-site (0.45 μm). At Red Buttes Lab, major inorganic anions (Cl^-, NO_2^-, NO_3^-, SO_4^{2-}; by ion chromatography), major inorganic cations (Ca^{2+}, K^+, Mg^{2+}, Na^+; by flame atomic absorption spectrophotometry), alkalinity (by H_2SO_4 titration), TA-N (by colorimetry), TN (digestion followed by colorimetry), dissolved organic carbon (by combustion), and total barium (by inductively coupled plasma-mass spectrometry) were analyzed according to standard methods (APHA et al. 1995). Bicarbonate was computed using a geochemistry speciation program. Concentrations of un-ionized ammonia (UIA) were calculated from temperature, pH and TA-N concentrations, according to USEPA (1999). Duplicate acid-preserved samples were collected from the same location in the stream and analyzed at ELI-G and ELI-B for TA-N (by colorimetry), NO_3^- (by ion chromatography), NO_2^- (by ion chromatography), and TN (by Kjeldahl). Blind samples of known concentrations of TA-N, NO_3^- and NO_2^- were analyzed at Red Buttes Lab and ELI to test analytical accuracy.

Data Analyses

To evaluate in-stream toxicity, we compared fish survival at each site to survival of the field control for each season. Similarly, survival in each beaker of both laboratory methods (ambient-pH WET tests and CO_2 pH-controlled WET tests) was compared to survival of each method's

well-water control. As recommended in the USEPA (2002b) flowchart for analysis of multi-effluent-concentration test data, we transformed percentage survival data using the angular transformation. If the number of replicates was unequal, a Wilcoxon Rank Sum test with Bonferroni adjustment was used to determine significance using Toxcalc 5.0.23F (Tidepool Scientific Software, McKinleyville, California, USA). When the number of replicates was equal, Steel's Many-One Rank test in Toxcalc 5.0.23F was used to determine significance. A site was considered non-toxic if survival did not differ significantly from the control (P>0.05). In the field in July/August, not all the FHM were accounted for at 96 h because muskrats tore into cages at Sites 2 and 3, presumably allowing fish to escape. Also, because some of the fish were small, they could not be found at some sites when the cages were pulled from the water -- probably because they were caught in mud on the sides of the cages. Therefore, percentage survival for those replicates was based on the number of fish that were confirmed alive or dead at 96 h. Because all 10 fish were missing from muskrat-torn cage 3 at Site 3 in July/August, that replicate was removed from the survival analysis.

The criteria maximum concentration (CMC) and criteria continuous concentration (CCC) for ammonia were calculated using Equations 3 to 5 in USEPA (1999: p. 83). We used the CMC equation for waters in which salmonid cold-water species are absent because salmonids are not normally found in ephemeral Beaver Creek. Then we calculated the ratio of TA-N (analyzed colorimetrically at ELI) divided by the CMC or the CCC. During July/August, we calculated the 4-d mean of the TA-N/CCC quotient at Sites 3 and 4 to determine if the mean quotient was <1.

For each field bout, we regressed the natural logarithm of ammonia concentration on pH, temperature and distance downstream from the CBNG outfall, and also regressed ln(TA-N) on temperature and downstream distance combined. The null hypothesis was that the slope of each regression was zero (α = 0.05).

Results and Discussion:

Toxicity Tests

The maximum air temperatures were 38, 22 and 11 °C and the minimum air temperatures were 20, 3, and 0° C, respectively in July/August, October and January. No significant rain or snow events occurred during the three field bouts. Effluent flows measured at the flume (Site 1) were 0.045, 0.024, and 0.061 m^3/s in July/August, October and January, respectively.

The closest CBNG discharges entering Beaver Creek were 30 km upstream and 14 km downstream. During the study period, Beaver Creek did not flow immediately upstream of the discharge point. Instead, in July/August only, standing water backed up ~45 m upstream from the discharge point; and in October and January, no water was in the stream bed upstream from the discharge point. Therefore, the study reach was only influenced by the discharge at Site 1. Downstream of the study reach, Beaver Creek was effluent-dominated and hydraulically connected to the Powder River during the entire study period.

The chemistry of the effluent and Beaver Creek water did not appear to cause acute toxicity within the 14-km study reach. Major losses of fish occurred only at Sites 1, 2 and 3 in

121

July/August, at Sites 5 and 6 in October (P<0.05 at both sites), and at Site 4 during January (P<0.05) (Fig. 8-3; Table 8-2 thru 8-4 and Appendix Tables B-1 to B-5 in Johnson 2007); and all those losses appeared to be caused by factors not related to water chemistry (see following paragraphs). The field controls and the handling controls had >80% survival in all field bouts.
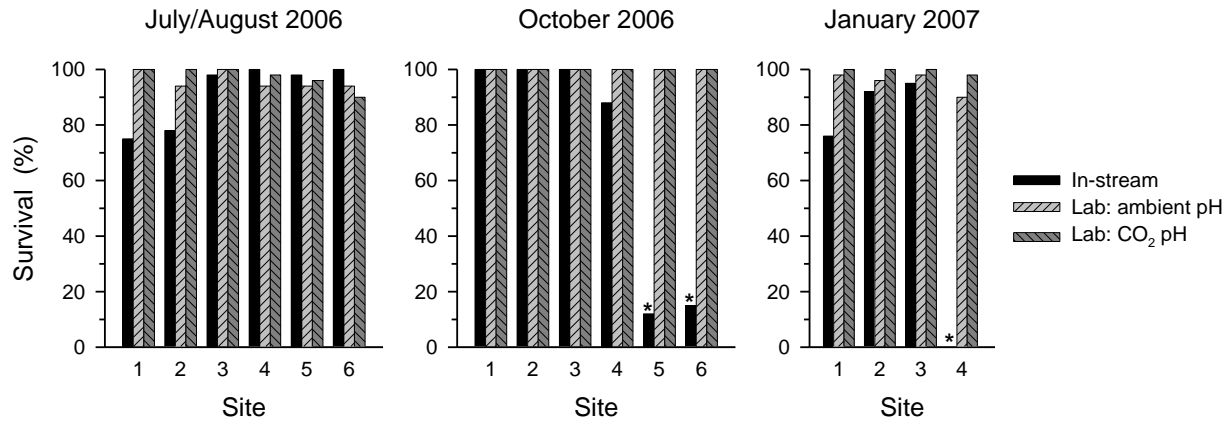

Figure 8-3: 96-h survival of fathead minnow (*Pimephales promelas*) larvae in water at Sites 1 to 6 in Beaver Creek, Wyoming, during three field bouts conducted from July 2006 through January 2007. In-stream = caged fish exposed *in situ* in Beaver Creek; Lab: ambient pH = fish exposed in beakers open to room atmosphere; Lab: CO_2 pH = fish exposed in beakers inside chambers containing elevated CO_2 concentrations; * = significantly less than field or laboratory controls (P<0.05). All three significant decreases in survival occurred when water temperatures were ≤2 °C on at least one morning. Sites 5 and 6 were not tested in January 2007 because the creek was frozen.

For unknown reasons, no fish survived in one cage at Site 1 in July/August; however, because 78, 100, 100 and 100% of the fish survived in the other four cages, the complete mortality in the one replicate did not appear to be related to water chemistry. At Sites 2 and 3 in July/August, muskrats scratched holes in the cages, allowing some fish to escape while all the remaining fish were alive and active.

At Sites 5 and 6 in October, the water temperature was <0.7 °C on 18 October; and at Site 4 in January, the water temperature was ≤2 °C on 26 and 27 January (Appendix Table C-1 and Appendix E in Johnson 2007). Hart (1947) reported the lower incipient lethal temperature (LILT; i.e., the minimum temperature at which 50% of the fish died) for FHM acclimated to 20 °C water was 1.5 °C, and the LILT for FHM acclimated to 30 °C was 10.5 °C. The FHM in that study were 1- to 2-year-old fish collected from the Don River in Thornhill, Ontario and then acclimated to 10, 20 or 30 °C water for 24 h. The FHM acclimated to 10 °C survived all low temperatures tested (i.e., the LILT was <0 °C). We are unaware of other LILT studies for FHM.

For several reasons, it is difficult to definitively conclude from Hart's (1947) study whether the low temperatures in Beaver Creek on some mornings killed our fish. For example, Hart's fish were much older than the FHM larvae in our study and thus might have been less sensitive to low temperatures; therefore, the LILT for our FHM larvae might have been >1.5 °C.

Additionally, Hart's fish were acclimated to a single temperature for 24 h before being exposed to low temperatures, whereas our caged larvae in Beaver Creek were exposed to highly variable temperatures during the 96-h exposures (<0.7-11.9 °C at Site 5 in October, <0.7-12.4 °C at Site 6 in October, and 1.0-8.5 °C at Site 4 in January; Appendix Table C-1 in Johnson 2007). We do not know how long our FHM larvae were exposed to the very low temperatures (e.g., $\leq$2.0 °C) at Sites 5 and 6 in Beaver Creek in October; but in January, the FHM larvae were exposed to temperatures $\leq$2.0 °C for ~2 h on day 4 (Appendix E in Johnson 2007). These uncertainties make the field data alone difficult to interpret. However, because (1) we used a presumably more sensitive life stage in our study than was used in Hart (1947) and (2) FHM larvae exposed to water collected from the same sites at the beginning of each field bout and maintained at 20 or 25 °C in the laboratory had $\geq$90% survival (Appendix Tables B-2 and B-4 in Johnson 2007), we conclude based on a weight of evidence that low water temperatures and not the water chemistry in Beaver Creek were the most likely cause of the deaths of the caged FHM larvae at Sites 5 and 6 in October and at Site 4 in January.

All lab controls had >90% survival, indicating acceptable exposure conditions in the laboratory studies. The pH of the water in the CO_2 pH-controlled test chambers did not increase more than 0.3 units from the pH at the beginning of the test to the end of the 96-h period, indicating acceptable pH control. No significant mortality occurred in the ambient-pH and CO_2 pH-controlled toxicity tests by 96 h (Fig. 8-3; Appendix Tables B-2 and B-4 in Johnson 2007). However, mortality in the ambient-pH beakers maintained in the water bath for an additional 48 h (i.e., for 96 h un-renewed) was greater than in the CO_2 pH-controlled beakers held an additional 48 h (Table 8-2 thru 8-4 and Appendix Tables B-3 and B-5 in Johnson 2007). The pH spikes and increased UIA in the ambient-pH beakers at 144 h (96 h since last renewal; Tables 2-5 to 2-8 in Johnson 2007) suggest the increased mortality probably was caused by ammonia. Although 144 h exceeds the USEPA (2002a) recommendation for a 96-h static-renewal test, survival in the beakers of well water (control) and the CO_2 pH-controlled test beakers was similar at 96 and 144 h (Table 2-4 in Johnson 2007).

The results of those extended-exposure toxicity tests support our hypothesis that pH drift can artifactually increase the toxicity of ammonia in CBNG produced waters tested in the laboratory. Because pH did not drift as much in the CO_2 pH-controlled tests, fish did not die when the exposure waters were not renewed for 96 h. Therefore, the CO_2 pH-controlled method appears to be a more acceptable method for testing CBNG produced water in the laboratory.

Overall, the lack of toxicity attributable to the chemistry of the CBNG effluent in the present study is consistent with Forbes' (2003) results. However, our toxicity results do not completely agree with results reported by USGS researchers (USGS 2006, Farag et al. 2007).

Farag et al. (2007) conducted in-stream toxicity tests in Beaver Creek during the same week as our July/August field bout. The Farag et al. (2007) site labeled "Upper Beaver" was only ~40 m downstream from our Site 6, but another CBNG outfall discharged into Beaver Creek between the two sites. Bicarbonate and TA-N concentrations were 1,646 mg/L and 0.5 mg N/L, respectively, at their site compared to 1,759 mg/L and <0.10 mg N/L, respectively, at our Site 6 in July/August. The increase in ammonia at the Upper Beaver site was most likely due to the influx of new CBNG water between Site 6 and that site. Because the HCO_3^- concentration at

Site 6 was greater than at the Upper Beaver site, HCO_3^- did not appear to have caused the higher toxicity reported by Farag et al. (2007).

Farag et al. (2007) reported 96-h toxicity (only 37% survival) to 2-d-old FHM larvae in in-situ cages at their Upper Beaver site but no significant toxicity (75% survival) to 6-d-old FHM larvae at the same site. In contrast, our in-stream toxicity test at Site 6 in July/August 2006 had 100% survival. The in-stream cages and protocol that Farag et al. (2007) used were the same as ours, except Farag (2007) had smaller size mesh on the cages, the cages were kept in a covered container (no light), and they were opened daily to record survival. Additionally, our FHM larvae were older than the larvae used by Farag et al. (2007).

Generally, younger fish are more sensitive to toxicants than are older fish (EPA 2002a). The EPA (2002a) guidelines for acute toxicity testing recommend 1- to14-d-old larvae for laboratory tests, whereas Burton (2005) recommended FHM larvae in in-situ cages be >7-d-old. The larvae used in our July/August field bout were 11 d old at test initiation compared to the 2- and 6-d-old larvae in Farag et al. (2007). Therefore, the significant difference in mortality between their 2-d-old larvae and their 6-d-old larvae at the Upper Beaver site probably was caused by an age-specific difference in sensitivity, but the difference in mortality between Farag et al.'s (2007) 2-d-old larvae at the Upper Beaver site and our 11-d-old larvae at Site 6 might have been caused by a combination of age-specific differences in sensitivity, site-specific differences in ammonia concentration, or differences in the study design.

In laboratory waters that were prepared to mimic water quality in the Tongue River and the Powder River, 96-h LC50s for early life stage FHM exposed to $NaHCO_3$ were 1,100 to 1,600 mg $NaHCO_3$ /L (USGS 2006). Consistent with those results, Mount et al. (1997) reported 96-h LC50s of $NaHCO_3$ to 1- to 7-d-old FHM ranging from <310 to1,220 mg/L. In contrast, we measured Na^+ concentrations ranging from 567 to 646 mg/L and HCO_3^- concentrations ranging from 1,637 to 1,818 mg/L in Beaver Creek (Table 8-1), with no acute toxicity attributable to water chemistry. This would seem to indicate that either (1) other components in Beaver Creek water or sediment mitigate toxic effects of $NaHCO_3$ to FHM or (2) the younger FHM larvae used by USGS (2006) and Mount et al. (1997) were more sensitive to $NaHCO_3$. The varying FHM life stages seined along a 24-km reach of Beaver Creek (Davis 2008; see also Figure 2-11 in Johnson 2007) demonstrate that FHM grow and probably reproduce in the CBNG product-water-dominated stream, yet adverse effects cannot be excluded. Additional field studies of the chronic effects (growth and reproduction) of CBNG product water using younger FHM larvae are needed to investigate that possibility.

Water Chemistry

In all three field bouts, pH, conductivity, Na^+ and Mg^{2+} increased from Site 1 to Site 6, but alkalinity, HCO_3^-, F^-, Cl^-, K^+ and DOC varied little among the sites (Tables 8-1 and 8-2). Barium concentration decreased downstream from the outfall as SO_4^{2-} increased. Calcium concentration also decreased downstream in July/August and October; however, a similar decrease was not evident in January because Sites 5 and 6 (where the decreases were most pronounced in previous months) were frozen. Total nitrogen concentration analyzed at ELI seasonally ranged from 3.2 to 3.6 mg N/L at Site 1 and was 1.2 mg N/L at Site 6 in October

(only month analyzed; Table 8-2), whereas TA-N concentrations ranged from 1.4 to 1.5 mg TA-N/L at Site 1 and from <0.1 to 0.2 mg TA-N/L at Site 6 (Table 8-4). All NO_2^- concentrations were <0.30 mg N/L, and all NO_3^- concentrations were <0.58 mg N/L.

Table 8-1: Water quality in Beaver Creek in the Powder River Basin, Wyoming in July/August and October 2006, and January 2007 and analyzed at the University of Wyoming's Red Buttes Laboratory in Laramie, Wyoming. DOC = dissolved organic carbon (mg/L).

