Wyoming Water Research Program
Annual Technical Report
FY 2006

Introduction

The NIWR/State of Wyoming Water Research Program (WRP) coordinates participation in the NIWR program through the University of Wyoming, Office of Water Programs. The primary purposes of the WRP are to support and coordinate research relative to important water resources problems of the State and Region, support the training of scientists in relevant water resource fields, and promote the dissemination and application of the results of water-related research. In addition to administrating the WRP, the Director of the Office of Water Programs serves as the University of Wyoming advisor to the Wyoming Water Development Commission.

State support for the research program includes direct funding through the Wyoming Water Development Commission and active State participation in identifying research needs and project selection and oversight. Primary participants in the WRP are the USGS, the Wyoming Water Development Commission (WWDC), and the University of Wyoming. A Priority and Selection Committee (P&S Committee)--consisting of representatives from agencies involved in water related activities in the State--solicits and identifies research needs, selects projects, and reviews and monitors progress. The Director of the Office of Water Programs serves as a point of coordination for all activities and serves to encourage research by the University of Wyoming addressing the needs identified by the P&S Committee. The State also provides direct funding (from the WWDC accounts) for the administration of the WRP through the Office of Water Programs, which was approved by the 2002 Wyoming Legislature.

The WRP supports faculty and students in University of Wyoming academic departments. Faculty acquire their funding through competitive, peer reviewed grants, submitted to the WRP. Since its inception in the year 2000, the WRP has funded a wide array of water related projects across academic departments. Each project represents the education of one or more students.

Research Program

The primary purpose of the Wyoming Institute beginning with FY00 has been to identify and support water-related research and education under what has been entitled the Wyoming Water Research Program (WRP). The WRP supports research and education by existing academic departments rather than performing research in-house. Faculty acquire funding through competitive, peer reviewed proposals. A goal of the WRP is to minimize administrative overhead while maximizing the funding allocated toward research and education. Another goal of the program is to promote coordination between the University, State, and Federal agency personnel. The WRP provides interaction from all the groups involved rather than being solely a University of Wyoming research program.

In conjunction with the WRP, an Office of Water Programs was established by Legislative action beginning July 2002. The duties of the Office, which provides for the administration of the Wyoming Institute, are specified by the legislation as: (1) to work directly with the director of the Wyoming water development office to identify research needs of state and federal agencies regarding Wyoming's water resources, including funding under the National Institutes of Water Resources (NIWR), (2) to serve as a point of coordination for and to encourage research activities by the University of Wyoming to address research needs, and (3) to submit a report annually prior to each legislative session to the Select Water Committee and the Wyoming Water Development Commission on the activities of the office.

The Wyoming Water Research Program (WRP) is a cooperative Federal, State, and University effort. All activities reported herein are in response to the NIWR program, with matching funds provided by the Wyoming Water Development Commission and the University of Wyoming. While the WRP is physically housed in the Civil and Architectural Engineering Department, the Director reports to the Vice President of Research. A State Advisory Committee (entitled the Priority and Selection Committee) serves to identify research priorities and select projects for funding. The Director coordinates all activities.

Land Use Impacts on Nitrogen Fixation in Jackson Hole Streams

Basic Information

Title:	Land Use Impacts on Nitrogen Fixation in Jackson Hole Streams
Project Number:	2005WY23B
Start Date:	3/1/2005
End Date:	2/28/2007
Funding Source:	104B
Congressional District:	1
Research Category:	Biological Sciences
Focus Category:	Surface Water, Nitrate Contamination, Ecology
Descriptors:	
Principal Investigators:	Robert O. Hall

Publication

Abstract

Pollution from excess nitrogen (N) threatens many freshwater and marine ecosystems with eutrophication. Rivers and streams play a central role in N cycling at the landscape scale because rivers provide an avenue to transport N from the terrestrial landscape to downstream ecosystems. Rivers are more than conduits and may play a strong role in transforming or storing N. Changing land use in the Western US may alter how streams transform and process N. Currently we are studying how contrasting land use may affect N cycling in streams in Jackson Hole, WY. We are examining how land use alters the removal and fate of nitrate-nitrogen using experimental addition of ^{15}N tracers. Missing from our studies is an understanding of how N fixation alters stream N budgets and cycling, and how land use may affect N fixation. In these streams, N-fixation (i.e., the creation of biologically available N from atmospheric N_2) may be a dominant pathway for N input . We hypothesize that unimpacted streams will have high rates of N-fixation that drives the stream N budget, while hydrologically impacted streams (e.g., irrigation ditches) and streams with elevated nitrate concentrations will have lower N fixation rates. We will measure N fixation in the context of summer stream N budgets in 9 streams in and around Jackson Hole that we are using as part of our larger study. The 3 land use types are reference (unimpacted; streams in Grand Teton National Park), irrigated cattle pasture (streams on the Snake River Ranch), and suburban (Jackson Hole Golf Club and 2 streams in condominium developments). We will measure N fixation rates in each of these 9 streams using the acetylene reduction method. In 3 streams, we will estimate the importance of N fixation in the context of a stream reach nitrogen budget that considers inputs and outputs of N combined with rates of internal processing.

Statement of Problem

Humans have dramatically increased the global fixation of N into the biosphere, and this N is responsible for the eutrophication of aquatic ecosystems ranging from the Gulf of Mexico to Lake Tahoe. Despite increased N concentrations and associated enrichment of coastal oceans, only a small fraction of N deposited on land reaches oceans via rivers. The fate of this missing N is unknown, and one possibility is that small streams may transform or remove a fraction of this N. Streams play a central role in the transport and fate of anthropogenically fixed N, as they are the primary avenue for transport to downstream ecosystems. Ecologists are now learning that streams are more than just a conduit, however, and can process and retain much of this N (Hall 2003). Streams can attenuate N concentrations from either long-term storage (M. A. Baker and R. O. Hall, unpublished manuscript) or from denitrification, i.e. the conversion of biologically available N to N_2 gas (Alexander et al. 2003).

The role of streams in transporting and transforming N is likely altered by land use practices that both increase N inputs to streams and alter stream geomorphology (e.g., making confined channels in urban streams; Paul and Meyer 2001) yielding lower water residence times and less proportional N removal. High N inputs to streams can also saturate biotic uptake (Royer et al. 2004), thus overwhelming the stream’s ability to act as a sink for N. Given a dramatic increase in urbanized land in western Wyoming (Parmenter et al. 2003), there is the potential for alteration of stream N exports from these areas.

Despite the large amount of research examining streams as transformers of N, there is almost no study of a central N transformation: N fixation. N fixation is the conversion of abundant, but mostly inert, dinitrogen (N_2) gas to biologically available N. Cyanobacteria are the primary N fixers in streams, and are abundant in many of our study streams. There is much knowledge of terrestrial N fixation, and indeed, terrestrial N fixation has been substantially increased from planting of leguminous crops (Vitousek et al. 1997). Less is known on N fixation is streams. Streams with low N concentrations may actually be net sources of N due to high rates of N fixation. Thus our interpretation of how streams cycle N from the landscape may be incorrect given that much of the N exported downstream may have been fixed in the channel itself, and not imported from the terrestrial component of the ecosystem. If streams do have high rates of N fixation and are net sources, of N stream ecologists will have to refine models of N use by streams, in that they may be next sinks for dissolved N, yet be a net source of new N to downstream ecosystems. N fixation can be an important source of N to certain aquatic ecosystems, dominating the N budget of eutrophic lakes and some wetlands (Howarth al. 1988). There are very few studies of N fixation in streams (Grimm and Petrone 1997); a review on N fixation by Howarth et al. (1988) did not include any measurements from streams or rivers. However, stream N budgets may be dominated by N fixation despite being open ecosystems, which have high rates of transport of N through the ecosystem. Indeed, N fixation may dominate stream N fluxes more than the well-studied process of denitrification.

Objectives

1. <u>Measure how land use and associated physical variables control N fixation rates in 9 streams.</u> Hypothesis: N fixation rates in these high light streams will be highest in streams with low ambient N concentrations. We measured N-fixation in 9 streams in 3 land-use types during summer 2005 and will repeat the 3 highest streams in 2006. We are currently developing experimental protocols to use $^{15}N_2$ to calibrate the acetylene reduction method; this method has not been attempted in streams. We will perform an extensive comparison of the $^{15}N_2$ method with the acetylene reduction method in the 3 streams with the highest N fixation rates.
2. <u>Measure the degree to which N fixation dominates reach-scale N budgets.</u> Hypothesis: In streams with high N fixation, N fixation will constitute a major fraction of the N budget in mid-summer. For 3 of the 9 streams, we created a short-term budget of N at the scale of a 500-m stream reach. In each reach we measured N inputs, outputs, and nitrate and ammonium uptake. Much of the data for the N budget will be collected as part of our ongoing LINX project. We have the associated N fixation data for these streams (Fig. 1), but we are currently analyzing the associated budget data collected as part of the LINX experiment.
3. <u>Examine controls of nitrogen and phosphorus on N fixation rates.</u> As a mechanistic test of the effects of high nitrate we performed the nutrient addition experiment described below in two streams with high rates of N fixation.

Methods and Results

Summer 2005, we measured nitrogen fixation rates using the acetylene reduction method in nine streams in three different land-use types in Grand Teton National Park and Jackson, WY (Reference-relatively unimpacted streams, Suburban-in residential areas, and Agricultural- irrigation return flow streams located on Snake River Ranch, Wilson, WY) (Figure 1). Reference and urban streams were not different, but this may be highly skewed due to high N-fixation occurring in the Golf course stream. The agricultural streams may not be low due to N concentrations, but rather the alteration of stream flow and fine sediments. Intermittent flow patterns and fine sediments may not be suitable habitat for N-fixing assemblages. The higher rates we measured are comparable to Sycamore Creek, Arizona (Grimm and Petrone 1997) and tropical systems (A.J. Ulseth and A.S. Flecker, unpublished) which are much higher than most lake, marine and estuarine systems (Howarth et al. 1988). Ambient nitrate concentrations varied among the 9 streams(Figure 2). Ambient stream nitrate concentrations exceeding 10µgN/L inhibited nitrogen fixation. Our results show that excessive N inputs could reduce nitrogen fixation occurring in these streams and suggest that N fixation is a process that only occurs in streams with ultra low rates of N fixation.

We measured denitrification, that is the conversion of biologically available nitrogen (as nitrate) back to N_2 gas (i.e. the biological opposite of N-fixation) in 9 stream in Jackson Hole, and 40 other streams across the country as part of the LINX2 experiment. Rates of N fixation equaled or greatly exceeded denitrification rates in all streams except Kimball Spring, on the Snake River Ranch. In streams with high N fixation (Ditch, Golf, Spread), denitrification was at least 100 times lower than N fixation. Thus these streams are a net source of N rather than a net sink, as is commonly believed for streams in highly polluted areas (Alexander et al. 2000). Our highest rate of nitrogen fixation ($4.2\ \mathrm{mg\ N\ m^{-2}\ h^{-1}}$) was higher than denitrification in all but 4 of the 49 streams measured across the United States, showing the rate of N fixation in Ditch Creek can exceed losses of N in streams highly polluted by nitrate with elevated rates denitrification.

To experimentally examine how nutrients regulate on N-fixing rates we incubated nutrient releasing substrates in Ditch Creek and Spread Creek during Summer 2006. Following Tank and Dodds (2003) we made nutrient diffusing substrates that are 64 cm^2 porous terracotta tiles embedded in agar medium containing high concentrations of nitrate(0.5M KNO_3), phosphate(0.5M NaH_2PO_4), both, or unamended controls. Five sites in each stream (Ditch and Spread) contained nutrient releasing substrates for each of the four treatments. The tiles were incubated in the stream for 6 weeks (the agar is replaced after 3 weeks) because N fixers are slow-growing. After 6 weeks we measured N fixation rates on each set of tiles using the acetylene reduction method. Nutrient effects are analyzed using 2 way analysis of variance following Tank and Dodds (2003).

Nitrogen and phosphorus are the two major nutrients necessary for growth of most organisms. Nitrogen fixing bacteria make nitrogen available by fixing gaseous nitrogen from the atmosphere. Nitrogen fixation is an energetically expensive process, so we hypothesize that the N-fixing bacteria do not fix nitrogen when nitrogen is readily available. Also, the N-fixing bacteria will thrive when phosphorus is added because they have access to an abundant supply of N from the atmosphere, thus it is likely that phosphorus is the element in shortest supply. Our experiments show that indeed nitrogen fixation was inhibited by the addition of nitrate (Figure 3), while the phosphorus addition increased nitrogen fixation four-fold. It is interesting to note that adding nitrogen and phosphorus together reduced N-fixation. The stimulatory effect of phosphorus is swamped out by adding extra nitrogen.

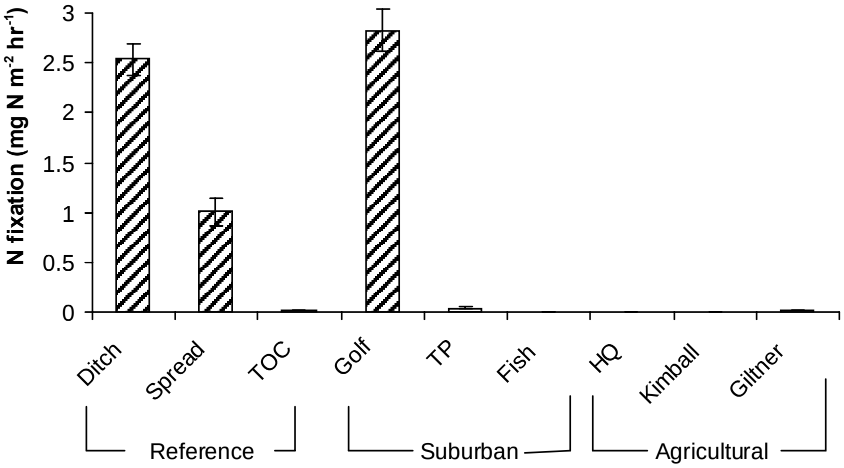

Figure 1. Mean stream nitrogen fixation rates (n ≥18). The results from summer 2005 nitrogen fixation measured using the acetylene reduction technique on 9 streams. Error bars represent standard error. TOC= Two Ocean Creek; TP= Teton Pines Waterway; HQ= Headquarters.