								Concentration (mg/L)								
Month	Site	Date	Time	Field pH	Hardness (as $CaCO_3$)	Alkalinity (as $CaCO_3$)	HCO_3^-	F^-	Cl^-	SO_4^-	Ba^{2+}	Ca^{2+}	K^+	Mg^2	Na^+	DOC (mg/L)
July/August	0	7/31/06	0555	8.90	NA	NA	1785	2.6	19.6	137	0.12	12	13	25	690	11.9
	1	7/31/06	0639	7.83	160	1414	1672	2.3	15.5	2	0.84	27	14	18	576	4.0
	2	7/31/06	0655	8.00	163	1409	1667	2.2	16.4	<1	0.86	26	14	18	575	4.3
	3	7/31/06	0730	8.24	164	1435	1651	2.0	13.5	<1	0.85	26	13	18	567	4.8
	4	7/31/06	0755	8.74	135	1406	1658	2.3	15.6	33	0.46	14	14	19	599	3.9
	5	7/31/06	0835	8.95	130	1454	1669	2.3	16.6	51	0.31	12	14	21	611	6.1
	6	7/31/06	0905	9.09	126	1472	1759	2.3	17.1	52	0.26	10	15	22	646	4.3
October	1	10/16/06	0730	7.39	159	1447	1765	2.1	15.4	<1	0.85	30	16	20	603	3.4
	2	10/16/06	0805	7.67	159	1479	1752	2.0	15.3	<1	0.84	30	16	20	598	4.1
	3	10/16/06	0845	7.91	167	1452	1746	2.1	14.8	8	0.82	31	16	20	598	4.7
	4	10/16/06	0930	8.24	177	1436	1714	2.0	15.9	74	0.56	29	16	24	613	4.3
	5	10/16/06	1020	8.45	183	1383	1660	2.1	14.4	136	0.35	22	16	29	620	4.9
	6	10/16/06	1100	8.56	168	1367	1637	2.1	16.5	144	0.28	18	15	28	623	5.2
January	1	1/23/07	0725	7.33	171	1494	1768	1.9	12.2	<1	0.85	31	16	20	601	4.0
	2	1/23/07	0900	7.91	173	1483	1784	2.1	12.3	<1	0.85	30	16	20	608	4.3
	3	1/23/07	1015	7.96	181	1494	1818	1.8	12.8	17	0.84	32	16	21	617	4.1
	4	1/23/07	1215	8.32	200	1457	1752	1.9	14.8	76	0.68	34	16	26	618	5.1

Table 8-2: Total nitrogen (TN) in Beaver Creek in the Powder River Basin, Wyoming analyzed at the University of Wyoming's Red Buttes Laboratory in Laramie, Wyoming (RB) and at Energy Labs Inc. in Billings, Montana (ELI). Total nitrogen was not analyzed in July/August 2006. At each site, duplicate samples were collected into two different bottles, one preserved (ELI) and one unpreserved (RB). Additional preserved samples collected throughout the week were analyzed at ELI. Complete data are in Appendix D in Johnson (2007).

| Month | Site | Red Buttes Lab[a] | | Energy Labs Inc.[a] | | |
		n	TN (mg N/L)	n	Average TN (mg N/L)[b]	S.D.
October	1	1	3.86	2	3.60[A]	0.14
	2	1	3.49	2	3.50[A]	0.00
	3	1	3.90	2	3.55[A]	0.07
	4	1	2.53	2	2.70[B]	0.14
	5	1	2.00	2	1.70[C]	0.00
	6	1	1.56	2	1.25[C]	0.07
January	1	1	3.34	3	3.23[A]	0.15
	2	1	3.52	3	3.13[A]	0.25
	3	1	3.62	3	3.17[A]	0.38
	4	1	3.06	3	3.03[A]	0.21

[a] RB analyzed TN using digestion by $K_2S_2O_8$, followed by colorimetry; whereas ELI analyzed TN using a Kjeldahl method.
[b] The same letter following the value indicates that the means of the ELI analyses did not differ significantly (P>0.05) among sites within the month.

Although pH increased as the CO_2-supersaturated produced water flowed downstream (Table 8-1), it did not increase as high as it would have if the same water had degassed in a beaker in the laboratory, probably because $CaCO_3$ precipitated in the stream and consequently buffered the pH. Ammonia concentration decreased in the creek (Table 8-1), probably because it was assimilated by plants and microbes. Calcium and Ba^{2+} decreased as SO_4^{2-} increased downstream (Table 8-1), probably due to dissolution of gypsum ($CaSO_4$) followed by precipitation of $CaCO_3$ and barite ($BaSO_4$). Alkalinity, F^-, Cl^-, K^+ and DOC varied little from Site 1 to Site 6 (Table 8-1), indicating little groundwater or precipitation influence. Overall, interactions with the atmosphere and stream substrate not replicated in a laboratory environment appeared to provide mitigating factors that helped decrease toxicity of the CBNG produced water to aquatic life.

Table 8-3: pH measured in Beaver Creek in the Powder River Basin, Wyoming; in stream water, on arrival at Red Buttes Laboratory in Laramie, Wyoming, and in one beaker of each method at WET test initiation, at 96 h, and at 144 h. NA = measurements not available; Y = yes; N = no.

Month	Site	Fish in beaker	pH Field	Arrival at Red Buttes	Initial (0 h)	Ambient-pH 96 h	Ambient-pH 144 h	pH-controlled 96 h	pH-controlled 144 h
July/August	1	Y	7.83	7.79	7.99	8.78	8.93	8.09	8.18
	2	Y	8.00	7.95	8.06	8.74	8.97	8.12	8.18
	3	Y	8.24	8.25	8.37	8.83	9.03	8.22	8.26
	4	Y	8.74	8.58	8.64	9.00	9.08	8.32	8.26
	5	Y	8.95	8.76	8.76	9.08	9.13	8.56	8.44
	6	Y	9.09	8.88	8.90	9.06	9.18	8.48	8.48
October	1	Y	7.39	7.71	8.00	8.82	9.05	8.06	8.10
	1	N	7.39	7.71	8.00	9.11	NA	8.24	NA
	2	Y	7.67	7.85	8.02	8.75	9.09	8.10	8.06
	2	N	7.67	7.85	8.02	9.16	NA	8.20	NA
	3	Y	7.91	8.10	8.27	8.90	9.07	8.27	8.30
	3	N	7.91	8.10	8.27	9.19	NA	8.32	NA
	4	Y	8.24	8.47	8.44	8.96	9.14	8.39	8.38
	4	N	8.24	8.47	8.44	9.18	NA	8.47	NA
	5	Y	8.45	8.68	8.66	9.05	9.10	8.58	8.35
	5	N	8.45	8.68	8.66	9.23	NA	8.55	NA
	6	Y	8.56	8.80	8.85	9.07	9.17	8.70	8.63
	6	N	8.56	8.80	8.85	9.25	NA	8.71	NA
January	1	Y	7.33	NA	8.12	9.08	9.23	8.13	8.17
	1	N	7.33	NA	8.12	9.38	9.45	NA	NA
	2	Y	7.91	NA	7.93	9.03	9.22	8.20	8.09
	2	N	7.91	NA	7.93	9.35	9.43	NA	NA
	3	Y	7.96	NA	8.24	9.06	9.28	8.21	8.25
	3	N	7.96	NA	8.24	9.38	9.44	NA	NA
	4	Y	8.32	NA	8.41	9.12	9.29	8.32	8.22
	4	N	8.32	NA	8.41	9.37	9.45	NA	NA

Table 8-4: Total ammonia nitrogen (TA-N) analyzed colorimetrically at Red Buttes Laboratory in Laramie, Wyoming (RB) and Energy Labs Inc. in Billings, Montana (ELI). At each site, duplicate samples were collected into two different bottles, one preserved (ELI) and one unpreserved (RB). Additional preserved samples collected throughout the week were analyzed at ELI. Complete data are in Appendix D in Johnson (2007).

| Month | Site | Red Buttes Lab | | Energy Labs Inc. | | |
		n	TA-N (mg N/L)	n	Average TA-N (mg N/L)[b]	S.D.
July/August	0	1	0.11	2	<0.1	NA
	1	1	2.40	2	1.45	0.21
	2	1	2.40	2	1.35	0.21
	3	1	2.33	2	1.20	0.00
	4	1	0.58	2	0.50	0.28
	5	1	0.00	2	<0.1	NA
	6	1	0.00	2	<0.1	NA
October	1	1	2.68	3	1.47	0.12
	2	1	2.68	3	1.50	0.00
	3	1	2.66	3	1.37	0.06
	4	1	1.49	3	0.97	0.15
	5	1	0.75	3	0.47	0.06
	6	1	0.36	3	0.20	0.10
January	1	1	2.60	3	1.40	0.20
	2	1	2.62	3	1.30	0.20
	3	1	2.63	3	1.27	0.21
	4	1	2.32	3	1.07	0.12

Natural logarithm of TA-N was significantly negatively related to the distance downstream from the discharge point in all three months (Table 2-14 in Johnson 2007). Additionally, ln(TA-N) was significantly positively related to water temperature in October and January but not in July/August. A consistent negative relationship existed between ln(TA-N) and pH in all three months, although it was only significant in July/August and October. When all three seasons were combined, ln (TA-N) was significantly related to a combination of distance and temperature (Table 2-14 in Johnson 2007). If the regression coefficients from that multiple linear regression are applied to the drainage, on average total ammonia concentrations decrease by ~18%/km (i.e., $e^{-0.201} = 0.818$) and by approximately 6%/°C (i.e., $e^{-0.058} = 0.944$). This regression coefficient for distance indicates that 90% of the original TA-N in the effluent would be removed after the effluent flowed 11.5 km downstream.

Means of the ratio of TA-N in Beaver Creek to the CMC or CCC less than one would indicate compliance with USEPA (1999) ammonia criteria. The acute criterion ratio (TA-N/CMC) was less than one at all sites in all three field bouts (Fig. 2-9 and Table 2-15 in Johnson 2007). The chronic criterion ratio (TA-N/CCC) with early life stage (ELS) present or absent was >1 at Sites 3 and 4 in July/August, but only the TA-N/CCC with ELS present ratio was >1 at Site 4 in October and January. The TA-N/CCC ratios with ELS present and absent exceeded 1 in July/August at Sites 3 and 4 in the afternoon, but not in the morning at the same location. However, the means of the TA-N/CCC ratio for the morning and afternoon single grab samples at Sites 3 and 4 over the 4-d period were 1.1 and 1.2, respectively; therefore, the waters at those sites exceeded the chronic criterion for ammonia.

The UIA concentrations in Beaver Creek were well below the FHM LC50s for UIA that are listed in Appendix 4 of USEPA (1999) (Figure 2-10 in Johnson 2007). Additionally, the TA-N concentrations in Beaver Creek in July/August (0-1.6 mg N/L) were lower than the seasonal ammonia limits in the Willow Creek watershed general permit (3.1 mg N/L in July and 2.2 mg N/L in August) (Table 2-16 in Johnson 2007).

Field Observations of Biota

Fish were seen at all sites in July/August and at Sites 2 and 3 in October and January (Appendix C in Johnson 2007). Toad metamorphs, adult toads, bull snakes, intermountain wandering garter snakes, and muskrats were also observed along Beaver Creek during the study periods. Turner (2007) observed early life stage boreal chorus frogs (*Pseudacris maculate*) and Woodhouse toads (*Bufo woodhousii*) near the outfall (Site 2). He concluded the amphibians were using portions of the river as breeding sites, where habitat was suitable. He also concluded the water in the arid landscape was a possible attractant and resource to the aquatic community (personal communication, Bill Turner, Wyoming Department of Game and Fish, Herpetological Coordinator, Laramie, Wyoming; February 1, 2007 – email correspondence). Davis (2008) found seven fish species along Beaver Creek (Table 2-17 in Johnson 2007). Fathead minnows of various sizes were at every site, suggesting growth and reproduction (Fig. 2-11 in Johnson 2007).

Combined, these observations suggest no overt adverse effects from CBNG effluent discharged into Beaver Creek during 2006-2007. However, the acute toxicity of Beaver Creek water to 2-d-old FHM larvae reported by Farag et al. (2007) indicates at least part of the aquatic community might be adversely affected. Therefore, more extensive ecological assessments would have to be conducted to evaluate community-level effects of CBNG effluent.

Ammonia Lability

In March 2007, NO_2^- and NO_3^- were below their detection limits (0.1 mg N/L), and the UIA concentrations were ≤0.01 mg N/L at top-of-pipe and 0.01 to 0.03 mg N/L at Site 2 (Table 3-2 in Johnson 2007). The TN and TA-N concentrations were considerably higher (up to 3.9 mg N/L at top-of-pipe and up to 2.8 mg N/L at Site 2). Because the TN and TA-N concentrations in paired filtered and unfiltered samples usually agreed within 0.2 mg N/L (Table 3-2 in Johnson 2007), herein we present results only for unfiltered samples.

At top-of-pipe, TN concentration ranged from 3.7 to 3.9 mg N/L, and TA-N (colorimetric) concentration ranged from 1.4 to 2.4 mg N/L over the 48-h period (Fig. 8-4a). Therefore, on average, ~50% of the TN (1.3-2.5 mg N/L) might have been organic nitrogen and available for ammonification (Fig. 8-4a). Results were similar at Site 2, for which TN concentration ranged from 2.3 to 2.8 mg N/L, and TA-N (colorimetric) concentration ranged from 0.5 to 1.3 mg N/L over the 48-h period (Table 3-2 in Johnson 2007). On average, ~60% of the TN (1.2-2.3 mg N/L) in that creek water might have been organic nitrogen and available for ammonification (Fig. 3-9 in Johnson 2007).

The TA-N concentrations analyzed at ELI on acid-preserved samples were consistently lower than the CAS, PERL/CAS and RB analyses on unpreserved or preserved samples (Fig. 8-4b for top-of-pipe; Table 3-4 and Fig. 3-8 in Johnson 2007 for Site 2). Although TA-N concentrations in the PERL analyses of unpreserved samples were similar to the ELI analyses of acid-preserved samples, the PERL analyses are inconclusive because that lab underestimated the concentration in a blind sample of known TA-N concentration by 43%.

A cooler containing acid-preserved samples packed at <4 °C was supposed to be shipped overnight by air to CAS; however, due to a shipping error, it arrived 5 d later in a truck with a temperature in the cooler of ~9 °C. The TA-N concentrations reported by CAS were 0.9 to 1.3 mg N/L higher than those reported by ELI for paired samples (Fig. 8-4b). Therefore, although the CAS sample was preserved, the increased temperature and delay of transport appear to have contributed to an increase in TA-N, probably from ammonification.
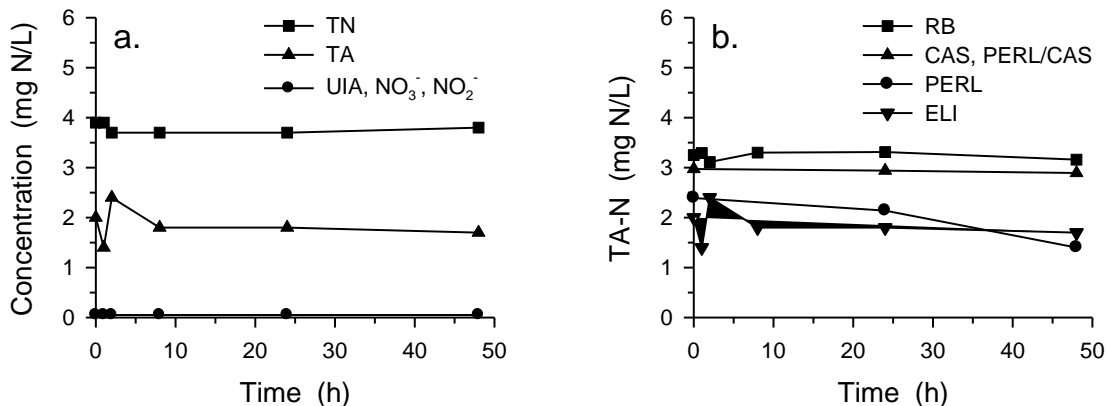
Figure 8-4: Concentrations of nitrogen-containing compounds in top-of-pipe samples of CBNG effluent flowing into Beaver Creek, Wyoming, in March 2007. (a) Total nitrogen (TN), total ammonia (TA), un-ionized ammonia (UIA), nitrate (NO_3^-) and nitrite (NO_2^-) analyzed in acid-preserved samples (TN and TA) and in frozen, unpreserved samples (NO_3^- and NO_2^-) by Energy Labs Incorporated (ELI). All UIA (calculated from temperature, pH and TA), NO_3^- and NO_2^- concentrations were <0.1 mg N/L. (b) Total ammonia concentrations analyzed by the University of Wyoming's Red Buttes Lab (RB), Columbia Analytical Services (CAS), Parametrix Environmental Research Lab (PERL), and ELI -- on acid-preserved samples using colorimetry (ELI), on unpreserved samples using colorimetry (RB and CAS), on initially unpreserved samples that were acid-preserved after receipt at PERL and then shipped to CAS for colorimetry (PERL/CAS), and on unpreserved samples using ion-selective electrode (PERL). The CAS and PERL/CAS analytical results overlap. Similar results for water collected from Site 2 are presented in Figures 3-8 and 3-9 in Johnson (2007).

In the March 2007 study, we intended to determine real-time TA-N concentrations using the RB samples, assuming that the TA-N concentration would be 'fixed' in the field by the addition of the colorimetric reagent (i.e., maintained until analyzed at RB). We anticipated that the 'fixed' RB TA-N concentrations would equal the acid-preserved ELI TA-N concentrations; however, the unacidified RB samples had higher TA-N concentrations (Fig. 8-4b), indicating ammonification probably occurred even after addition of the colorimetric reagents to the water.

These results clearly demonstrate that ammonification can occur within 24 h in unpreserved and/or improperly transported samples. Nitrogen budgets indicated that one or more organic nitrogen species might be a significant component of the TN, because the summations of TA-N, UIA, NO_3^- and NO_2^- concentrations were less than TN (Fig. 8-4a; and Fig. 3-9 in Johnson 2007). Therefore, ammonification in unpreserved CBNG effluent probably increased the TA-N concentrations during transport and/or storage.

In summary, refrigerated unfiltered, acid-preserved samples transported within 24 h of collection and analyzed using colorimetry appear to have the least biased TA-N concentrations. Although, we cannot evaluate whether some ammonification also occurred in acid-preserved samples, we conclude that acid preservation at least minimized the amount of ammonification.