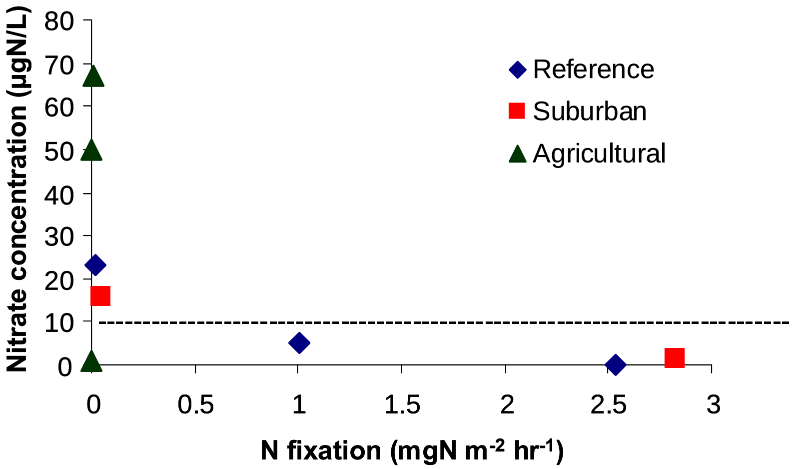

Figure 2. Ambient stream nitrate concentrations exceeding 10µgN/L have low nitrogen fixation rates. The only exception from this study is Headquarters which has 0.7 µgNO_3-N/L and 0.002mg N m^{-2} h^{-1} nitrogen fixation rate. Headquarters has predominately silt substrate and intermittent flow.

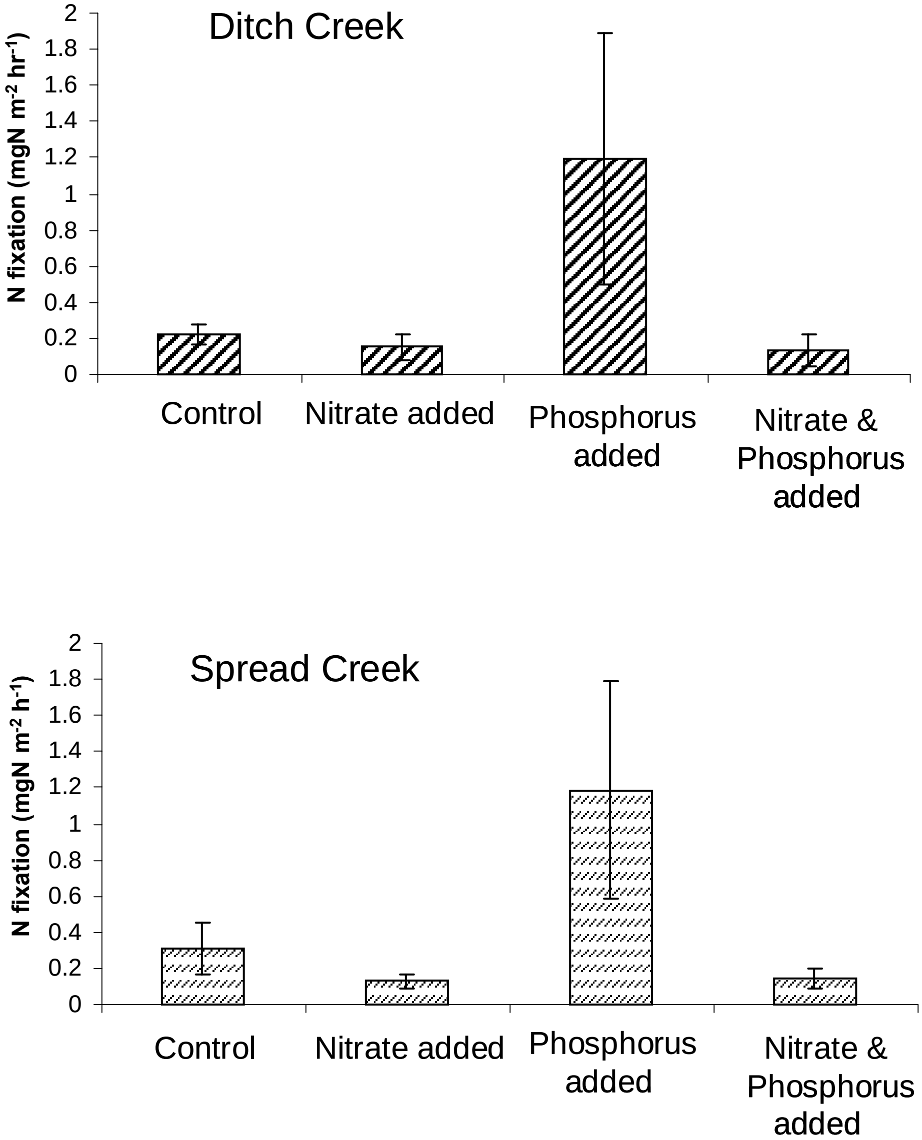

Figure 3. Ditch Creek and Spread Creek mean treatment nitrogen fixation rates (n=5). Error bars represent 95% confidence intervals. Addition of nitrogen inhibits N-fixation, while addition of phosphorus stimulates N-fixation.

We compared N-fixation to ammonium uptake, and nitrate uptake, biweekly from the end of June through September 2006 (Figs. 4 and 5). Nitrogen fixation rates greatly exceeded rates of ammonium cycling in Ditch Creek. This stream has nitrogen fixation rates among the highest in the literature, but like our 2005 data rates were among the highest measured in the literature and peaked during the warmest part of July. Nitrogen fixation rates throughout the summer season were 10 to 100 times greater than uptake rates. Thus, N-fixation dominated internal cycling of nitrogen.

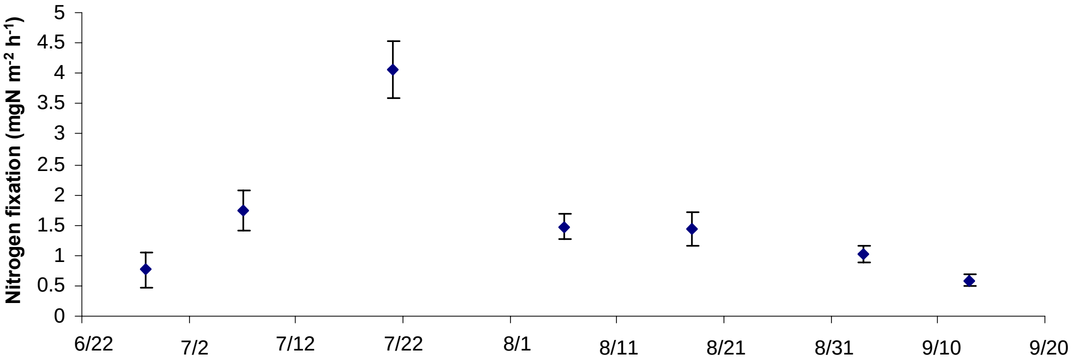

Figure 4. Nitrogen fixation in Ditch Creek measured throughout the 2006 summer season. Error bars represent 95% confidence intervals (n=18).

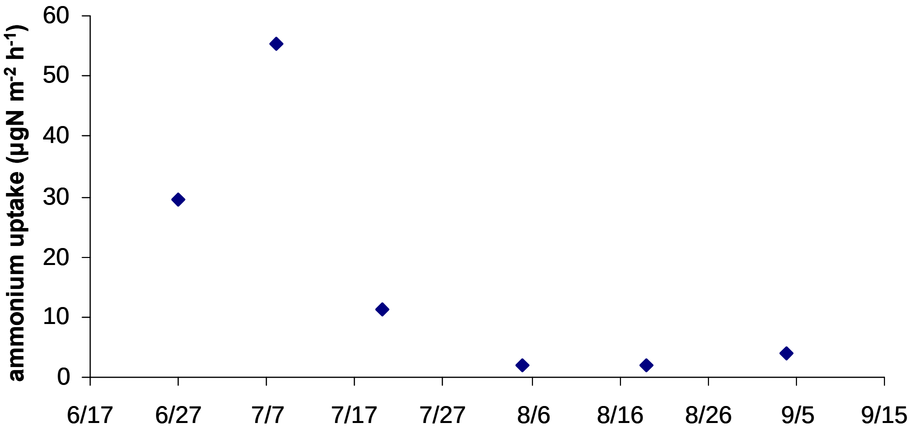

Figure 5. Ammonium uptake throughout the 2006 summer season. These measurements are in smaller units(μgN m^{-2} h^{-1}) than nitrogen fixation (mgN m^{-2} h^{-1}). Nitrogen fixation rates are at least 10 to 100 times higher than ammonium uptake rates showing that the creation of new nitrogen by fixation great exceeds the rate at which N is cycled in Ditch Creek.

Student Support

Lisa Kunza (Neerhof) was funded for 2 years towards a Ph.D. in the department of Zoology and Physiology. Lisa started graduate school in Fall 2004, and has performed two summers of fieldwork on this project. Undergraduate students were hired to assist with field work and lab work. During summer 2005 we hired Jon Hefner, a junior from Nebraska in the Dept. of Zoology and Physiology. Marci Trana, a University of Wyoming student was hired in Fall 2005 to assist with lab work. Additionally using National Science Foundation funds we hired Leslie Henry, a Research Experience for Undergraduates student who examined how nutrients control N fixation. Leslie is a Biology major at UW from Cody, WY. We hired Marley Vaughn from June through

September 2006 to assist with fieldwork. Marley was an undergraduate from the University of Oregon, and she is from Wilson, WY.

Additional Financial Support

This project was conducted in tandem with a National Science Foundation funded project examining mechanisms of nitrate removal from streams (Lotic Intersite Nitrogen eXperiment 2). In addition to this project we received additional funds ($5000) for a Research Experience for Undergraduate student (Leslie Henry). Lisa Kunza also received funds ($4000) from the University of Wyoming EPSCoR program to develop a method to calibrate acetylene-derived measures of N fixation using isotopically labeled $^{15}N_2$ gas.

Products

Lisa presented a talk in June 2006 at the national meeting of the North American Benthological Society entitled "High Nitrogen Fixation in Wyoming Streams". She will present another talk entitled "The Contribution of Nitrogen Fixation to Nitrogen Cycling in Ditch Creek, WY throughout the Summer Season" at the national meeting of the North American Benthological Society in June 2007. Two manuscripts are currently in preparation. A third manuscript and Lisa's dissertation will be completed by 2008.

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Real-Time Monitoring of E. Coli Contamination in Wyoming

Basic Information

Title:	Real-Time Monitoring of E. Coli Contamination in Wyoming
Project Number:	2005WY24B
Start Date:	3/1/2005
End Date:	2/29/2008
Funding Source:	104B
Congressional District:	1
Research Category:	Water Quality
Focus Category:	Water Quality, Methods, None
Descriptors:	
Principal Investigators:	Paul E. Johnson

Publication

1. Johnson, P.E., A.J. Deromedi, P. Lebaron, P. Catala, and J. Cash, 2006. Rapid detection and enumeration of Escherichia coli in aqueous samples using Fountain Flow Cytometry, Cytometry, 69A, 1212-1221.

Abstract

This project will demonstrate the feasibility of economical, simultaneous, real-time detection of individual Escherichia coli and their viability in surface waters. The Clean Water Act requires states to monitor surface waters for fecal coliforms or specifically for *E. coli*. Fecal coliform monitoring is an indicator of the sanitary quality of the water and can determine the extent of fecal contamination in the water from warm-blooded animals. A low-cost, portable, highly sensitive, self-contained single cell detection system for *E. coli* enumeration is being developed for rapid monitoring of surface waters, including streams, rivers, and lakes. With first-year USGS/WWDC funding, the P-I and his team have demonstrated and significantly improved an innovative technique for detection of pathogenic microorganisms in surface water, economically and in real time. This technology is based on LED-induced fluorescence of antibody- and DNA-labeled cells. *The project will demonstrate the detection of individual E. coli simultaneously in two wavebands in order to detect and determine viability of individual microorganisms.* The suspended bacteria are stained using both an immunofluorescent antibody and a fluorescent cell viability label. The resulting aqueous sample is passed as a stream in front of an LED, which excites the fluorescent labels (Figures 1 and 2). The resulting fluorescence is measured with a CCD or CMOS imager using an innovative integration scheme (called *Fountain Flow*), giving a dramatically higher signal-to-noise ratio than conventional techniques. In addition, we are investigating the extension of the fountain flow technology to imaging, to provide increased discrimination capability among *E. coli*, other biological particles, and small geological particles.

Objectives

The major tasks of this project are to: 1.) fabricate and test a two-color, LED-illuminated detection system in order to simultaneously detect and determine the viability of *E. coli*, 2.) perform laboratory measurements on quantified *E. coli* samples to determine the detection efficiency and sensitivity of the two-color monitoring system, 3.) enumerate *E. coli* in stream and lake water samples using both our proposed method and the standard method currently recommended by the US Environmental Protection Agency, 4.) determine the feasibility of a rare-cell, fountain flow *imaging* system based on an extension of our current technology, and 4.) fabricate and test a prototype fountain flow imaging system for proof of concept.

Progress Report, Second 12 Months of Funding

We are testing and engineering improvements on a low-cost, portable, highly sensitive, self-contained single cell detection system for *E. coli* in surface waters, which will greatly exceed the current testing procedures in both speed and reliability. The goal of this project is the development of 1) a low-cost, rapid (<< 1 hour test), sensitive (< 5 cells/ml), portable, easy to use system for *E. coli* detection in raw surface water. Our objectives are to: 1) develop and test a system for simultaneous detection and viability testing of *E. coli* and 2) develop and test a proof-of-concept prototype for multi-spectral high resolution FF imaging. This proof of concept will allow for the design and fabrication of a remote monitoring system that will automatically screen water in real time. Alternative methods necessitate the shipping of bulk water samples or concentrates to laboratories and labor-intensive screening technologies, which may include bulk water concentration, incubation, and culturing. These factors combine to impede overall routine monitoring for fecal coliforms in the field and preclude widespread, routine screening of surface waters.