Conclusions:

The chemistry of CBNG effluent and Beaver Creek water did not cause acute toxicity to 11- to 15-d-old FHM larvae, either in in-stream or laboratory toxicity tests. Although another in-situ study conducted in Beaver Creek suggested possible $NaHCO_3$ toxicity to younger FHM larvae (Farag et al. 2007), no toxicity occurred in the present study with waters containing slightly higher $NaHCO_3$ concentrations. However, FHM are not among the most sensitive species to NH_3 and $NaHCO_3$, and the FHM larvae used in the present study (11- to 15-d old) might not have been as sensitive to NH_3 as the younger larvae used by Farag et al. (2007).

Field observations of aquatic plants and animals suggest no overt adverse effects from CBNG effluent discharged to Beaver Creek during the 2006-2007 study periods.

For CBNG-related waters in the Powder River Basin, CO_2 pH-controlled WET tests are more appropriate than ambient-pH WET tests in which the pH can increase considerably.

The biogeochemistry of the interactions between the CBNG produced water and the Beaver Creek ecosystem helped mitigate toxic effects to aquatic organisms by buffering the pH gradually downstream from the outfall, thus helping maintain a lower pH than expected in the bicarbonate-rich CBNG-related waters. This is important because increased pH (especially >9.0) increases the percentage of un-ionized ammonia, thus leading to greater potential toxicity at a specified total ammonia concentration. The super-saturated-CO_2 effluent maintained a lower pH at the outfall, where total ammonia concentration was elevated. As the water flowed downstream, the CO_2 degassed and the pH began to increase gradually due to precipitation of $CaCO_3$. Dissolution of $CaSO_4$ resupplied the Ca^{2+}, allowing even more $CaCO_3$ precipitation and formation of $BaSO_4$, thus decreasing Ba^{2+} as the effluent flowed toward the Powder River. The $CaCO_3$ precipitation buffered the effluent-dominated stream to pH 8.0-8.5. This compares to pH 9.0-9.5 in the laboratory ambient-pH beakers, in which the pH continued to increase as the CO_2 degassed -- because little $CaCO_3$ was available to precipitate in the original effluent, and Ca^{2+} was not resupplied in the beakers by dissolution of $CaSO_4$.

Total ammonia nitrogen concentrations decreased at a rate of 18%/km along a downstream gradient in Beaver Creek, probably due to assimilation by bacteria and algae -- thus increasing primary production in the drainage. Because ammonia is more toxic at higher pH and the pH along Beaver Creek did not increase significantly before the ammonia decreased considerably, the ammonia might be interpreted from one perspective as a benefit to the ecosystem. However, because the potentially most toxic combinations of pH and ammonia occurred at intermediate distances downstream from the discharge point in the study reach, the USEPA (1999) chronic criterion for ammonia was sometimes exceeded.

Ammonification of what appears to be organic nitrogen in CBNG effluents can occur during transport and storage of unpreserved samples, thus potentially biasing WET tests by increasing ammonia concentrations in the water samples by the time they arrive at the laboratory. This can even occur if the water is acidified but not stored at ≤4 °C. The apparent ammonification that occurred in ≤24 h in the present study indicates that even static-renewal WET tests started immediately after an effluent or stream water is collected will have elevated TA-N concentration

before the end of the first 24 h of exposure, much less before the end of the customary 48-h exposure-water renewal period. Therefore, when selecting appropriate tests to measure toxicity of CBNG-related waters and/or when interpreting results of toxicity tests conducted with those waters, regulatory and management agencies should consider the possibility that ammonification might occur while the waters are transported from the stream to the laboratory or even if they are temporarily stored in the field before beginning flow-through toxicity tests.

In this study, only acute toxicity was investigated. Chronic toxicity studies will be needed to examine the effects of CBNG-related waters on reproduction and growth of aquatic life.

References:

APHA (American Public Health Association), AWWA (American Water Works Association) and WEF (Water Environment Foundation). 1995. *Standard Methods for the Examination of Water and Wastewater*. 19th Edition. APHA, Washington, District of Columbia, USA.

Burton Jr., G.A. 2005. Standard guide for assessing freshwater ecosystem impairment using caged fish or invertebrates for tiered diagnosis of stressors. American Society for Testing and Methods Draft (ASTM). Dayton, Ohio, USA. [Email allen.burton@wright.edu.]

Clearwater, S.J., B.A. Morris and J.S. Meyer. 2002. A comparison of coalbed methane product water quality versus surface water quality in the Powder River Basin of Wyoming and an assessment of the use of standard aquatic toxicity testing organisms for evaluating the potential effects of coalbed methane product water. University of Wyoming, Laramie, Wyoming, USA.

Davis, W.N. 2008. Effects of coalbed natural gas development on fish assemblages in tributary streams in the Powder River Basin, Montana and Wyoming. M.S. thesis, Montana State University, Bozeman, Montana, USA.

De Bruin, R.H., R.M. Lyman, R.W. Jones and L.W. Cook. 2004. Coalbed Methane in Wyoming, Information Pamphlet 7 (2nd revision). Wyoming State Geological Survey, Laramie, Wyoming, USA.

Farag, A., D. Harper and D. Skaar. 2007. National Pollution Discharge Elimination System: Potential toxicity of the major salt (sodium bicarbonate) from coalbed natural gas discharge water to aquatic life of the Tongue and Powder River drainages in Montana and Wyoming. Progress report submitted to U.S. Environmental Protection Agency (Project IAG #14-953964010) and U.S. Bureau of Land Management (Project Agreement #KAI061019).

Hart, J.S. 1947. Lethal Temperature relations of certain fish of the Toronto region. *Transactions of the Royal Society of Canada* 41:57-71.

Johnson (now Heath), L.A. 2007. Longitudinal changes in potential toxicity of coalbed natural gas produced water along Beaver Creek in the Powder River Basin, Wyoming. M.S. thesis, University of Wyoming, Laramie, Wyoming, USA.

Meyer, J.S., S.J. Clearwater, T.A. Doser, M.J. Rogaczewski and J.A. Hansen. 2007. *Effects of Water Chemistry on the Bioavailability and Toxicity of Waterborne Cadmium, Copper, Nickel, Lead, and Zinc to Freshwater Organisms.* SETAC Press, Pensacola, Florida, USA.

Mount, D.R. and D.I. Mount. 1992. A simple method of pH control for static and static-renewal aquatic toxicity tests. *Environmental Toxicology and Chemistry* 11:609-614.

Mount, D.R., D.D. Gulley, J.R. Hockett, T.D. Garrison and J.M. Evans. 1997. Statistical models to predict the toxicity of major ions to *Ceriodaphnia dubia*, *Daphnia magna* and *Pimephales promelas* (fathead minnows). *Environmental Toxicology and Chemistry* 16:2009-2019.

Rice, C.A., M.S. Ellis and J.H. Bullock. 2000. Water co-produced with coalbed methane in the Powder River Basin, Wyoming: Preliminary compositional data. U.S. Geological Survey Open-File Report 00-372, Denver, Colorado, USA.

Russo, R.C. 1985. Ammonia, nitrite, and nitrate. pp. 455-471 in: G.M. Rand and S.R. Petrocelli (eds.). *Fundamentals of Aquatic Toxicology*. Hemisphere Publishing Corporation, New York, New York, USA.

Turner, W. 2007. Survey of herptefauna of the Powder River Basin. Unpublished report, Wyoming Game and Fish Department, Laramie, Wyoming, USA.

USEPA (U.S. Environmental Protection Agency). 1999. *1999 Update of Ambient Water Quality Criteria for Ammonia*. EPA 822-R-99-014. USEPA, Washington, DC, USA.

USEPA (U.S. Environmental Protection Agency). 2002a. *Methods for Measuring the Acute Toxicity of Effluents and Receiving Waters to Freshwater and Marine Organisms*. Fifth Edition. EPA-821-R-02-012. USEPA, Washington, DC, USA.

USEPA (U.S. Environmental Protection Agency). 2002b. *Short-term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Freshwater Organisms*. Fourth Edition. EPA-821-R-02-013. USEPA, Washington, DC, USA.

USGS (U.S. Geological Survey). 2006. Toxicity of sodium bicarbonate to fish from coal-bed natural gas production in the Tongue and Powder River drainages, Montana and Wyoming. USGS Fact Sheet 2006-3092. USGS, Reston, Virginia, USA. http://pubs.usgs.gov/fs/2006/3092/.

WDEQ (Wyoming Department of Environmental Quality). 2003. Whole effluent toxicity (WET) testing of coalbed methane (CBM) produced water in northeastern Wyoming. Water Quality Division, WDEQ, Cheyenne, Wyoming, USA.

WDEQ (Wyoming Department of Environmental Quality). 2004. Coal bed methane discharge WET testing implementation approach. Memo written by Todd Parfitt, September 27, 2004. WDEQ, Cheyenne, Wyoming, USA.

Task 9 – Enhanced Risk Assessment of West Nile Virus Resulting from Coalbed Natural Gas Production Waters

Scott Miller[9]

Water disposal methods such as pond storage and in-channel releases that are associated with coalbed natural gas production (CBNG) have increased the amount of standing water in the Powder River Basin, Wyoming. These standing waters have been shown to be potential larval habitats for the *Culex tarsalis* mosquito, the primary vector of West Nile Virus (WNV) in Wyoming. This paper presents findings from a research effort focused on identifying environmental and anthropogenic risk factors for WNV associated with CBNG production. There were two areas of emphasis in this project: the first was a field research program in which pond and streams created by coalbed natural gas activities were investigated for the presence or absence of mosquito larvae, specifically *Culex tarsalis*; the second was a suite of research into the use of high resolution and medium resolution remote sensing imagery for the detection of water bodies and suitable larvae habitat.

Methods:

Field Research

A field campaign was carried out in the Powder River basin of north-central Wyoming in the late summer and early fall of 2006. A total of 64 ponds and streams were sampled for the presence or absence of mosquito larvae. Subsampling at the 64 sites was taken for replication and to ensure that a complete survey of the quality of the habitat was performed. This subsampling resulted in a total of 796 total sites being visited. The overall goal of the field campaign was to identify suitable larvae habitat for the *Culex tarsalis* mosquito, the primary vector of West Nile virus in Wyoming. Previous field seasons had revealed that mosquitoes prefer to lay eggs in relatively stagnant water protected from wind, with abundant organic matter. There does not seem to be a correlation between water quality and larval habitat quality.

A brief summary of the data collected in the field follows: Where mosquito larvae were identified as present, larvae were captured and brought back to University of Wyoming lab for identification to the species level. Field notes were taken as to the amount and extent of vegetation, whether the pond was steep walled, leaky, and if vegetation was present, whether it went all the way to the water edge or was somewhat disconnected from the water. Secondarily, if other aquatic micro invertebrates were identified their presence was noted. Lastly, field photographs and differentially corrected GPS data were taken at each of the sample sites. Previous field experiments had revealed difficulties in carrying out effective sampling for mosquitoes on private and public lands. First, many ponds and outfalls from coalbed natural gas wells have been treated for mosquito larvae. However, virtually no records are taken as to what and where exactly the treatments have occurred. In most cases, operators simply report that all ponds are treated with larvicide. Many of the ponds and river bodies where mosquito larvae have occurred in the past were blocked by private access. Much of the land in the study area is a

---

9 Department of Renewable Resources. University of Wyoming, Laramie, WY. email: SNMiller@uwyo.edu

typical Western checkerboard ownership pattern with private and public lands co-mingled throughout the study area. Our goal was to identify the presence or absence of mosquito larvae independent of whether the ponds have been treated. This required identifying ponds where we could definitively state whether the ponds had or had not been treated and if they had been treated at what time.

Sampling sites were identified in the summer of 2006 through a series of phone and personal interviews with landowners in the Powder River basin. We identified landowners who could provide consistent and open access to water bodies that had been produced solely through oil and gas development activities. Furthermore, each of the landowners stipulated that no mosquito control would take place on the water bodies in question prior to or during the field campaign. This was intended to ensure that false negatives were removed and that mosquitoes had no barrier to egg laying or larval production in the study cites. Each of the landowners provided written permission to access their lands, and at the conclusion of the field campaign the landowner was sent a letter detailing the findings of the study, including whether or not mosquitoes were found in their water bodies and identification of mosquito species that were found.

Once a range of suitable potential habitat areas were identified in discussion with the various landowners, a GIS study was undertaken to identify and randomly locate sampling areas from within those potential sites. High resolution NAIP (1.5M) photographs were downloaded from the state of Wyoming, which allowed us to identify potential ponds, streams and slow-moving water areas. The 64 sample sites were randomly selected from the these water bodies. GPS locations of the 64 sites were downloaded to a high resolution GPS unit capable of differential correction (Trimble proXRS). Field crews were dispatched to these sites in late July through late September 2006. The field campaign was timed to coincide with predicted high numbers of mosquito larvae and with the maximum expected rate of transmission of West Nile virus, which typically occurs at this time in Wyoming as temperatures reach a threshold where the virus is capable of being transmitted.

Upon arrival at each of the field sites, a short reconnaissance was carried out. The purpose of this reconnaissance was to visually assess the variability of the landscape and to determine the expected number of subsampling points required to capture the variability. If the site in question was a pond, variability was determined by inspecting the range and quality of vegetation surrounding the pond, whether or not vegetation came close to be water's edge, and whether the pond was consistent in construction. If this setting in question was a stream, then the criteria for variability focused primarily on the range and quality of vegetation and the amount of standing water within the stream reach. At each location, a minimum of 5 and a maximum of 20 points were sampled depending on the abundance of available habitat, with no two points closer than 10 m from each other.

Protocols, taken at each subsample point were as follows:

1. Type and intensity of vegetation was assessed and recorded.
2. If at a pond, steepness of wall was noted.
3. Whether or not vegetation encroached all the way to the water's edge was noted.

4. Emergent vegetation was identified and noted as present or absent.
5. The presence or absence of any mosquito larvae was noted.
6. If a mosquito larvae was identified it was captured using a small net and fixed in a small bottle using preservative in the field.
7. Other aquatic micro invertebrates were noted as present or absent.
8. A differentially corrected GPS point was taken.
9. A digital camera photograph was taken.

Mosquito larvae retrieved from the field were transported back to the SAWLS lab at University of Wyoming and identified to the species level using a dissecting microscope. All field and laboratory data were taged and entered into AE spatially explicit GIS database.

Remote Sensing at Multiple Scales

A variety of approaches were used to increase the resolution and accuracy of identifying small-scale water bodies and a potential larval habitat. The development of remote sensing techniques for larval habitat identification used in this effort is detailed in Zou et al. (2006). We classified a range of remote sensing products, including Landsat 7 (30 m resolution), Quickbird (2.4 m), Landsat-Enhanced Thematic Mapper Plus (ETM+; both 30 m and 15 m), and ASTER (15 m).

Improvement on Habitat Identification with Landsat and Quickbird Imagery

The Zou et al. (2006) techniques were improved upon in this effort at classifying 30 m resolution Landsat data into vegetation and water bodies that could be used to identify suitable habitat. Emergent vegetation is a critical condition for the identification of suitable habitat, as is the presence of water. However, larger water bodies such as open discharge ponds are rendered unacceptable due to the fact that wind action and lower organic contents reduce the suitability for larval growth and maturation. A set of GIS rules were used to refine the selection of suitable sites, such that steep slopes and pre-existing large waterways were excluded. This is a conservative approach to estimating habitat since it restricts the identification to only small bodies of water with abundant vegetation and low slopes using relatively coarse data.

The use of Landsat imagery showed an overall increase in *C. tarsalis* habitat of 75% from 1999-2004. An accuracy assessment using field data and high-resolution aerial photography showed that the classifier can identify likely habitat for ponds larger than 0.8 ha (2 acres) with generally satisfactory results (72.1%) with a lower detection limit of 0.4 ha (1 acre) that is due to the relatively coarse 30m resolution of the imagery.

To address the issue of temporal change and spatial scaling both conventional (Landsat 5 TM: 30 m multispectral) and high resolution data (Quickbird: 2.4 m multispectral and 0.5 m panchromatic; and SPOT: 12 m multispectral) were collected over the field sites for 2005 and 2006 seasons. These data were classified following the rules set forth by Zou et al. (2006) with suitable results found for the identification of larval habitat. The contrast in use of Quickbird and Landsat imagery is detailed in Figure 9-1. As expected when using high resolution imagery, small-scale features are more readily detectable. Channels and small impoundments larger than approximately 50 sq. m (0.005 ha, or 0.01 acres) can be identified, compared to a lower limit of

4 ha (10 acres) with Landsat. This range is more suitable for accurately resolving micro-habitats that form a high percentage of the *C. tarsalis* habitat in the study area.
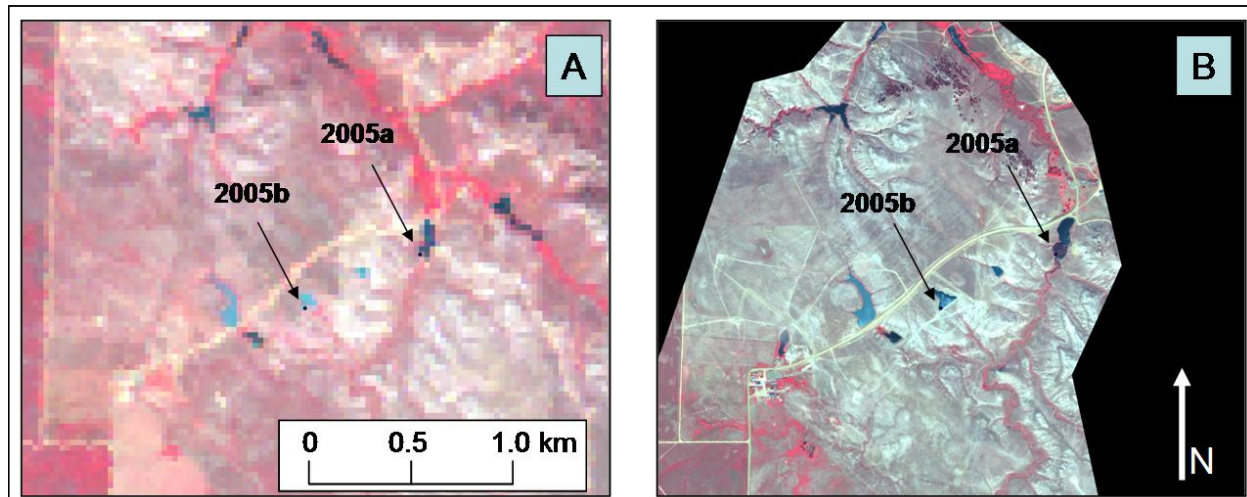
Figure 9-1: Comparison of false color composite remote sensing imagery covering a portion of the 2005 field research area. Figure 1a is Landsat imagery (30 m); Figure 1b is Quickbird multispectral bands (2.4 m) with arrows in both panels indicating the same positive habitat sites detected in the field. Landsat imagery was able to detect the larger site (2005a) but unable to detect the smaller site (2005b) while Quickbird was able to detect both.