In the 12-months of year 2 funding, we have:

- successfully fabricated a two-color detection system for detection of microorganisms,
- continued successful proof of concept experiments for a fountain flow (FF) imaging system, using a syringe pump to consistently stop fluorescent beads in the focal plane of the FFC,

- collected data on the two-color detection of amoebae in natural river water,
- drafted a paper on the previously mentioned detection of amoebae in natural river water, using LED illumination, to be submitted to the Journal of Applied Microbiology (JAM),
- published a paper on the detection of *E. coli* in water to the journal Cytometry,
- published a paper on the detection of amoebae in natural river water using LED-illumination, against a background of organic detritus, in the Journal of Applied Microbiology, and
- have pending a patent application for the software control of FF.

The paper that we have written and are about to submit to JAM concerns the use of Fountain Flow Cytometry (FFC) for detection of protozoa in raw water with a two-color LED-illuminated FFC system. The system was tested with a flow throughput of 10 ml/minute and amoebae concentrations of 0.06 to 3 amoebae/ml. Two dyes were used, Chemchrome V6, a viability dye, and and R Phycoerytherin immunolabel. Detections were made in two colors, simultaneously using two cameras and two LED illuminators. Water samples for the Tech River (France) were sampled and tested for background autofluorescence from organic and non-organic material. These experiments show that two-color simultaneous measurements allow us to successfully separate living amoebae at 0.5 to 4 amoebae/ml from background detritus and that we will be able to separate E. coli detections from background detritus. Our final experiment in this series, this summer, will be to detect E. coli at low concentrations in natural river water.

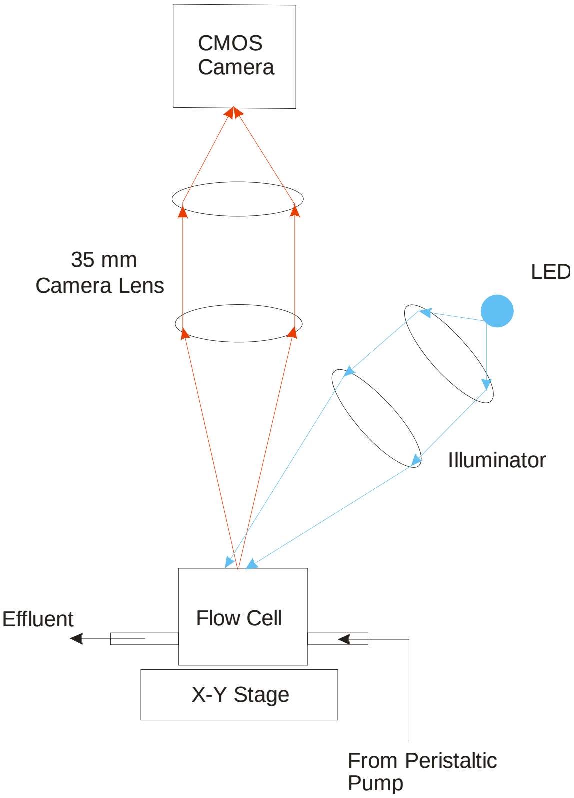


Figure 1. *Schematic diagram of an LED-illuminated epifluorescent Fountain Flow Cytometer. A sample of fluorescently tagged cells flows through the flow cell toward the CMOS camera and fore-optics. The cells are illuminated in the focal plane by an LED. When the cell(s) pass through the CMOS camera focal plane they are imaged by the camera and lens assembly through the transparent flow cell window, and a filter that isolates the wavelength of fluorescence emission. The fluid in which the cells are suspended then passes by the window and out the flow cell drain tube.*

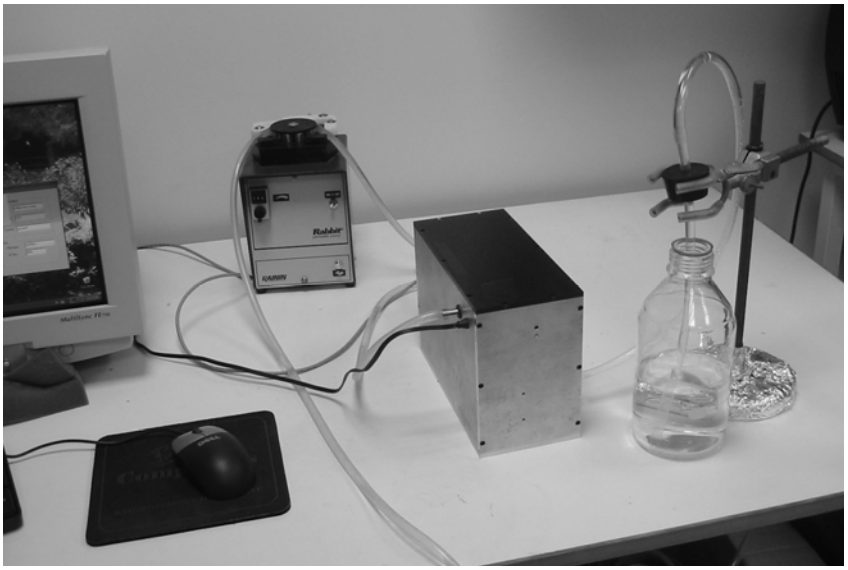


Figure 2. *The Wyoming Biodetection System Fountain Flow Cytometer, shown with peristaltic pump, and sampling reservoir*

Student Support

During Year 2, the P-I employed one former undergraduate Pre-Med student, Chris Havens (BS graduate 2006), and one geology student, Joseph Johnson (provisional graduate student), in this research. The interaction among personnel of varying backgrounds has provided a highly educational experience for everyone in research biodetection technology.

Publications in Preparation (and other project products) from Year 2

Manuscripts (in preparation or submitted)

Johnson, P.E., Deromedi, A.J., Lebaron, P., Catala, P., Havens, C., and Pougnard, C. 2007. *High throughput, real-time detection of Naegleria lovaniensis in natural river water using LED-illuminated Fountain Flow™ Cytometry*, in press, J Applied Microbiology.

Johnson, P.E., Havens, C., Lebaron, P., and Catala, P. *High Throughput, Real-Time Detection of Naegleria lovaniensis in Aqueous Samples using Two-Color Fountain Flow™ Cytometry,* to be submitted to Journal of Applied Microbiology.

Invited Presentations

2006 Asilomar Cytometry Development Workshop

1. *High-Throughput-Axial Imaging Flow Cytometry with LED illumination*
2. *Imaging Flow Cytometry*

2006 Select Water Committee Meeting, Wyoming State Senate

1. *Detection of Pathogenic Organisms in Wyoming Surface Water*

Innovative Technology Development to Maximize Beneficial Use of Produced Water from Coal Bed Natural Gas Operations in the Powder River Basin, Wyoming

Basic Information

Title:	Innovative Technology Development to Maximize Beneficial Use of Produced Water from Coal Bed Natural Gas Operations in the Powder River Basin, Wyoming
Project Number:	2005WY25B
Start Date:	3/1/2005
End Date:	2/28/2007
Funding Source:	104B
Congressional District:	1
Research Category:	Biological Sciences
Focus Category:	Treatment, Geochemical Processes, Water Use
Descriptors:	
Principal Investigators:	George Floyd Vance, Girisha K. Ganjegunte, Ronald C. Surdam

Publication

1. Ganjegunte, G.K. and G.F. Vance, 2006. Deviations from the empirical sodium adsorption ratio (SAR) and exchangeable sodium percentage (ESP) relationship. Soil Science 171:364-373.

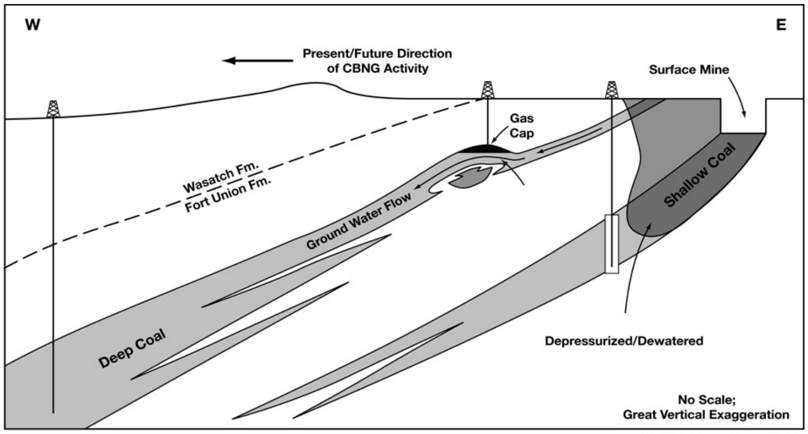
Abstract

Wyoming has experienced rapid growth in the development of its coalbed natural gas (CBNG), resources. One of the most contentious issues surrounding CBNG production is how to deal with the co-produced water that must be removed to allow coal seams to degas? A Wyoming CBNG task force has been formed to investigate alternative uses of water produced during CBNG production. One area of interest has been the beneficial use of CBNG co-produced waters in order to enhance gas production and environmental sustainability. The primary concern with CBNG produced waters is the amount and influence sodium (Na^+) (as defined by the sodium adsorption ratio (SAR)) has on soils, vegetation, wildlife and livestock in different environments, e.g., streams, agricultural lands, rangelands, and other ecosystems. We have researched the development of a water treatment system based on cation exchange between natural zeolites and CBNG waters. Research indicates that there is a significant reduction in the amount of Na^+ and a lowering of SAR in CBNG produced waters after these waters are processed with the zeolitic materials. Our research included three primary tasks: 1) determination of cation exchange capacity (CEC), exchangeable cations, and opportunities of selected zeolites deposits; 2) evaluation of cation exchange reactions between CBNG produced water and natural zeolites to reduce CBNG water SAR's; and 3) design of a water treatment scenario based on cation exchange between natural zeolites and CBNG produced waters. Studies on the exchange and kinetic reactions between CBNG waters and Ca-zeolites were conducted to formalize and quantify the exchange process. Industry, land owners, and downstream users will benefit from this new method of reducing Na^+ and lowering SARs of CBNG waters.

Introduction

Development of CBNG in the Powder River Basin (PRB) of Wyoming and Montana has increased dramatically in the past 10 years, resulting in significant CBNG production as well as many environmental and regulatory issues (Ayers 2002, McBeth *et al.* 2003, RIENR 2005). One of the issues involves the release of copious quantities of groundwater removed to recover the natural gas (King *et al.* 2004c, Vance *et al.* 2004, Vance 2006). Not only are the thick coal seams in the PRB rich in natural gas, they are also important regional aquifers (Wheaton and Olson 2001, Wheaton and Metesh 2002). In order to produce the absorbed natural gas from the coals, formation pressures must be reduced by removal of water. Existing data strongly suggests that CBNG activities in the PRB will expand west into deeper coals (Figure 1), that the quality of water from the coal will deteriorate, and that the volume of the water per well will increase significantly (BLM 2003). CBNG stakeholders in the PRB have focused on the disposal of the water. As a consequence a very contentious atmosphere has evolved around CBNG activities. Most of the contention surrounding CBNG water would be eliminated if a significant portion of the waters could be put to beneficial use (King *et al.* 2004c, Vance *et al.* 2004).

WDEQ's NPDES permits/enforcement and BLM's drilling permits take into consideration water management issues relating to CBNG activities. In addition, the WO&GCC's permitting and reclamation of off-channel reservoirs and the WSEO water rights issues also involve CBNG activities throughout Wyoming. Estimates suggest CBNG production from the relatively thick coal seams in the PRB will reach a peak of about 5.0 Bcf/d by 2008, which will require more than 25,000 wells. Clearly, these estimates are becoming reality, with the amount of both gas and CBNG water increasing at a rapid rate. The BLM's Environmental Impact Assessment (EIS) for the PRB had allowed unlined, off-channel reservoirs so the water can be disposed by evaporation and/or infiltration into the alluvium (BLM 2003). Estimates suggest only 2% of the water subjected to off-channel storage is available for beneficial use (i.e., livestock water). To many stakeholders in the arid PRB believe this "preferred" water disposal procedure is a waste of an important and valuable resource – water!



Modified from Ayers (2002)

Figure 1. Early coal bed natural gas (CBNG) wells in the PRB were located in depressurized strata adjacent to surface mines around Gillette, WY. Presently CBNG activity is moving to the west and exploiting deeper and thicker coalbeds (i.e., Big George coalbed).

Water treatment is an important issue for maintaining the viability of the CBNG industry in the PRB and the rest of the western United States (Vance 2006). In the future, the CBNG industry will either improve water disposal options by developing new or improved technologies, or be faced with interminable litigation and delay. The most important aspect of the produced water from the deeper coals is the significant increase in the SAR. For comparison, water produced from shallow coals near Gillette, WY have SAR's ranging from 6 to 12, whereas the water produced from the deeper coals near Sheridan, WY have SAR's ranging from 45 to 60. In the eastern (i.e., shallow coals) portion of the PRB, discharge of CBNG produced water is limited to SARs of 10 or less for the northeastward flowing Belle Fourche and Cheyenne River drainages. For the northward flowing Powder River, the SAR default limit is 7. CBNG produced water significantly degrades to the north and west, particularly with respect to SAR, and the water quality requirements for the receiving streams become more stringent.