Pan-sharpened Landsat Imagery for Identification of Small Waterbodies

A cloud-free, Landsat-Enhanced Thematic Mapper Plus (ETM+) image acquired on 13 July, 2001 was obtained from the WyomingView archive. This image was acquired prior to the SLC failure of the Landsat 7 satellite, and was preprocessed at the US Geological Survey (USGS) satellite data processing facility at Sioux Falls, South Dakota, for geometric and radiometric distortions. They were rectified to the Universal Transverse Mercator projection system (zone 13) and NAD83 datum, GRS80 spheroid. The image was clipped, using the study area boundary, and a subset was generated consisting of six multispectral bands and one panchromatic band. Using a principal component analysis (PCA) algorithm, the multispectral bands were merged with the panchromatic band of the Landsat data. PCA-based merging was chosen because it causes less distortion of spectral characteristics than techniques.

Very high-resolution (1 m) ortho-rectified colour infrared aerial photographs for Campbell, Johnson and Sheridan counties were used to manually identify and map waterbodies in the study area. These data were downloaded from the WyGISC data server. Heads-up digitizing of 701 waterbodies was accomplished in ArcGIS desktop software (ESRI, Redlands, CA, USA). Candidate ponds were evenly distributed throughout the study area, using a 100-ksq. m grid system. A trained photo interpreter digitized small, medium and large waterbodies within each of the 90 grids. Although obviously submerged vegetation was included as part of a waterbody, emergent or dry land vegetation was not. No waterbodies were located in some grids. The 701 digitized waterbodies ranged in size from 12.7 to 69 808 ksq. m. The waterbodies were randomly chosen in either a calibration or a validation set. Three hundred fifty of these polygons were used

to refine image classification efforts, while the remaining 351 were reserved for validating the results.

Data collected in the field on waterbody shape, scale, water quality and color, as well as the vegetation characteristics and near-water and upland types, were used to train the photo interpreter. Although previously collected maps of known waterbodies were used as reference data to identify waterbodies in the Landsat image, they were not used to assess the accuracy of the classified images. Field crews used a global positioning system to collect information regarding the location of waterbodies.

Based on their brightness values, pixels in the original Landsat image were assigned to clusters through a successive image classification process. Using an ISODATA classification, 100 spectrally homogenous clusters were generated. Clusters corresponding to non-waterbodies (e.g. bare ground, vegetated areas) were excluded from the classified image, with the remaining pixels corresponding to water classes being again classified. This method enabled better separation between different types of waterbodies in the study area (e.g. clear water) from those with suspended materials. Completion of this process resulted in generation of a digital map consisting of standing waterbodies. This process was repeated for the pan-sharpened Landsat imagery.

Both the 30-m and the 15-m classified images were compared to a subset of 351 randomly selected points from the overall set of 701 photo-interpreted polygons, in order to assess the accuracy of both the overall ability to detect water (presence/absence), and the estimation of the water surface area. Producer accuracies were computed for each image. Producer accuracy allows us to assess the effectiveness of the classified image to successfully map a known feature. A producer accuracy of 78%, for example, denotes that the classified image was able to correctly identify the feature 78 of 100 times. The overall difference in the omission error between the 30-m and 15-m pan-sharpened classified images was calculated to determine the relative overall efficacy of the approaches. Verification data were further sorted by area, and the two classified images were compared to the verification data at a range of scales. This analysis allowed determination of a threshold scale where the benefits of pan-sharpened imagery were significantly better than the 30-m multispectral imagery.

Area estimates obtained from the 30-m and 15-m imagery were compared to the photo-interpreted area estimates at a range of scales. A subset of 59 waterbodies was selected by including every sixth data from the 351 verification data. Image-derived area estimates were compared to the photo-interpreted waterbodies grouped into four categories, based on the equivalent number of Landsat pixels. These categories were termed very small (<900 sq. m), small (between 901 and 3600 sq. m), medium (between 3601 and 8100 sq. m) and large (>8100 sq. m). Small waterbodies (>900 and ≤3600 sq. m) were further subdivided into three subclasses, in order to gain further insights into the benefits of merged data. These subclasses corresponded to the number of 30-m pixels: 901–1800 sq. m; 1801–2700 sq. m; and 2107–3600 sq. m. This approach allowed the determination of the lower limit of suitability for using either standard or pan-sharpened Landsat imagery to estimate water surface area. Pearson's correlation coefficient was calculated for each size category, in order to determine the degree of agreement between the area estimates derived from images and the photo interpretation.

Use of ASTER Data for Mapping Waterbodies and Habitat

Two ASTER images acquired on 28 August 2006 were purchased from the US Geological Survey's EROS Data Center in Sioux Falls, SD (USA). Data were geo-referenced to UTM NAD83 (zone 13) projection, and delivered in GeoTIFF format. ASTER images were converted to ERDAS Imagine format (Leica Geosystems, Atlanta, GA), and combined to create a single digital file to cover the entire study area. A cloud-free Landsat image (path 35; row 29 – WRS2), acquired approximately 15 minutes prior to the ASTER scene, was obtained in ERDAS Imagine format from WyomingView and Landsat images were subset to match the geographic extent of the study area. Several groups of cumulus clouds moved into the study area from the east and were present in the ASTER image. Previous studies have shown that presence of clouds and their shadows in satellite images diminish their usefulness for identifying and mapping landscape features. Other than using cloud-free images, masking the pixels representing clouds and their shadows can minimize issues associated with feature misclassification. Identifiable clouds and their shadows were masked in the ASTER image using heads-up digitizing, and removed from subsequent analyses. Small and thin clouds that are typical of changing atmospheric conditions in this area proved hard to visually discriminate in the ASTER imagery; it is likely that several of these clouds were not identified and masked and may have negatively influenced the results.

The Iterative Self Organizing Data Analysis Technique (ISODATA) algorithm was used to generate two separate sets of clusters from ASTER and Landsat images. An infrared over red ratio band was added to each image's original spectral bands in order to minimize the influence of topography. ISODATA algorithm groups pixels based on spectral similarity; where variations exist within a feature (i.e. different types of water bodies or vegetation) they may be assigned to different clusters. These clusters have to be assigned to a land cover feature (water, forest, etc) using field collected and ancillary data. An advantage of ISODATA and other unsupervised classification algorithms is that not all land cover classes have to be interpreted in a single step. An image can be successively classified and at the end of each classification step some land cover classes can be identified. Pixels corresponding to those classes that are identified are removed from the image and the remaining pixels are classified. This process is repeated until all the pixels are assigned to a land cover feature class.

Color aerial photographs obtained through the National High Altitude Photography (NHAP) at 1 m spatial resolution were downloaded from the Wyoming geospatial data clearinghouse. These geo-referenced images (UTM projection, zone 13, projection NAD83) were displayed in ArcGIS software. Water bodies in the study area were digitized using photo-interpretation techniques and their boundaries stored as a shape file. Field data and photographs obtained in the summer of 2006 regarding water bodies, water quality, and color were used to train the photo-interpreter. Previously published maps and location of CBNG wells were used as ancillary information while interpreting the aerial photos. This resulted in 322 water bodies throughout the study area, and they were further classified according to its surface area and color (clear and black, green, and turbid/muddy).

To evaluate the suitability of ASTER and Landsat derived classified maps two types of accuracies were calculated. The first metric, termed producer accuracy, estimates the number of instances, expressed as a percentage, that water features are correctly identified. Omission error

[100% - producer accuracy] provides insights about the suitability of a remotely sensed data for mapping water and other landscape features. For example, if the omission error associated with water bodies is high, the interpretation is that more water bodies are present in the landscape than are identified in the image. The second metric, user accuracy, estimates the numbers of instances, also expressed as a percentage, other features in the landscape are misclassified as water.

Common misclassified features include shadows cast by clouds and hill slopes on forests and other features. Commission error [100% - user accuracy] provides insights about the utility of the classified image from a user's perspective. For example, high commission errors are interpreted that numerous non-water bodies have been misclassified as water. Classified images with high omission and commission errors have low utility for scientific and management purposes. First, the 322 verification data that were sorted by type (clear, green, and turbid) and producer accuracy values for these three types of water bodies were computed. Second, within each type of water body, verification data were sorted by the size of the water bodies into three size categories (901-3600, 3601-8100, and >8100 sq m) as in the other portion of this effort and producer accuracy values were calculated for each size class. Finally, producer accuracies for water bodies in that smallest size category were further broken down into size classes equivalent to Landsat pixel footprints (901-1800, 1801-2700, and 2701-3600 sq m) were calculated to quantify the advantage of higher spatial resolution data (ASTER) for detecting very small water bodies.

User accuracy values for the satellite images were computed by randomly selecting water bodies respectively from the ASTER and Landsat derived images. Water bodies identified in the image were compared to the 1 m color NHAP county mosaic to ascertain the presence of the water bodies. If a water body was present in the ASTER (or Landsat) classified image and also in the NHAP count- mosaic it recorded as a correct classification. User accuracy values were computed for the size categories described above. Producer and user accuracy values were compared for each type and size class using the test of 2-proportions and the corresponding Z values. One tailed tests were used to determine whether the proportion of correctly identified water bodies in the ASTER image was significantly (alpha level of 0.05) higher (for producer accuracy) or lower (for user accuracy) than the corresponding values in the Landsat image.

Results and Discussion:

Field Research Findings

Mosquito larvae were found at 29 of the 63 locations (46%) and all but one of those positive locations had *C. tarsalis* larvae. This indicates that, at least during late summer, most mosquitoes in the region are potential West Nile Virus vectors. *C. tarsalis* larvae were much less common at reservoirs (23%) than in drainages (90%) (Table 9-1).

Table 9-1: Presence of *C. tarsalis* larvae according to CBNG water discharge technique.

	CBNG Reservoir Locations	CBNG Drainage Locations
C. tarsalis present	10 (23%)	18 (90%)
C. tarsalis absent	33 (77%)	2 (10%)
Total	43	20

Vegetation parameters suggest a correlation between recently flooded dryland grass species and *C. tarsalis* presence. Another important factor is sufficiently shallow (<12 cm) and stagnant water. In other words, if water is channelized and moving quickly through drainages, mosquito habitat is minimized. Two confounding variables were identified in our initial field seasons. First, it was impossible to conclusively track the deployment of mosquito control devices in discharge ponds and channels. Second, the absence of larvae in the field is not necessarily indicative of inadequate habitat, especially when similar sites are identified with abundant larvae.

Pan-sharpened Landsat Imagery for Identification of Small Waterbodies

Two iterations of unsupervised classification were required to map the waterbodies. During the first iteration of analysis of the 30-m multispectral data, eight clusters representing waterbodies were extracted from the classified image. The shadows cast by mountains and steep slopes exhibit spectral characteristics similar to waterbodies, often being misclassified as water. In the second iteration, these eight clusters were classified and removed to achieve a better separation among waterbodies and shadows. Although the second iteration reduced the misclassification of shadows to a certain extent, it was not able to completely eliminate it. Water in the Powder River and tributaries had different spectral reflectance values, compared to water stored in reservoirs, ponds and lakes, and was readily identified where the riparian canopy was not complete. Mapping waterbodies in the pansharpened imagery was accomplished in one classification iteration.

The overall results illustrated a moderate improvement in the use of pan-enhanced imagery. In the 30-m multispectral classified image, 172 locations out of the 351 (49%) photointerpreted waterbodies were correctly classified (Fig. 9-2). In the 15-m pan-sharpened image, 209 locations (60%) were correctly classified as waterbodies. Thus, merging multispectral and panchromatic bands resulted in an 11% increase in producer accuracy. This analysis includes all waterbodies independent of size, with the results being degraded because of the inclusion of very small ponds and reservoirs in the analysis. Large waterbodies (>8100 sq. m) were accurately mapped for both resolutions; the producer accuracies for both 30-m and 15-m were 96%. The 30-m multispectral data are highly suitable at this scale, and there is no demonstrable benefit to merging it with higher resolution data (Fig. 9-2). For medium-sized waterbodies (>3600 and ≤8100 sq. m) there was a 7% increase in the producer accuracy of the pansharpened imagery.

The benefits of merging data are marginal for mapping this class of waterbodies. There was an 18% increase in the producer accuracy for small waterbodies (>900 and ≤3600 sq. m) when 15-m merged data were used. For very small waterbodies (<900 sq. m), however, the performance of both 30-m and 15-m imagery had very low producer accuracy values (<15%). These results indicate that these very small bodies are below the detection limit of both the standard and the

pan-sharpened data, which require higher resolution data (<10 m). Analysis of the three subclasses within the small waterbody class reveals further distinctions in accuracies. In the 901–1800 sq. m category, the merged image was able to correctly identify 18% more photo-interpreted waterbodies than the 30-m image (Fig. 9-3). There was a 25% increase in the producer accuracy for the merged imagery in the 1801-2700 sq meters category. In the 2700 and 3600 sq meters category, the producer accuracy for the merged image was 8% more than the 30 m multispectral data. These results demonstrate that the benefits of merged data were more pronounced for the water bodies ranging between 1801 and 2700 sq meters than any other classes analyzed in this study.
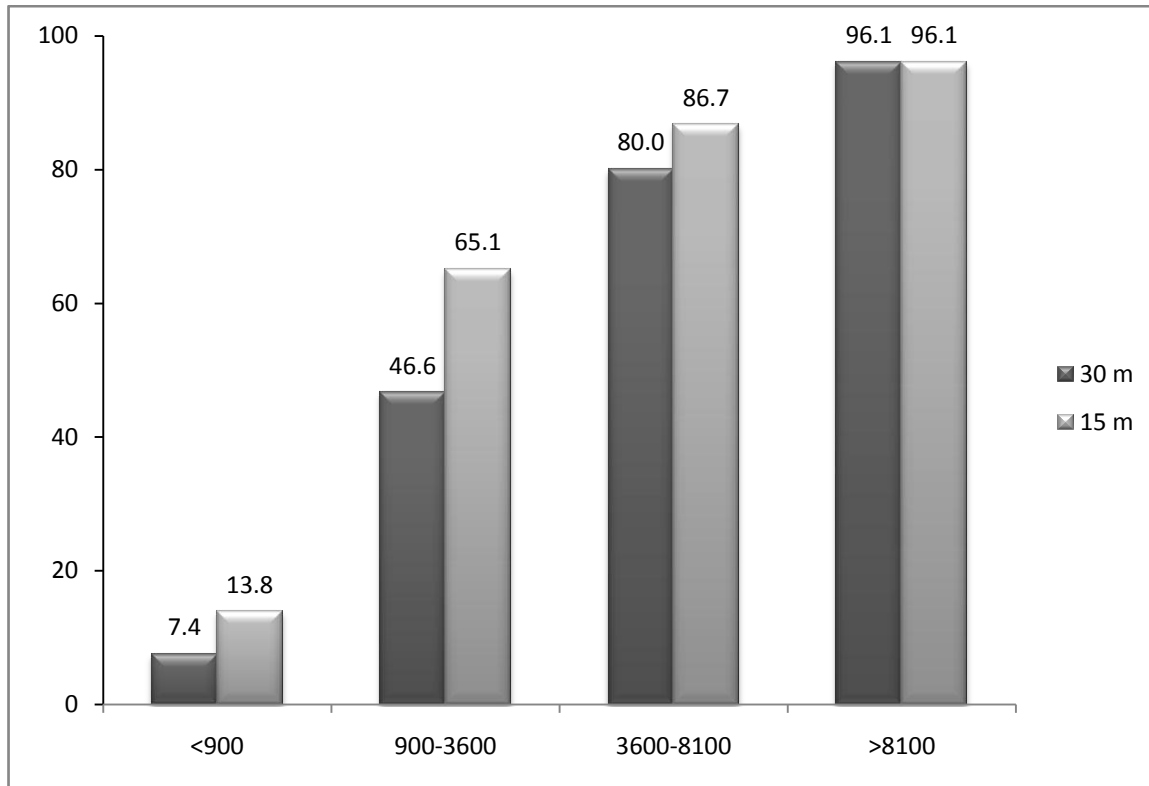
Figure 9-2: Classification (producer) accuracy for classified multispectral (30-m) and pan-sharpened (15-m) images, stratified by the size of observed waterbodies.
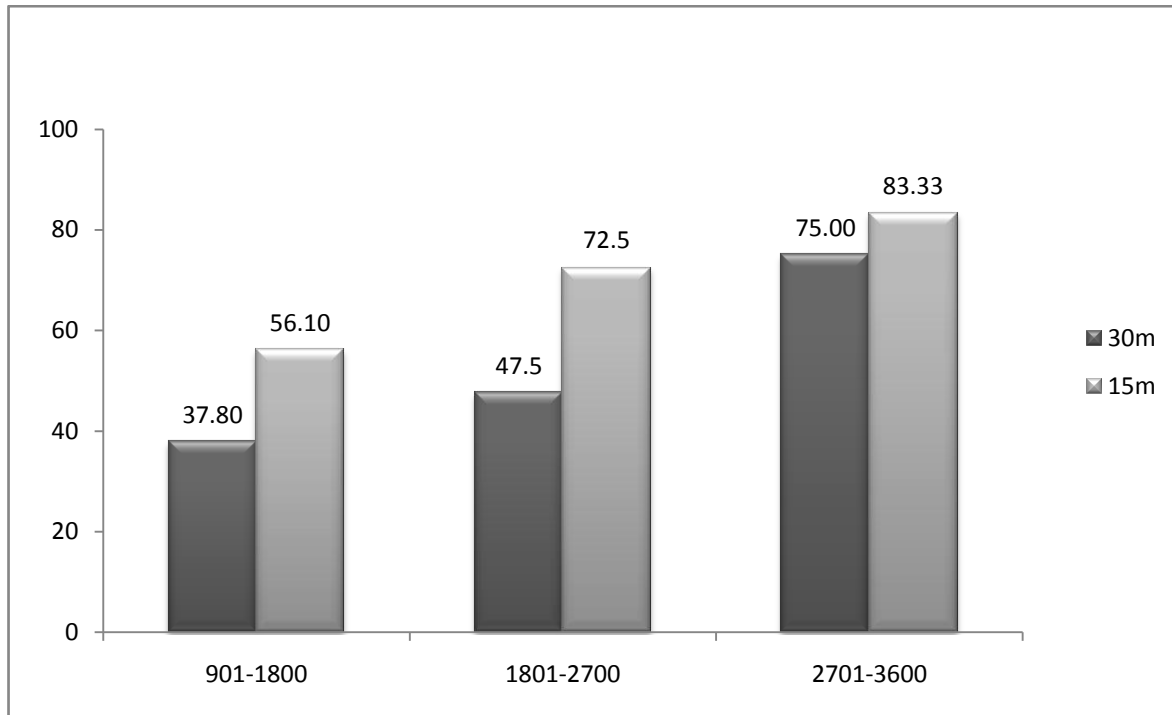
Figure 9-3: Producer accuracy for classified multispectral (30 m) and pan-sharpened (15-m) images for the three subclasses within small waterbody class (901–3600 sq. m).