CBNG waters have been used as a source of irrigation water in the PRB (King *et al.* 2004a,b, Vance *et al.* 2004). Soils in PRB are dominated by smectitic clays, and nearly 41% of the PRB area is covered with soils characterized by poor drainage (BLM 2003, Ganjegunte *et al.* 2005). Application of CBNG waters with high SAR's can have negative impacts on soil physical and chemical properties (Ganjegunte *et al.* 2005). Irrigating soils with high SAR water can result in dispersion of soil clay particles and organic matter, resulting in surface crusting, reduced infiltration, and lower hydraulic conductivity, which could lead to poor vegetation growth (Vance and Stevens 2003, Ganjegunte *et al.* 2004). In order to avoid permanent damage to fragile PRB agricultural and rangeland ecosystems, it is necessary to reduce the Na^+ concentrations in the CBNG water so that it can be used safely for irrigation (i.e., crop production) or discharged to natural drainages (i.e., recreation and wildlife).

The technology researched in this project evaluated the use of natural zeolites as cation exchangers to achieve targeted SAR levels in CBNG produced waters. If this technology is utilized, a significant portion of CBNG water may be available for beneficial use (Vance *et al.* 2007). The University of Wyoming and Wyoming State Geological Survey will continue to pursue research that will evaluate a technology to treat CBNG produced water and improve its beneficial usage. The essential treatment is the removal of Na^+ from the produced water. With only Na^+ removal, most of the produced water could be used in some beneficial capacity. To accomplish this goal many technologies have been suggested (Rawn-Schatzinger *et al.* 2003). All of the suggested technologies have both promise and problems, but most importantly they are often too expensive. The solution to the problem is to find a practical, cost-effective and efficient method to treat the CBNG produced water in the PRB – not the best or ideal water management plan, but a practical water treatment technology that allows a significant portion of the CBNG produced water to be available for beneficial use.

Statement of Results and 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. Therefore, although accurate cost estimates for utilizing zeolite will not be possible until field experiments are completed, we conclude that zeolite is probably the only large volume, low-cost, and easily disposable cation exchanger available.

The technology researched for resolving the problem of CBNG Na-rich waters is based on the use of natural clinoptilolite in cation exchange columns or beds to achieve targeted SAR levels in CBNG produced waters. The mineral name clinoptilolite as used in this project covers the heulandite-group zeolites. Typically the two end members of this group of zeolites, heulandite and clinoptilolite, are defined on the basis of thermal stability (i.e., heulandite being stable at higher temperatures than clinoptilolite). Ratterman and Surdam (1981) have demonstrated that with respect to thermal stability there exists a suite of intermediate members of the group. This demonstration is important to our research because the intermediate members have CaO/Na_2O ratios ranging from 0.4 to 4.9 (Sheppard and Gude, 1973). Moreover, Ratterman and Surdam (1981) showed that these intermediate zeolite-group members are found in many zeolite-rich deposits (i.e., altered tuffaceous deposits). A survey of the literature suggests that the intermediate members are common in the zeolite deposits (Sheppard and Gude, 1968, 1969, 1973; Surdam and Sheppard, 1978; Ratterman and Surdam, 1981). A major aspect of our research focused on the utilization of intermediate relatively Ca-rich clinoptilolites as the solid cation exchanger in the treatment of CBNG produced water. This will require material from a natural zeolite-rich deposit that is >75% clinoptilolite, is Ca-rich (i.e., Ca > Na) or that can be made Ca rich through Ca saturation, and has a cation exchange capacity (CEC) of 1.75 meq/gm or greater. These values are all within the range of parameters observed for natural clinoptilolite characteristics (Sameshima, 1978; Stonecipher, 1978; Kastner and Stonecipher, 1978; Iijima, 1978; Hay, 1995; Ogihara and Iijima, 1989).

Objectives

The primary objective of our research was to evaluate the development of a water treatment alternative that maximizes the beneficial use of CBNG produced water. In order to accomplish this objective, research was conducted according to three tasks that included:

Task 1.0 – Determine cation exchange capacities (CEC), exchangeable cations, and volumetrics of selected zeolite deposits, *Task 2.0* – Evaluation of the potential for cation exchange reactions between CBNG produced water and natural zeolite deposits to reduce CBNG water SAR's, and

Task 3.0 – Design an economic, viable water treatment scenario based on cation exchange between natural zeolite and CBNG produced waters.

Materials and Methods

Zeolites are hydrated aluminosilicates of the alkaline and alkaline-earth metals. About 40 natural zeolites have been identified during the past 200 years, the most common are analcime, chabazite, clinoptilolite, erionite, ferrierite, heulandite, laumontite, mordenite, and phillipsite (Table 1). More than 150 zeolites have been synthesized, which are primarily zeolites A, X, Y, and ZMS-5. Natural and synthetic zeolites are used commercially because of their unique adsorption, ion-exchange, molecular sieve, and catalytic properties.

Natural zeolites exhibit distinctive CEC and adsorption properties, and have been effectively utilized to remove toxic elements from polluted waters (Barrer 1978, Collela 1996, Pansini 1996, Mumpton 1999, Duong *et al.* 2005, Wingenfelder et al. 2005). 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, whereas chabazite selectivity is Tl > Cs > K > Ag > Rb > NH_4 > Pb > Na = Ba > Sr > Ca > Li (Mumpton, 1999, 2000). The slightly higher preference of Na^+ over Ca^{2+} of clinoptilolite zeolites makes them a better choice for removing Na^+ from CBNG waters (Table 1).

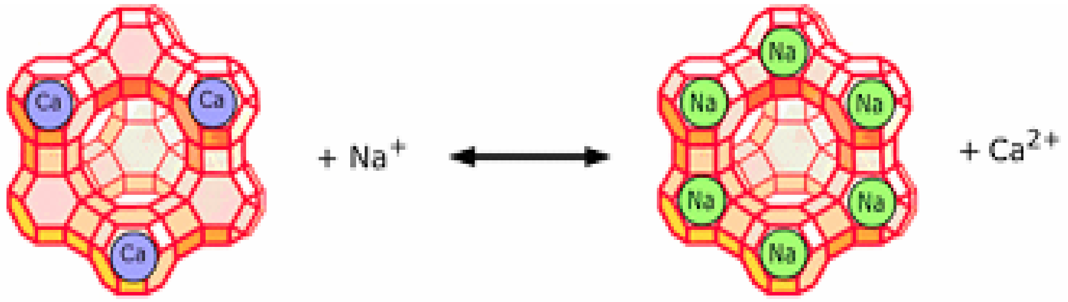


Table 1. Ideal cation exchange capacity of some natural zeolite: data calculated using the unit cell formula **(**Inglezakis 2005)

Zeolite	**Cation Exchange Capacity (CEC) (meq/g)**
Chabazite	3.84
Clinoptilolite	2.16
Erionite	3.12
Ferrierite	2.33
Heulandite	2.91
Laumontite	4.25
Mordenite	2.29
Phillipsite	3.31
Faujasite	3.39

Commercial zeolite deposits in the United States 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. 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.

In 2002, nine companies mined natural zeolites in the United States. Two additional companies involved in zeolites during 2002 sold from stocks or purchased zeolites from other producers for resale. Chabazite was mined in Arizona and clinoptilolite was mined and processed in California, Idaho, Nevada, New Mexico, Oregon, Texas, and Wyoming. New Mexico produced the greatest amount of zeolite in 2002. Total domestic production of zeolites was estimated to be 46,000 metric tons (t) compared with an estimated 36,400 tonne in 2001.