For small and medium sized water bodies (901-8100 sq meters) the agreement between the area estimates obtained from both 30 m multispectral and 15 m pan-sharpened imagery with the photo-interpreted were poor (Table 9-2). However the correlation coefficient values for the pan sharpened imagery showed marginal improvements. For large water bodies (>8100 sq m), the agreement between the photo-interpreted areas values and the corresponding values derived from 30 m image was high (r=0.94). This agreement increased (r=0.97) when the photo-interpreted area estimates were compared to the estimates derived from the pan-sharpened imagery.

Table 9-2: Area under each class, and the agreement (Pearson correlation coefficient, r) between the photo-interpreted area and the area estimates of water bodies derived from multispectral and pan-sharpened imagery.

Size class Sq meter	Area (sq meter)		
	Photo-interpreted	30 m multispectral	15 m pan-sharpened
901-3600	61590	57600 (r=0.35)	56025 (r=0.49)
3601-8100	64482	44100 (r=0.34)	45675 (r=0.40)
>8101	313944	324000 (r=0.94)	315675 (r=0.97)

Spectral reflectance values of water bodies were distinctly different from the rest of the land cover features and the iterative ISODATA classification technique was adequate to identify and map them. Image classification algorithms also separated static water bodies (lakes, ponds and reservoirs) from running water in the Powder River and larger tributaries. In the 30 m multispectral data, shadows cast by the hills were often misclassified as water, while the pan-

sharpening process minimized spectral confusion between water bodies and shadows. One of the benefits of using pan-sharpened imagery is the reduction in spectral confusion or overlap between water bodies and shadows.

Results obtained in this study highlight the value of 30 m multispectral data for mapping water bodies greater than 8100 sq meters. Multispectral data were able to correctly identify 96% of the water bodies in this size category and the results were identical to the ones obtained with the pan-sharpened imagery. The presence of suspended solids and other biological materials in a water body may alter its spectral reflectance values and resulted in their misclassification. The fact that Landsat data could be used to identify almost all of the large water bodies is encouraging and suggests that agencies can use Landsat or similar medium resolution data for periodic monitoring. In the medium size category (3600 – 8100 sq meters), improvement in the producer accuracy with the use of pan-sharpened imagery was marginal (7% increase). However the added benefit of using pan-sharpened imagery is the reduction in the misclassification of non-water bodies such as shadows, which reduces the number of false positives.

These results also highlight the value of pan-sharpened imagery for mapping small water bodies especially in small size (901 – 3600 sq meters) category. Producer accuracy in this category increased to 65% (from 47%) when pan-sharpened imagery was used for identifying water bodies. Further stratification and subsequent analysis within this size category demonstrated that for water bodies that were larger than 2700 sq meter, producer accuracies greater than 72% can be achieved. In the 2701-3600 sq meters size category, the producer accuracy increased from 75% to 83%. For mapping very small water bodies (<1800 sq meters) higher spatial resolution data are necessary as water bodies of this size could not be distinguished. These results indicate that the ability to map smaller water bodies increases with the use of pan-sharpened Landsat data and producer accuracies greater than 80% can be achieved for water bodies larger than 2700 sq meters. For water bodies larger than 3600 sq meters results were similar and very good using either technique.

Area estimates obtained from the multispectral and pan-sharpened imagery for water bodies less than 8100 sq meters were not comparable to the photo-interpreted estimates. This could be due to the pixilated nature of the image data and the limitation posed by the pixel size. Also, several water bodies had narrow, convoluted shapes and in several instances only one or two images of these water bodies were correctly identified. This resulted in discrepancies between the more precise photo-interpreted boundary and the satellite image mapped boundary. Based on the results from this study, reliable estimates from Landsat image could be obtained for water bodies that are larger than 8100 sq meters.

In addition to Landsat, other sources of medium resolution data include SPOT image – 20 m multispectral bands and a 2.5 panchromatic band, and the Indian Remote Sensing ResourceSat (IRS P6) – 24 m multispectral bands and 5 m panchromatic band. These images are comparatively more expensive than the Landsat, but could be viable alternatives until the launch of the next Landsat (expected launch date 2012).

Use of ASTER Data for Mapping Waterbodies and Habitat

Spectral reflectance values of water bodies identified using ASTER data were different from the spectral values of other landscape features; however there were some overlap with features such as shadows. Including the near infrared to red ratio band in each image minimized spectral confusion caused by shadows but did not eliminate it completely. During the first classification iteration, water bodies and spectrally overlapping landscape features were extracted from the ASTER image. In the second iteration most of the water bodies were extracted and mapped. Similarly water bodies in the Landsat image were extracted and mapped in two classification iterations.

Producer accuracy values of the ASTER classified image were higher than the Landsat image in two of the three types of water bodies (Figure 9-4). Classification using ASTER image correctly identified 89% of the clear water bodies in comparison to 69% identified by the Landsat image ($Z = 3.97$; $p < 0.005$). Furthermore, classification using ASTER correctly identified 87% of the green water bodies, in comparison to the 64% that were correctly identified by the Landsat image ($Z = 4.37$; $p < 0.000$). However for the turbid/muddy water bodies the producer accuracy in the ASTER image (82%) was higher although not statistically different ($Z = 1.83$; $p < 0.1$) than the producer accuracy in the Landsat image (74%).
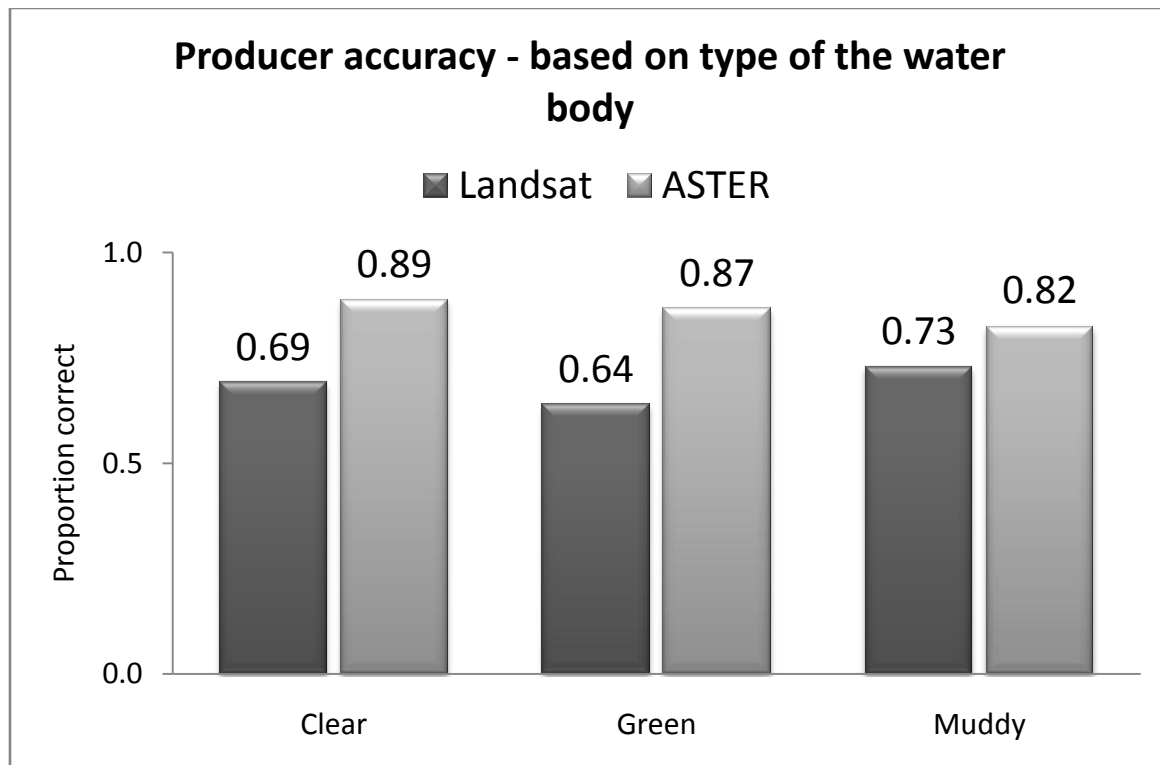
Figure 9-4: Producer accuracy values for water bodies (by type) computed from the Landsat and ASTER derived classified images. Proportions of correctly identified water bodies were significantly higher (at 0.05 level) in the clear and green category, however were not significant for muddy category.

Producer accuracy values of the three types of water bodies (clear, green and muddy) were evaluated over three primary area classes (901 – 3600 sq m, 3601 – 8100 sq m, and > 8100 sq m). Among the clear water bodies in the 901 – 3600 sq m and 3601 – 8100 sq m size categories the ASTER derived image had significantly higher producer accuracy values (65% and 95%) than the corresponding Landsat image (18% and 70%) (Table 9-3). However, for the large water bodies (> 8100 sq m) both ASTER and Landsat derived images had comparable producer accuracy values (Z = 0.59; p < 0.3). A similar pattern was also identified in green water bodies (Table 9-3). The classified ASTER image had statistically higher producer accuracy in the 901 – 3600 sq m and 3601 – 8100 sq m size categories, whereas for large water bodies (> 8100 sq m) differences in producer accuracy values were not statistically significant between the ASTER and Landsat derived images. On the other hand, among the muddy water bodies ASTER derived image had significantly higher producer accuracy only in the 901 – 3600 sq m size category (Table 9-3). For the remaining two categories of water bodies, the producer accuracy of the Landsat derived image was higher than the ASTER derived image, but not statistically significant.

Table 9-3: Producer accuracy for the water bodies in the classified Landsat and ASTER images by color and area of water bodies.

	Landsat	ASTER	Z-value	p
Color: clear				
Size = 901-3600 sq m	17%	65%	3.17**	0.001
Size = 3601-8100 sq m	70%	95%	2.20*	0.014
Size >8100 sq m	94%	97%	0.59	0.277
Color: green				
Size = 901-3600 sq m	39%	78%	3.91***	0.000
Size = 3601-8100 sq m	62%	91%	3.45**	0.001
Size >8100 sq m	95%	95%	0.00	1.000
Color: turbid (brown)				
Size = 901-3600 sq m	51%	79%	3.29**	0.001
Size = 3601-8100 sq m	93%	89%	-0.74	0.771
Size >8100 sq m	95%	86%	-1.07	0.857

In the 901-3600 sq m category accuracy values of the ASTER derived image were higher than the Landsat derived image (Figure 9-5). For the water bodies 901 – 1800 sq m in size, the classified ASTER image had significantly higher (Z = 4.90; p < 0.000) producer accuracy (55%) than the Landsat image (10%). Similarly the producer accuracy of the ASTER image (85%) was significantly higher (Z = 3.94; p < 0.000) than the accuracy of the Landsat image (44%) in the 1801-2700 sq m category. Finally, in the 2701 – 3600 sq m water bodies ASTER image had significantly higher (Z = 3.94; p < 0.05) producer accuracy (80%) than the Landsat image (63%). These results demonstrate the higher spatial resolution ASTER image can correctly identify significantly more water bodies, especially in the smaller size categories, than the Landsat image.
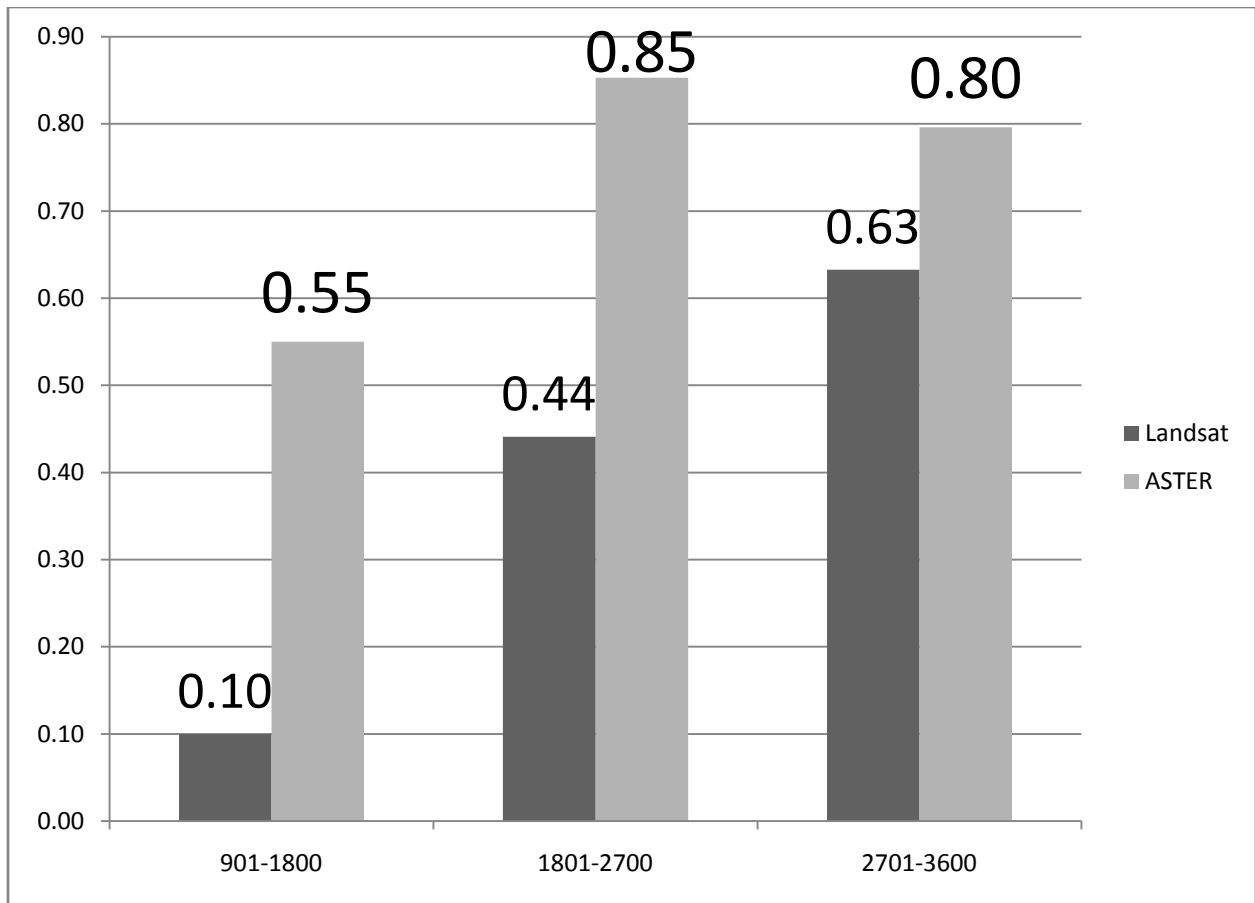
Figure 9-5: Producer accuracy values for water bodies (by size in sq m) computed from the Landsat and ASTER derived classified images. Proportions of correctly identified water bodies in the ASTER image were significantly higher (at 0.05 level) in the three size categories.

User accuracy values of the ASTER derived image in three of the four size categories were lower than the corresponding values in the Landsat derived image (Table 9-4). Among the 1801-2700 sq m size category 15% of ASTER derived and 4% in Landsat water bodies were found to be incorrect and this difference was statistically significant (p = 0.044). In the 2701-3600 sq m size category, misclassification in ASTER and Landsat images were 16% and 7% respectively, although this difference was not statistically significant (p = 0.087). In the 3601-8100 sq m size category, the misclassification in ASTER and Landsat images were 6% and 1% respectively, and this difference was also not significant (p = 0.112). For large water bodies (> 8100 sq m) there were no misclassification in the ASTER and Landsat derived images.

Table 9-4: User accuracy for the water bodies in the classified Landsat and ASTER images by color and area of water bodies.

	Landsat	ASTER	Z-value	p
Size = 1801-2700 sq m	96%	85%	-1.7	0.044
Size = 2701-3600 sq m	93%	84%	-1.36	0.087
Size = 3601-8100 sq m	99%	94%	-1.21	0.112
Size >8100 sq m	100%	100%	n/a	n/a

Higher spatial resolution ASTER data could correctly identify more water bodies that were categorized as being either clear or green, especially in smaller size categories. ASTER data also showed some improvement, albeit not significant, in comparison to Landsat data for identifying muddy or turbid water bodies. High producer accuracy values associated with identifying clear and green water bodies (89% and 87% respectively) demonstrates that ASTER can be used to identify majority of the water bodies that are either clear or are green due to submerged or floating vegetation – the presumed source of the green color. There were several irregularly shaped water bodies (i.e. long and elongated) in the study area that the ASTER data were better able to correctly identify in comparison to Landsat data due to the smaller pixel size of the ASTER image. In contrast, Landsat data were not adequate for recording the spectral values from narrow and elongated water bodies. ASTER data could correctly identify more water bodies using standard and commonly applied image processing techniques which requires minimal training data for the calibration of the classification algorithm. These data can be obtained relatively easily from existing maps or limited field surveys. For periodic monitoring and mapping ISODATA image processing algorithm is more advantageous in comparison to other complex image processing methods such as mixed-pixel separation approaches that require extensive field surveys, intensive training data, and skilled remote sensing specialists.

The presence of clouds and more importantly their shadows in ASTER or similar data can negate the gains achieved in terms of high producer accuracy and increased detection limit. Cloud shadows present in the ASTER data were misclassified as water, necessitating the heads-up digitizing of spatial masks to exclude cloud and cloud shadows prior to accuracy assessment. An alternative approach is to utilize automated cloud and cloud shadow detection algorithms to screen and mask out such pixels. However information required to generate these automated masks are collected for 90 x 90 m blocks, which results in a loss of information on the 15 m data; therefore automated cloud screening algorithms should be used selectively to eliminate cloud contaminated pixels.

For the 3601-8100 sq m water bodies that were either clear or green, ASTER data had significantly higher producer accuracies in comparison to Landsat data. These results are encouraging since the producer accuracy values associated with ASTER data were more than 90% and could be used for routine monitoring and mapping applications. One approach to improving the accuracy could be to use even higher spatial resolution data (such as 10 m SPOT satellite data) that might be able to capture several narrow impoundments build across small

streams to store water. However costs associated with acquiring ASTER data are much lower which might be an important issue for mapping large geographic areas on a periodic basis. Within the 901-3600 sq m water bodies, ASTER data correctly identified more water bodies than Landsat data. Further analysis revealed that though ASTER data correctly identified more water bodies in the 1801-2700 sq m category, it also misclassified other features in the study area as water bodies. In other words, while the ASTER data successfully identified more water bodies in this size category, other landscape features were mistakenly classified as water bodies. ASTER derived images could overestimate the water bodies in the landscape which reduces their precision. Landsat data, on the other hand, identified 44% of the water bodies in this size category but did not classify non water bodies as water. High user accuracy values (> 90%) associated with Landsat images implies fewer misclassifications of non water bodies as water which could be useful for sampling purposes.

Both ASTER and Landsat data could identify approximately the same number of water bodies that were more than 8100 sq m. This area corresponds to nine pixels in a Landsat scene and represents a relatively large and presumably homogenous area in which mixed pixels are not a significant concern. Landsat data can be effective for mapping and monitoring and water bodies (> 8100 sq m) for large geographic areas since a Landsat image covers 9 times more land surface area than an ASTER image and has a lower per-area cost.

Mapping the interface between water and vegetation or areas suitable mosquito larvae habitat from these satellite images was somewhat limited using the spectral information. These images were acquired in late-summer to coincide with the oviposition time of the mosquitoes. Through enhancements and digital classification of the ASTER images we were able to map the interface between water and vegetation. However edges along the cloud shadow were also grouped with this class (please refer to the commission error discussion above). Cloud screening algorithms used in this study were able to identify only some of the clouds but their shadows were not.

In Figure 9-6a water bodies appear in various shades of grey. Water bodies absorb most of the infrared radiation hence they appear dark in color. However presence of biological and or chemical materials could alter its reflectance characteristics. The pond that appears in the bottom right hand corner of this image in light (or pale) blue color could be due to turbidity in this pond. Areas highlighted in light blue color (Figure 9-6b) are the suitable mosquito larval habitats. The reflectance properties of these pixels were a combination of water and vegetation. However it is worth noting that the turbid water body (described in Figure 9-6a) was not classified as a water body in this image (omission error). Absence of spectral information in the blue and mid-infrared region somewhat limited ASTER's ability to map turbid water bodies.

Figure 9-6a: ASTER image displayed in color infrared combination.	Figure 9-6b: Classified (processed) ASTER image that highlights water bodies in dark blue and the interface between water and vegetation in light blue.
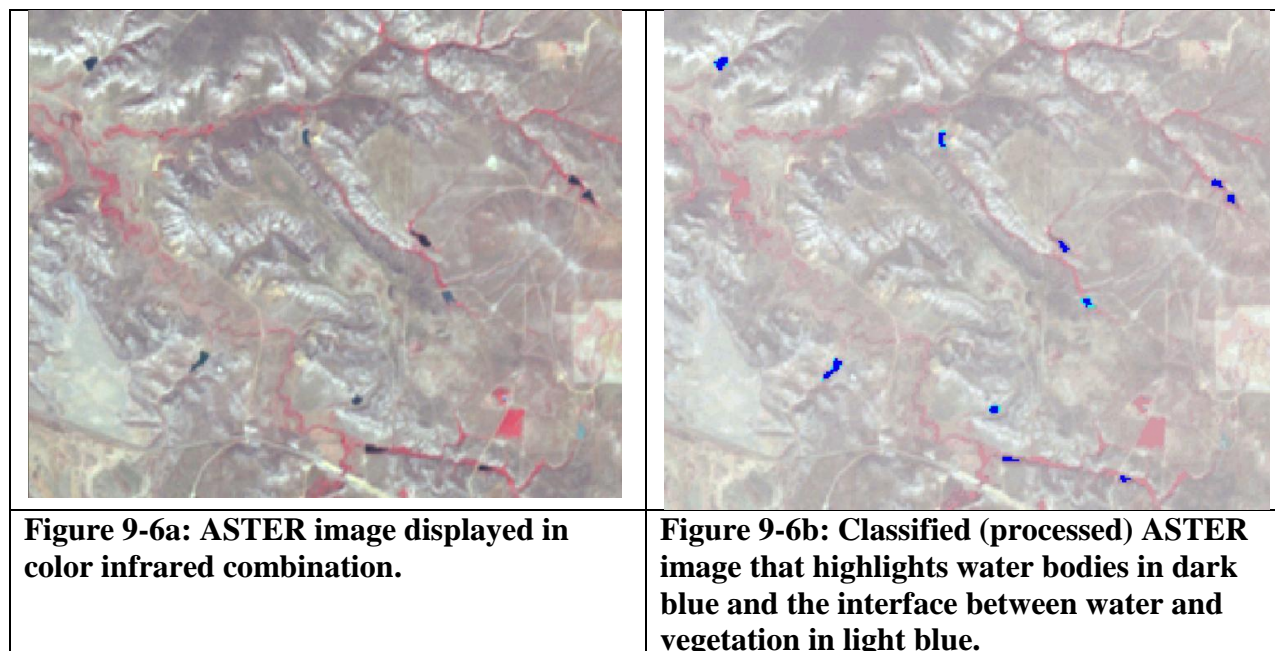
In this late-summer image there were fewer interfacing areas of water and vegetation. During this time of the year, water levels in several ponds and lakes are often lower in comparison to their spring and early-summer levels following snow-melt and run-off. Therefore there were fewer areas (or pixels) in which water and vegetation occurred together. In other words more pixels in the satellite images were classified either as water or vegetation. Also vegetation starts to senescence in late summer leading to decreased contrast between sparsely vegetated areas and bare ground. In the second study, both ASTER and Landsat images acquired in late summer (August 2006) were used and the prevailing ground conditions associated at that time could have limited our ability to map interface between water and vegetation, i.e., mosquito larvae habitat. One approach to overcome this limitation would be to perform sub-pixel classification of the satellite image rather than a per-pixel classification. Sub-pixel classification algorithms (for example, fuzzy logic) would not force each pixel to either water or vegetation. Sub-pixels classifications assign probability values for each pixel pertaining to its membership to water and vegetation. Therefore it is possible for a pixel to have simultaneous memberships in both water and vegetation whereas per-pixel classification methods used in this study had to assign the pixels either of the classes and not both.

Conclusions:

A GIS-based habitat classification model for *C. tarsalis* mosquito larvae has been built for the Powder River Basin, Wyoming, using Landsat remote sensing data and a rule-based spatial modeling system. This approach produces a conservative estimate of suitable habitat due to restrictions in minimum detection size and resolution. High resolution data sets have been tested and found to be superior in identifying suitable habitat that was missed using the Landsat data. A multi-year field campaign has served to refine the conditions for suitable habitat and assist in the definition of landscapes at risk for enhanced production of *C. tarsalis* mosquito, and the field data are currently being used to refine the GIS-based model.

Co-produced waters associated with CBNG production in the Powder River Basin have increased *C. tarsalis* larvae habitat. This increase in suitable habitat is implicated in an increased risk to wildlife, livestock, and people to West Nile Virus. Effective management of co-produced waters can reduce larval habitat since field efforts have found that the greatest abundance of larvae are found in small drainage systems with abundant vegetation and slow moving waters, while relatively few larvae were identified in reservoirs or channelized streams.

Higher spatial resolution ASTER data, despite having fewer spectral bands, were able to identify more water bodies in comparison to Landsat data. Based on the results obtained in this study we recommend that ASTER data can be used for mapping water bodies that are either clear or have green floating vegetation. However the utility of ASTER data for mapping very small water bodies (< 2700 sq m) was somewhat diminished due to the misclassification of non water bodies as water. Extensive field data for calibration and advanced classification algorithms, such as pixel unmixing, might be undertaken to improve the classification accuracies of ASTER data.

Results obtained in this study also underscore the importance of acquiring data in additional spectral regions (i.e. higher spectral resolution) in addition to the higher spatial resolution data. Increased spectral resolution could reduce the spectral confusion between the landscape features and increase the producer and user accuracies of the land cover maps. We conclude that the additional spectral information collected by Landsat reduced commission errors at small scales. In order to improve the detection and minimize the over-prediction of smaller landscape features, satellite imagery that contains both high spatial and spectral resolution data are needed.

This study demonstrates the usefulness of higher spatial resolution ASTER data in monitoring product water related to coalbed natural gas activities and their linkage to mosquito habitat increases.

Reference:

Zou L., Miller S. N. & Schmidtmann E. T. (2006) Mosquito larval habitat mapping using remote sensing and GIS: implications of coalbed methane development and the West Nile virus. *J. Med. Entomol.* **43**, 1034–41.

Task 10 – A Legal History of Policy Actions Affecting CBNG Development and Management in Wyoming

Melinda Harm Benson[10]

Numerous agency, industry and NGO decisions have guided the development of coalbed natural gas (CBNG) extraction in Wyoming's Powder River Basin (PRB). Wyoming hosts an estimated 31.7 trillion cubic feet of CBM reserves, 79% of which are located in the PRB (Quillinan, 2006). Wyoming produced a record-setting 178.6 BCF of CBM in the first half of 2006, equivalent to slightly less than 29.8 BCF per month, on average. At this rate, annual production could exceed 355 BCF (Quillinan, 2006). At the end of June 2006, 22,701 wells existed in the PRB, 16,554 of which were producing wells. Although CBM production has increased in the PRB, drilling has decreased 20% from 2007. Current projections are for about 51,000 wells by 2013. (Quillinan, 2006).

To assess the ongoing PRB play and how management and policy decisions have resulted in landscape changes and socio-economic behaviors, several project investigators at the University of Wyoming worked to identify nodes or junctures of critical decisions and resultant effects from a systems perspective. The goal was to provide an assessment of the legal landscape, which often led to economic, hydrologic, and ecologic landscape changes, that might provide a sound basis for the identification of recommendations for more effective and integrated adaptive basin management for CBM production in future developments.

Methods:

A review of the legal and policy framework under which the regulatory and agency decisions were made in the PRB was performed in order to better understand and provide a timeline for the key decisions made governing the PRB development. A comprehensive analysis, which includes federal and state laws, legal decisions, executive orders, and agency actions, was developed utilizing queries on legal search engine Westlaw. Where possible, free, on-line versions of these materials were then identified and placed on an interactive timeline that is now available on the Wyoming Energy Resource Information Clearinghouse website: http://www.weric.info/tl/timeline.htm.

Results and Discussion:

Once the comprehensive review was completed, the team identified five key policy drivers, or critical junctures, considered to have altered the course of CBNG development in the PRB. The following is a detailed account of four of the five chosen drivers. One of the selected drivers, the deregulation of natural gas pricing under the Natural Gas Wellhead Decontrol Act of 1989 in which "first sales" of natural gas were to be free of any federal price regulations and subsequent FERC Orders No. 436 (1985) and 636 (1992) is not discussed here.

---

[10] Current Address: Department of Geography. University of New Mexico, Albuquerque, NM
. email: mhbenson@unm.edu

They are: (1) the multi-tiered litigation over whether the Bureau of Land Management adequately analyzed the impacts of CBNG development as required under the National Environmental Policy Act (NEPA), (2) the State of Wyoming's policy of encouragement to rapidly accelerate CBNG development on state lands early in the PRB play, (3) a series of federal administrative decisions, initially implemented by the Bush Energy Policy and subsequent codified by the Energy Policy Act of 2005, facilitating and expediting the PRB play, and (4) the State of Wyoming's designation of CBM water production as a "beneficial use" under its state water law.

These drivers provided the basis for an interdisciplinary assessment of how these events actually influenced changes in the economic and ecological landscape and provided an opportunity to examine what potential interventions/policy changes could assist future development in the PRB and other basins.

1. Litigation over Wyoming BLM NEPA Analysis for Leasing CBNG Development

When CBNG initially came onto the scene, it came quickly, and little was known about its environmental impacts and how they would compare with conventional natural gas development. One major hurdle involved with the development of CBNG was the requirement that the major federal agency involved, the BLM, comply with its obligation to assess the environmental impacts under the National Environmental Policy Act (NEPA). The BLM is the federal agency responsible for management of federally owned mineral interests, including CBNG.

Nationally, BLM manages 261 million surface acres and 700 million sub-surface acres of mineral estate. In Wyoming, it is responsible for 18.4 million surface acres and 41.6 million acres of subsurface mineral estate. Of these, 4.7 million acres are in the Powder River Basin.

NEPA requires the BLM and other federal agencies to take a "hard look" at the environmental consequences of their actions and to develop alternatives to those actions based on their environmental review. (42 U.S.C. 4332) At the time when technological advancement first made CBNG commercially viable, the BLM had in place existing environmental documents that had included NEPA reviews for actions authorizing leasing oil and gas development in the Powder River Basin. However, because these documents predated the commercial advancement of CBNG technology, they did not contemplated the extraction of CBNG or analyze its unique impacts.

In an effort to address this, the BLM issued leases for CBNG development using the existing NEPA analysis but BLM also issued several post-leasing NEPA documents, most significantly the Wyodak EIS, specifically addressing the impacts of CBNG development.

Environmentalists argued that these documents were insufficient in their analysis because they did not include a pre-leasing analysis. NEPA, they argued, requires a hard look *before* the agency makes a decision. In the absence of a pre-leasing analysis of the impact of CBNG, they argued, the BLM failed to comply with NEPA.

Environmental groups appealed the agency's actions to the Interior Board of Land Appeals, an administrative court inside the U.S. Department of Interior. The IBLA agreed with the environmentalists and concluded the requirements of NEPA had not been satisfied prior to issuing the leases. It held that the BLM failed to consider the unique impacts of CBNG development when it made its leasing decisions.

> [T]he record amply demonstrate[s] that the magnitude of water production from CBM extraction in the Powder River Basin creates unique problems and that CBM development and transportation present critical air quality issues not adequately addressed [in existing, pre-leasing NEPA documents]. Because the [these documents] failed to take the requisite hard look at the impacts associated with CBM extraction and development, which clearly are relevant matters of environmental concern in this case, BLM could not rely on that document to satisfy its NEPA obligations for the proposed leasing decisions at issue here.

BLM responded by asking the IBLA to reconsider its decision, arguing that "the United States is losing valuable [CBM] and related royalties each month through drainage caused by CBM wells on private and state tracts adjacent to Federal lands" (Interior Board of Land Appeals, 2002). Seemingly unimpressed, the IBLA instead granted the environmentalists' request that future leasing under the current NEPA documents be halted and until an appropriate NEPA analysis was completed (Interior Board of Land Appeals, 2002).

Industry groups successfully challenged the IBLA decision in federal district court. Their victory was short lived, however, as Judge Brimmer's decision was then appealed to the 10th Circuit Court of Appeal. The Tenth Circuit reinstated the IBLA's initial holding that the BLM was required to analyze the impacts of CBM development before leasing the parcels (Pennaco Energy, Inc. v. U.S. Dept. of Interior, 2004). In the end, the BLM never did conduct a preleasing analysis. Instead, the BLM ultimately resolved the issue by conducting an Environmental Assessment examining an alternative of revoking the leases and then rejecting that alternative (Bureau of Land Management, 2005).

2. Wyoming's "Go Blue letter"

In November of 1999, the State of Wyoming took a significant step toward encouraging development of CBM on state lands. At the time, development on land with federal minerals lands was proceeding relatively slowly, as the BLM issued numerous Environmental Assessments (EAs) to address a rapidly growing number of proposals to drill for this new form of natural gas while also meeting its obligations under NEPA (Kesterke, 2007).

When the BLM exceeded its development scenarios under its initial EAs, it was forced to halt development until new NEPA analyses were completed (Kesterke, 2007; Zander 2007). As the BLM became further backlogged with permit applications, Wyoming stepped forward to encourage operators to develop on state owned lands, lands where NEPA does not apply and leasing procedures are relatively streamlined. It did so by issuing the famous "Go Blue Letter" to industry operators, informing them that Wyoming was eager to "work with you as operator/lessee or potential lessee on State lands, to get the biggest bang from your drilling buck"

(State of Wyoming, 1999). "Blue" is in reference to the fact that, on land ownership maps, state lands are traditionally demarcated in blue. In essence, the letter was an open invitation to develop on state land. By opening the door with a more streamlined process, the state accelerated development on state lands (Duffy, 2005).

3. President Bush's Energy Policy and Subsequent Energy Act of 2005

The Bush Administration's National Energy Policy (NEP), drafted by Vice President Dick Cheney and the "Energy Task Force" was released in May 2001. It outlined the various steps that the Administration believed the country ought to take in order to rectify the energy problems facing the nation, particularly the United States' dependence on foreign oil. This policy was the foundation of the Energy Policy Act of 2005, signed into law by President Bush in 2005 (Public Law 109-58, 119 Stat. 594. 2005; Bryner, 2002).

The National Energy Policy (NEP)
The NEP articulated five overarching goals: (1) modernizing conservation, (2) modernizing the energy infrastructure, (3) increasing energy supplies, (4) accelerating protection of the environment, and (5) increasing energy security. Included in the Administration's policy were discussions of CBNG. Of these, the goal of increasing domestic fuel supplies was of paramount concern. Among the 105 specific recommendations, there was a clear emphasis on streamlining the permitting and regulatory process for oil and gas development.

The NEP touted CBNG as the future of energy in the United States and referred to the fact that it is cheaper to drill and extract and burns cleaner. The Task Force recommended that the President encourage Congress to expand current tax credits to include methane projects.

The Administration began implementing a number of the NEP recommendations through Executive Orders. There were two main Executive Orders that accompanied the NEP: Executive Order 13212 and Executive Order 13211 (Morgan, 2007). Executive Order 12212 directed the BLM to expedite permits and other federal actions necessary for energy-related project approvals. This order also directed BLM to take into consideration the impact of the Bush National Energy Policy.

In response to this Executive Order, the BLM issued a series of Instructional Memoranda (IMs) to BLM Field Offices. These memoranda advised the BLM on how to implement the NEP. BLM IM 2003-233 discussed the integration of the Energy Policy and Conservation Act (EPCA) into the land use planning process. It reaffirmed the BLM`s "commitment to not unduly restrict access to the public lands for energy exploration and development" and of the goal of "expedit[ing] their review of permits or take other actions necessary to accelerate the completion of energy-related projects" ¨including through reassessment and modification of constraints to oil and gas leasing. It established seven priority areas, including the PRB (Morgan, 2007).

BLM IM 2003-234 was issued to eliminate "undue restrictions on access to federal lands for exploration and development." It required a review of all existing lease stipulations to determine whether they were "necessary and effective." It also directed that, to the extent to which

stipulations where not found effective, the agency must consider waiver, exceptions or modifications.

Executive Order 13211 required agencies to prepare a "statement of energy effects" for any agency action that could adversely impact energy supply and distribution and also required the agencies to discuss potential alternatives to avoid those effects. In October 2001, the BLM created an Energy Office to better enforce the Bush NEP.

The Energy Policy Act of 2005
The Energy Policy Act of 2005 essentially codified the NEP. It includes several provisions affecting access to federal lands and addressed continuing concerns over delays in the permitting process. Specifically, Section 365 established federal "permit streamlining" pilot projects in seven BLM field offices in the five western states where seventy percent of APDs are processed (Public Law 109-58, § 365, 119 Stat. 594, 2005). The idea was to implement new management strategies to further expedite the processing of permits, including the approach of placing employees from other federal agencies in the BLM offices to provide an increased focus on the permitting of APDs (Clarke, 2005).

The legislation also established a BLM permitting processing Improvement Fund designed to allow a share of mineral rental revenue to be deposited into the Fund and then be immediately available for the coordination of oil and gas development at the pilot offices. In 2005, it was estimated by BLM officials that an additional 19 million dollars would be available in rental revenue to keep up with the demand for issuing APDs. Special U.S. Treasury accounts were established so that the pilot offices are able to access the funds (Clarke, 2005).

Financial Resources for Permitting
Former BLM officials argue that the main impact of these policies were monetary (Kesterke 2007; Zander, 2007). Increased financial resources allowed the BLM to almost quadruple it staff and process more permits to drill (Kesterke, 2007; Zander, 2007). In 2001, the Buffalo Field Office received BLM's "Award for Excellence" for issuing more drilling permits than all other BLM offices in the country combined. The 2005 Energy Bill expanded already substantial acceleration in the approval of drilling applications, with additional funding and more experience in management modifications resulting in approving 7,018 APDs in FY 2005 (Clarke, 2005).

4. Wyoming's Decision to Designate CBM Production a "Beneficial Use" of Water

One major issues associated with the development of CBNG is how to manage and regulate the water discharges associated with its extraction. In contrast to conventional natural gas development, CBNG development results in relatively large quantities of co-produced water. Water management issues are a matter of both quality and quantity.

In Wyoming, like most Western states, water is the property of the state, and individuals are allowed to use this resource only if they can put it to beneficial use (Ruckelshaus Institute, 2005).   The SEO is charged with administering the water resources of the state through a permit system. The permit application requires that the proposed beneficial use of the water be identified.

Wyoming recognizes CBNG water production as beneficial use and places regulation of CBNG by project water under the jurisdiction of the Office of the State Engineer. This is unique among Western states. Darin (2005) provides a detailed, comprehensive analysis of the approaches of various states and reports that, in most western states, CNG byproduct water is regulated by each state's Oil and Gas Commission and therefore exempted from traditional water allocation permitting requirements.

The impact of having CBNG water regulated by the SEO rather than the state Oil and Gas Commission has never been fully explored. Some argue that, if the state proceeds with the designation of CBNG byproduct water as a beneficial use, that designation should be further refined and that even more traditional uses of water such as irrigation of agricultural lands have a limit on the amount of water that can be reasonably consider beneficial use (Fox & MacKinnon, 2007). CBNG operators, under this reasoning, could be held to a "best technology available" standard that encouraged industry to use the least amount of water necessary to produce CBNG and that the state should promulgate regulations that addresses the interrelationship between water quantity and water quality. Perhaps in response to these and other critics, the State Engineer's office recently modified its permit conditions to reflect a threshold water-to-gas ratio of 10 barrels per mcf. Operators will be required to demonstrate that they will achieve the required ratio in the first two to three years of water production (Office of the State Engineer, 2008).

References:

Bryner, Gary C. *The National Energy Policy: Assessing Energy Policy Choices*, U. Col L. Rev. (2002).

Bureau of Land Management. Environmental Assessment Oil and Gas Leasing Buffalo Field Office 070-05-064 (August 22, 2005).

Bureau of Land Management. Instruction Memorandum 2003-233 (Jul 28, 2003).

Bureau of Land Management. Instruction Memorandum 2003-234 (Jul 28, 2003).

Kathleen Clarke. BLM Oil and Gas Activities-Part 1. Hearings before the Senate Appropriations Subcommittee on Interior and Related Agencies (October 25, 2005).

Darin, Thomas. *Waste or Wasted: Rethinking the Regulation of Coalbed Methane Byproduct Water in the Rocky Mountains: A Comparative Analysis of Approaches for Coalbed Methane Produced Water Quantity Legal Issues in Utah, New Mexico, Colorado, Montana and Wyoming.* 17 J. Envtl. L. & Litig. 281 (2002).

Duffy, Robert J. *Political Mobilization Venue Change and the Coal Bed Methane Conflict in Montana and Wyoming*, 45 Nat. Res. J. 409, 431 (2005).

Fox, Kate & MacKinnon, Anne. Demanding Beneficial Use: Opportunities and Obligations for Wyoming Regulators in Coalbed Methane, 6 Wyo. Law Rev. 369 (2006).

Interior Board of Land Appeals. Wyoming Outdoor Council, et al., 156 IBLA 347, 357 (April 26, 2002).

 Interior Board of Land Appeals. Wyoming Outdoor Council, et al., 157 IBLA 259 (October 15, 2002).

Kesterke, Alan. Personal Communication (December 19, 2007).

Morgan, Ann. Energy Policy Act of 2005 Oversight, Hearings on H.R. 6 Before the Committee House Natural Resources Subcommittee on Energy and Minder Resources, April 18, 2007.

Pennaco Energy, Inc. v. U.S. Dept. of Interior, 377 F.3d 1147 (10th Cir. 2004).

Quillinan, Scott. Energy Specialist Wyoming State Geological Survey, Wyoming Mineral Update: Coalbed Natural Gas (January-June 2006).

Ruckelshaus Institute of Environment and Natural Resources. Water Production from Coalbed Methane Development in Wyoming: A summary of Quantity, Quality and Management Options-Final Report (December, 2005).

State of Wyoming, Office of State Lands and Investments. "Go Blue" Letter. (November 18, 1999).

State of Wyoming. Office of the State Engineer's Press Release: *"A permit to appropriate ground water in order to produce coal-bed methane gas carries with it an expectation that the production of gas will occur in a timely fashion." December 18, 2007. Accessed at: http://seo.state.wy.us/Press/2007/121807.aspx.*

U.S. White House, National Energy Policy." http://www.whitehouse.gov/energy/2001/National-Energy-Policy.pdf.

Zander, Richard. Personal Communication. (December 19, 2007).

GRAPHICAL MATERIALS LIST

List of Tables

BIBLIOGRAPHY

The following is a list of publications and presentations resulting from this funding.

Task 1
Not applicable.

Task 2
Puckett, K.A., 2008, Uncertainty quantification in predicting deep aquifer recharge rates, with applicability in the Powder River Basin of Wyoming, M.S. Thesis, University of Wyoming, Laramie, WY 82071, USA

Task 3
Tentative Title: Coalbed Methane: Energy and Environment; Editors: K.J. Reddy and Lusha Transtand; Publisher: Nova Science Publishers, Inc. New York; Tentative Data of Publication: June 2009

Milligan C. L., and K.J. Reddy. 2007. Monitoring the Quality of CBNG Produced Water Across the Powder River Basin, WY. 2007 National Water Quality Conference, Savanna, Georgia, U.S. Department of Agriculture and Cooperative Research and Extension Service, Washington, January 29-February 1st, 2007.

Reddy, K.J., R. E. Jackson, C. L. Milligan. 2007. (Invited) Coalbed Natural Gas (CBNG) Produced Water Quality Across the Powder River Basin, Wyoming: Beneficial Uses. Colorado State University Department of Chemical and Biological Engineering Seminar Series, Fort Collins, Colorado, March 23rd, 2007.

Milligan C. L., and K.J. Reddy. 2007. Water Quality of CBNG Produced Water In The Powder River Basin, Wyoming. University of Wyoming Graduate School Symposium, Laramie, Wyoming, April 4th, 2007.

Milligan C. L., and K.J. Reddy. 2007. Monitoring of Trace Elements in CBNG Disposal Ponds Across the Powder River Basin, Wyoming. American Society of Mining and Reclamation's 24th Annual Conference, Gillette, Wyoming. June 4-7th, 2007.

Reddy, K.J., and R.E. Jackson. 2007. (Invited, Keynote Presentation) Coalbed natural gas produced water: Geochemistry and beneficial uses in semi-arid environment. Special Symposium: Coal and Coal Combustion By-products, 9th International Conference on Biogeochemistry of Trace Elements, Beijing, China.

Milligan C.L. and K.J. Reddy. 2007. Monitoring the Quality of CBNG Produced Water and Associated Sediments across the Powder River Basin, Wyoming. American Water Resources Association Annual Conference, Albuquerque, New Mexico. Scheduled for November 12-15th, 2007.

Milligan, C.L., and K.J. Reddy. 2007. Monitoring the Quality of CBNG Produced Water and Determining Beneficial Uses across the Powder River Basin, Wyoming. 2008 National Water Quality Conference, U.S. Department of Agriculture and Cooperative Research and Extension Service, Washington, D.C. Scheduled for February 2nd-7th, 2008.

Milligan, C.L., K.J. Reddy, and G. Paige. 2008. Monitoring the Quality of CBNG Produced Water and Determining Beneficial Uses across the Powder River Basin, Wyoming. Sparks, Reno, NV. February 2nd-7th, 2008. National Water Quality Conference, U.S. Department of Agriculture and Cooperative Research and Extension Service, Washington, D.C.

Milligan, C.L., and K.J. Reddy. 2007. Monitoring the Quality of CBNG Produced Water Across the Powder River Basin, WY. Abstract: In Proceedings of 2007 National Water Quality Conference, U.S. Department of Agriculture and Cooperative Research and Extension Service, Washington, D.C.
http://www.usawaterquality.org/conferences/2007/PPTs&Posters/Poster/MilliganWY.pdf

Milligan C. L., and K.J. Reddy. 2007. Monitoring of Trace Elements in CBNG Disposal Ponds Across the Powder River Basin, Wyoming. In Proceedings of Thirty Years of SMRCA and Beyond, National Meetings of American Society of Mining and Reclamation, 3134 Montavesta Road, Lexington, Kentucky, 40502.

Milligan, C.L., and K.J. Reddy. 2007. Monitoring the Quality of CBNG Produced Water and Determining Beneficial Uses across the Powder River Basin, Wyoming. Abstract: Submitted for 2008 National Water Quality Conference, U.S. Department of Agriculture and Cooperative Research and Extension Service, Washington, D.C.

Raisbeck, M.F., S.L. Riker, C.M. Tate, R.E. Jackson, M.A. Smith, K.J. Reddy, and J.R. Zygmunt. 2007. Water quality for Wyoming livestock and wildlife: A review of the literature pertaining to health effects of inorganic contaminants. Department of Veterinary Sciences and Renewable Resources, University of Wyoming, Wyoming Department of Game and Fish, and Wyoming Department of Environmental Quality, pp107.
http://deq.state.wy.us/wqd/WQD_home/Announcements/final%20draft_1.pdf

Jackson, R.E., and K.J. Reddy. 2007. Geochemistry of CBNG produced water in Powder River Basin: Salinity and Sodicity. Water, Air, and Soil Pollution. DOI:10.1007/s11270-007-9398-9, May 3rd, 2007. http://www.springerlink.com/content/e11m0777845n7226/fulltext.html

Jackson, R.E., and K.J. Reddy. 2007. Trace element chemistry of coalbed natural gas produced water in the Powder River Basin, Wyoming. Environmental Science and Technology. DOI: 10.1021/es062504o. 20 July, 2007.
http://pubs.acs.org/cgi-bin/abstract.cgi/esthag/2007/41/i17/abs/es062504o.html

Milligan, C.L., and K.J. Reddy. 2008. Monitoring the Quality of CBNG Produced Water and Determining Beneficial Uses across the Powder River Basin, Wyoming. Abstract: 2008 National Water Quality Conference, U.S. Department of Agriculture and Cooperative Research and Extension Service, Washington, D.C.

Task 4

Brinck, L., 2006. Water and soil quality issues associated with coal bed natural gas development using strontium isotopes as a natural tracer. 2006 EPA Graduate Fellowship Conference, Washington DC Sept. 24-27, 2006.

Brinck, E.L., and Frost, C.D. 2007. Detecting infiltration and impacts of introduced water using strontium isotopes. Ground Water, v. 45, 554-569, doi:10.1111/j.1745-6584.2007.00345.x.

Brinck, E.L,, Frost, C.D., 2007. Using strontium isotopes to evaluate CBM irrigation amendments. 30 Years of SMCRA and Beyond, National Meeting of the American Society of Mining and Reclamation, Gillette WY June 2-7, 2007. R.I. Barnhisel (ed.), published by ASMR, 2134 Montavesta Road, Lexington KY 40502.

Brinck, Elizabeth L., 2007. Assessing Potential Environmental Impacts from Coal Bed Natural Gas Produced Water Using Strontium Isotopes, Ph.D. dissertation, University of Wyoming, 119p.

Brinck, E.L., Frost, C.D., Evaluation of amendments used to prevent sodification of irrigated fields. Applied Geochemistry, in revision September 2008.

Brinck, E.L., Drever, J.I., and Frost, C.D., 2008. The geochemical evolution of water co-produced with coal bed natural gas in the Powder River Basin, Wyoming. Environmental Geosciences, in press July 2008.

Carter, S.A., Mailloux, J., Frost, C.D., Sharma, S., Meredith, M.T., 2007. Isotopic and geochemical characterization of the Powder River, Wyoming and Montana. 30 Years of SMCRA and Beyond, National Meeting of the American Society of Mining and Reclamation, Gillette WY June 2-7, 2007. R.I. Barnhisel (ed.), published by ASMR, 2134 Montavesta Road, Lexington KY 40502.

Carter, S.A., and Frost, C.D., 2007. Isotopic and geochemical characterization of the Powder River, WY and MT: refining assimilative capacity models. Geological Society of America Abstracts with Programs, v. 39, abstract 177-8, p. 482.

Carter, S. and Frost, C., 2008. Identification And Regulation Of Coal Bed Natural Gas Co-Produced Water In Surface Waters, Powder River Basin, Wyoming And Montana, Geological Society of America Abstracts with Programs, v. 40, to be presented in Houston, October 2008.

Carter, S.A., 2008. Geochemical analysis of the Powder River, Wyoming/Montana and an assessment of the impacts of coalbed natural gas co-produced water. M.S. thesis, University of Wyoming, 146 p.

Mailloux, J., Frost, C.D., 2007. Nd and Sr isotopic mass balance of dissolved, suspended and bed load of the Powder River, WY and MT: insights into weathering processes in an arid watershed. Geological Society of America Abstracts with Programs v. 39, abstract 177-9, p. 482.

Mailloux, J., Ogle, K., Frost, C., 2008. Using a Bayesian statistical model to determine the amount of coalbed natural gas co-produced water in the Powder River, Wyoming and Montana, Geological Society of America Abstracts with Programs, v. 40, to be presented in Houston, October 2008.

Mailloux, J., Ogle, K., Frost, C., Using a Bayesian statistical model to determine the amount of coal bed natural gas co-produced water in the Powder River, Wyoming and Montana, manuscript submitted to Water Resources Research, September 2008.

Sharma, S., Frost, C.D., 2007, Tracking CBNG co-produced water using stable carbon isotope of DIC-an innovative approach. Geological Society of America Abstracts with Programs, v. 39, abstract 42-13, p. 116.

Sharma, S., and Frost, C.D., 2008. Tracing coal bed natural gas co-produced water using stable isotopes of carbon. Ground Water v 46 no 2, 329-334.

Task 5
Sajtar, E.T. and Bagley, D.M. 20XX, Electrodialysis Reversal: Process and Cost Approximations for Treating Coal-Bed Methane Waters, submitted to Desalination.

Sajtar, E.T. and Bagley, D.M. 20XX, Reverse Osmosis Cost Approximating and Sensitivity Analyses. To be submitted to Desalination.

Sajtar, E.T. 2007. Getting the Salt Out: Technologies and Costs for treating CBM Produced waters. American Water Works Association and Water Environment Federation 4th Annual Rocky Mountain Student Conference. May 14, 2007. University of Colorado at Boulder.

Sajtar, E.T. Bagley, D.M. Johnson, D.W. 2007. Getting the Salt Out: Technologies and Costs for treating CBNG Produced waters in the Powder River Basin. American Society of Mining and Reclamation (ASMR) Annual Conference. June 5, 2007. Gillette, Wyoming.

Task 6
Xie, X., Presentation at the National Meeting of the American Society of Mining and Reclamation: Aspects of coalbed methane water and oil recovery, June 2-7, 2007, Gillette, Wyoming.

Morrow, N.R., Presentation at the Enhanced Oil Recovery Institute Commission Meeting: Low salinity waterflooding, May 24, 2007, Laramie, Wyoming.

Pu, H., Xie, X. and Morrow, N.R., "Application of coalbed methane water to oil recovery from Tensleep sandstone by low-salinity waterflooding," paper SPE 113410 presented at the 2008 SPE Improved Oil Recovery Symposium, April 21 – 23, 2008, Tulsa, Oklahoma.

Xie, X., Pu, H. and Morrow, N.R., "Aspects of coalbed natural gas water and oil recovery," R.I. Barnhisel (ed.) Published by ASMR, 3134 Montavesta Rd., Lexington, KY 40502.

Task 7

Ganjegunte, G.K., R.W. Gregory, G.F. Vance and R.C. Surdam. 2005. Innovative technology to reduce sodium concentrations in saline-sodic coalbed natural gas waters: Use of natural zeolites. Presented at the American Society of Agronomy/Soil Science Society of America Annual Meetings, Salt Lake City, UT. Agronomy Abstracts CD p. 149

Ganjegunte, G.K., L.A. King and G.F. Vance. 2008. Cumulative soil chemistry changes from application of saline-sodic waters. Special Issue: Environmental impacts and sustainable reuse of degraded water reuse. Journal of Environmental Quality 37:S-128-S138 (Invited Special Issue)

Ganjegunte, G.K. and G.F. Vance. 2005. Evaluation of changes in soil chemistry from leaching saline-sodic waters through Powder River Basin soils: A column study approach. Presented at the American Society of Agronomy/Soil Science Society of America Annual Meetings, Salt Lake City, UT. Agronomy Abstracts CD p. 212

Ganjegunte, G.K., G.F. Vance, R.W. Gregory, and R.C. Surdam. 2006. Utilization of zeolite for reducing sodium and salt concentrations in saline-sodic coalbed natural gas waters. In: R.S. Bowman and S.E. Delap (Eds.) Zeolite =06 - 7th International Conference on the Occurrence, Properties, and Utilization of Natural Zeolites, Socorro, NM, 16-21, July, 2006. ICOPUNZ Abstracts pp. 111-112.

Ganjegunte, G.K., G.F. Vance, R.W. Gregory and R.C. Surdam. 2006. Utilization of zeolite for reducing sodium and salt concentrations in saline-sodic coalbed natural gas waters. Presented at the Soil Science Society of America Annual Meetings, Indianapolis, IN. Agronomy Abstracts CD 534.

Ganjegunte, G.K., G.F. Vance and L.A. King. 2005. Tracking salt and sodium build-up due to irrigating with coalbed natural gas product water: Soil solution lysimeter and soil saturation paste extract studies. Presented at the 22nd National American Society of Mining and Reclamation Symposium Annual Meetings, Breckenridge, CO. In: R. Barnhisel (ed.) Raising Reclamation to New Heights, Lexington, KY CD pp. 378-387.

Johnston, C,R., S. Jin, G.F. Vance and G.K. Ganjegunte. 2006. Impacts of coalbed natural gas co-produced water on cropland irrigated soils in the Powder River Basin, Wyoming. Presented at the 10th Billings Land reclamation Meetings and 23nd National American Society of Mining and Reclamation Symposium, Billings, MT. In: R. Barnhisel (ed.) Reclamation: Supporting Future Generations, Lexington, KY pp. 301-316.

Johnston, C.R., G.F. Vance and G.K. Ganjegunte. 2007. Irrigation with coalbed natural gas co-produced waters: Changes in soil physical and chemical properties. Presented at the Soil Science Society of America Annual Meetings, New Orleans, LA. Agronomy Abstracts CD 304-6.

Johnston, C.R., G.F. Vance and G.K. Ganjegunte. 2008. Irrigation with coalbed natural gas co-produced water. Agricultural Water Management 95 (11): November issue.

King, L.A. 2006. Land Application with Saline-Sodic Coalbed Natural Gas Co-Produced Waters in Wyoming=s Powder River Basin: Impacts to Soil and Biological Properties. Ph.D. Dissertation, University of Wyoming

King, L.A., G.F. Vance and G.K. Ganjegunte. 2005. Use of coalbed natural gas (CBNG) waters: Soil and plant responses. Presented at the 22nd National American Society of Mining and Reclamation Symposium Annual Meetings, Breckenridge, CO. In: R. Barnhisel (ed.) Raising Reclamation to New Heights, Lexington, KY CD pp. 607-622.

King, L.A., G.F. Vance and G.K. Ganjegunte. 2005. Saline-sodic water impacts to soils and vegetation. Presented at the 22nd National American Society of Mining and Reclamation Symposium Annual Meetings, Breckenridge, CO. In: R. Barnhisel (ed.) Raising Reclamation to New Heights, Lexington, KY CD pp. 623-625.

King, L.A., G.F. Vance and G.K. Ganjegunte. 2006. Land application of saline-sodic coalbed natural gas (CBNG) co-produced waters: soil and vegetation impacts. Presented at the 10th Billings Land reclamation Meetings and 23nd National American Society of Mining and Reclamation Symposium, Billings, MT. In: R. Barnhisel (ed.) Reclamation: Supporting Future Generations, Lexington, KY pp. 344-361.

Vance, G.F. 2006. Management of saline-sodic waters from coalbed natural gas production. Presented at the Special Symposium ΑManagement and Use of Waters of Altered or Impaired Quality@ at the Soil Science Society of America Annual Meetings, Indianapolis, IN. Agronomy Abstracts CD 103-5. (Invited)

Vance, G.F. 2008. Land application and treatment of coalbed methane co-produced waters: Soil properties and water management. Soil and Water Conservation Service Conference, Estes Park, CO. (Invited)

Vance, G.F. and others. 2008. The Future of Coal: Upstream Issues. National Commission on Energy Policy (in layout process)

Vance, G.F., G.K. Ganjegunte, and M.A. Urynowicz. 2006. Ion exchange reactions of natural zeolites: Adsorption, exchange kinetics, and desorption. In: R.S. Bowman and S.E. Delap (Eds.) Zeolite =06 - 7th International Conference on the Occurrence, Properties, and Utilization of Natural Zeolites, Socorro, NM, 16-21, July, 2006. ICOPUNZ Abstracts pp. 238-239.

Vance, G.F. L.A. King and G.K. Ganjegunte. 2008. Soil and plant responses from land application of saline-sodic waters: Implication of management. Special Issue: Environmental impacts and sustainable reuse of degraded water reuse. Journal of Environmental Quality 37:S-139-S148 (Invited Special Issue)

Vance, G.F., H. Zhao, M.A. Urynowicz, G.K. Ganjegunte and R.W. Gregory. 2007. Reduction in coalbed methane (CBM) water sodicity using zeolites. Presented at the 24th National American Society of Mining and Reclamation Symposium, Gillette, WY. In: R. Barnhisel (ed.) 30 Years of SMCRA and Beyond, Lexington, KY pp. 837-844.

Vance, G.F., H. Zhao, M.A. Urynowicz, R. Gregory and G.K. Ganjegunte. 2007. Use of zeolites for treating natural gas coproduced waters in Wyoming, USA. Special Symposium "Environmental Impact and Sustainability of Degraded Water Reuse." Presented at the Soil Science Society of America Annual Meetings, New Orleans, LA. Agronomy Abstracts CD 230-19. (Invited)

Zhao, H. and G.F. Vance. 2007. Treatment of coalbed methane produced water using zirconium phosphate to maximize its beneficial use. Presented at the Soil Science Society of America Annual Meetings, New Orleans, LA. Agronomy Abstracts CD 327-2.

Zhao, H., G.F. Vance, G.K. Ganjegunte, and M.A. Urynowicz. 2008. Use of zeolites for treating natural gas co-produced waters in Wyoming, USA. Desalinization Journal 228:263-276.

Zhao, H., G.F. Vance, M.A. Urynowicz and R.W. Gregory. 2008. Integrated treatment process using a natural Wyoming clinoptilolite for remediating produced waters from coalbed natural gas operations. Applied Clay Science (Available online doi:10.1016/j.clay.2008.03.007)

Zhao, H., G.F. Vance, M.A. Urynowicz, G.K. Ganjegunte, and R.W. Gregory. 2007. An Integrated Process using Wyoming Zeolite for Treating Saline-Sodic Waters Produced from Coalbed Natural Gas Operations. Presented at the 44th Clay Minerals Society Meeting, Santa Fe, NM. Clay Mineral Society Abstracts 44:174.

Zhao, H., G.F. Vance, M.A. Urynowicz, R.W. Gregory and G.K. Ganjegunte. 2007. Processes using zeolites for treating waters produced from coalbed natural gas operations. Presented at the Soil Science Society of America Annual Meetings, New Orleans, LA. Agronomy Abstracts CD 307-6.

Task 8
Johnson, L.A., C.J. Boese and J.S. Meyer. 2007. Longitudinal Changes in Potential Toxicity of Coalbed Natural Gas Produced Water along Beaver Creek in the Powder River Basin, Wyoming. Presented at Wyoming Game and Fish Department Four State Meeting, Sheridan, WY. 24 April.

Johnson, L.A., C.J. Boese and J.S. Meyer. 2007. Longitudinal Changes in Potential Toxicity of Coalbed Natural Gas Produced Water along Beaver Creek in the Powder River Basin, Wyoming. Presented at Annual Meeting of the American Society of Mining and Reclamation, Gillette, WY. 5 June.

Johnson, L.A., C.J. Boese and J.S. Meyer. 2007. Longitudinal Changes in Potential Toxicity of Coalbed Natural Gas Produced Water along Beaver Creek in the Powder River Basin, Wyoming. Presented at the Twenty-eighth Annual Meeting of the Society of Environmental Toxicology and Chemistry. Milwaukee, WI. 11-15 November.

Johnson, L.A. 2007. Longitudinal Changes in Potential Toxicity of Coalbed Natural Gas Produced Water along Beaver Creek in the Powder River Basin, Wyoming. M.S. thesis, University of Wyoming, Laramie, WY.

Task 9
Zou L., Miller S. N. & Schmidtmann E. T. (2006) Mosquito larval habitat mapping using remote sensing and GIS: implications of coalbed methane development and the West Nile virus. *J. Med. Entomol*. 43, 1034–41.

Task 10
Abebe, N.A., and F.L. Ogden, (2008) Peak Sediment Flow Scaling in a Small Hortonian Watershed, Eos Trans. AGU, 89(53), Fall Meet. Suppl., Abstract H53B-1057.

ABBREVIATIONS AND ACRONYMS

BFR: Belle Fourche River
BLM: Bureau of Land Management, U.S.
CAS: Columbia Analytical Services, Inc.
CBM: coalbed methane (same as coalbed natural gas, used interchangeably in this report)
CBM-DTC: coalbed methane demineralization treatment cost
CBNG: coalbed natural gas (same as coalbed methane, used interchangeably in this report)
CCC: criteria continuous concentration
CEC: cation exchange capacity
CHR: Cheyenne River
CI: confidence interval
CMC: criteria maximum concentration
DIC: dissolved inorganic carbon
DO: dissolved oxygen
DOE: Department of Energy
EBCT: empty bed contact times
EC: electrical conductivity
ECEC: effective cation exchange capacity
ED: electrodialysis
EDR: electrodialysis reversal
ELI-B: Energy Laboratories, Inc. – Billings
ELI-G: Energy Laboratories, Inc. – Gillette
EOR: enhanced oil recovery
EPA: Environmental Protection Agency, U.S.
FHM: fathead minnow
HEEPM^{TM}: high efficiency electro-pressure membranes
IX: ion exchange
LILT: lower incipient lethal temperature
LPR: Little Powder River
MCL: maximum contaminant level
OOIP: original oil in place
ORP: oxidation-reduction potential
PERL: Parametrix Environmental Research Laboratory
PR: Powder River
PRB: Powder River Basin
PV: pour volume
RB: Red Buttes Laboratory
RO: reverse osmosis
SAR: sodium adsorption ratio
SWAT: Soil and Water Assessment Tool
TA-N: total ammonia nitrogen
TCLP: toxicity characteristics leaching procedure
TDS: total dissolved solids
TN: total nitrogen
TR: Tongue River

IUA: un-ionized ammonia
USGS: U.S. Geological Survey
WET: whole efficient toxicity
WGFD: Wyoming Game and Fish Department
WHO: World Health Organization
WOGCC: Wyoming Oil and Gas Conservation Commission
WRDS: Water Resources Data Systems, University of Wyoming
WYDEQ: Wyoming Department of Environmental Quality
WYGISC: Wyoming Geographic Information Science Center, University of Wyoming
WYPDES: Wyoming Pollutant Discharge Elimination System

National Energy Technology Laboratory

626 Cochrans Mill Road

P.O. Box 10940

Pittsburgh, PA 15236-0940

3610 Collins Ferry Road

P.O. Box 880

Morgantown, WV 26507-0880

One West Third Street, Suite 1400

Tulsa, OK 74103-3519

1450 Queen Avenue SW
Albany, OR 97321-2198

2175 University Ave. South

Suite 201

Fairbanks, AK 99709