Selection of Materials

Zeolite samples were collected from several deposits in Nevada, California, New Mexico, Idaho and Wyoming (Table 2). These sites were chosen based on reported chemical analysis and CEC of these zeolite deposits. Additionally, three of the sites are active zeolite mines (Ash Meadows, NV, Bear River, Idaho and St. Cloud, NM). Two sites are currently inactive but have been active in the recent past (Mud Hills, CA, and Fort La Clede, WY) and presumably could be reopened at minimal cost. Following are brief descriptions of the sample locations and their geologic setting, along with their CEC.

Table 2. Natural zeolite samples (Clinoptilolite-Dominant) obtained for this study.

Sample	CEC (meq/g)	Source, location
AM1	1.60	Ash Meadows, Nye County, NV
FC1	1.36	Fossil Canyon, San Bernardino County, CA
FC2A	1.88	Fossil Canyon, San Bernardino County, CA
FC2B	1.96	Fossil Canyon, San Bernardino County, CA
MH1	1.71	Mud Hills, San Bernardino County, CA
SC1	0.62	St. Cloud, Sierra County, NM
BRZ1a	1.29	Bear River, Franklin County, ID
BRZ1b	1.21	Bear River, Franklin County, ID
FL1a	1.92	Fort LaClede, Sweetwater County, WY
FL1b	2.15	Fort LaClede, Sweetwater County, WY

Extensive research was carried out in an effort to identify target locations with favorable mineralogy, chemistry, and sufficient volume to sustain a mining operation capable of supplying enough material for water treatment described herein. Zeolite beds should be of sufficient thickness (several meters or more), laterally extensive with minimal dip and should also be covered by a minimum of overburden.

Following are brief descriptions of the most promising sample locations and their geologic setting and history, along with mention of the chemistry and CEC of the samples. CEC determinations were performed by Dr. Steve Boese of the UW Department of Geology and Geophysics. Other information sources are as noted. See Tables 1 and 2 for CEC.

The Ash Meadows zeolite deposit is located in Amargosa Valley, Along the California-Nevada border between Las Vegas and the Death Valley area of California. The zeolite is situated in a gently dipping sequence of altered lacustrine deposits in Inyo County, CA and extends in to Nye County, NV. The deposits are believed to have originated as late Tertiary tuffaceous (Pleistocene) ash fall deposits that settled into a large lake referred to as Lake Tecopa (Sheppard and Gude, 1968). The vitric material in the ash fall deposits was later altered and zeolitized by reactions between the siliceous matrix of the ash with the saline-alkaline waters of the lake and, to some extent meteoric waters (Sheppard and Gude, 1968). The zeolite mined at Ash Meadows has a CEC value of 1.60 meq/g with major cation weight percentages of 3.73% K_2O, 3.47% Na_2O, and 0.97% CaO.

Approximately 160 km to the southwest of Ash Meadows is the Mud Hills area containing zeolites in the Barstow Formation of Miocene age. This formation contains lacustrine and fluvial deposits with tuff making up approximately 2% of the stratigraphic section. As is thought to be the case with the Ash Meadows zeolites, the zeolites in the Barstow formation are believed to have formed by diagenetic reactions between the vitric material in the tuff with the lake waters and to some extent, connate waters ((Sheppard and Gude 1969). The tuff beds range in thickness from 0.3 to >2 m (Sheppard and Gude 1969). We collected samples from the area of the inactive Mud Hills zeolite mine and also in the Fossil Canyon area to the west of the Mud Hills mine approximately 8 km. The CEC value of the Mud Hills sample is 1.71 meq/g. with major cation values of 1.63% K_2O, 3.57% Na_2O, and 1.41% CaO. Fossil Canyon was also of interest because of its high Ca content of 2.25 wt% (Shepard and Gude 1969). CEC values for the Fossil Canyon zeolite samples range from 1.88 – 1.96 meq/g. Major cation weight percentages are 1.63% K_2O, 3.57% Na_2O, and 1.41% CaO.

Samples were also collected from the St. Cloud zeolite mine near Winston, NM. The St. Cloud zeolite deposit is located approximately 6 km south of Winston, NM within the Winston graben. The Oligocene-Miocene Little Mineral Creek tuff, which is a rhyolitic ash flow, hosts the commercial grade clinoptilolite. This ash flow is overlain by the unconsolidated conglomerates of the Santa Fe formation (Austin and Bowman 2002). Diagenesis of the ash flow deposits in an environment favorable to high silicon activity, i.e., a saline alkaline lake but with some apparent ground water influence (Pat Freeman, personal communication) resulted in the clinoptilolite beds.

The St. Cloud zeolite deposit crops out along nearly 2.5 miles of strike, and extends laterally in zones ranging from approximately 250-500 m (Austin and Bowman 2002). The zeolite is white to buff in color, with very homogenous and continuous beds up to 7.5 m thick where it is mined. Estimated reserves are 16 Mt (St. Cloud Zeolite website, accessed February 22, 2007, White *et al.* 1996).

The chemistry of the mined zeolite at St. Cloud is relatively high in Ca, at 2.71 – 6.1 (Austin and Bowman 2002) but with a slightly lower CEC of 0.62 meq/g. The mined zeolite product at St. Cloud contains 74 wt % clinoptilolite (Austin and Bowman 2002). Major cation weight percentages are 3.44% K_2O, 0.44% Na_2O, and 2.87% CaO.

At the Bear River zeolite mine, located just a few km northeast of Preston, outcrops of the Pliocene Cache Valley Formation of the Salt Lake Group host a major zeolite deposit. This region is found in the SE corner of the Riverdale 1:24,000 USGS quadrangle. Bear River Zeolite has controlled the deposit since 2001 and is actively expanding operations with new processing equipment. Most of their zeolite is sold for animal feed, air and water filtration, and as pozzolan, a material added to Portland cement to increase the long-term strength of concrete (Janotka *et al.*

2003). Much of their market is currently foreign, with common shipments to Peru, the Dominican Republic, Europe, and Canada.

The Bear River deposit crops out over a relatively large area (several km^2) consisting of numerous large hills. Beds are very homogenous and continuous with a total thickness of approximately 200 m) in some instances. The zeolite is colored a light, pastel gray-green due to iron impurities. The weathered surface is rusty to buff in color, and in most cases the deposit is covered with 3-5 m of soil. This soil has been found to be extremely fertile due to the ammonium-fixating properties of the zeolite. There is commonly good zeolite exposure on the hilltops, and estimated reserves are at 175 to 625 million tonne (Mt) (Lawrence, 2007, personal communication).

Samples collected from the quarry wall by the WSGS and Bear River Zeolite confirm a purity of 85-92% clinoptilolite with a balance of chalcedony. The chalcedony occurs in centimeter-scale dark green bands within the zeolite, lowering the CEC in localized areas due to the higher concentration of silica. Bear River Zeolite has also identified areas of variable CEC within the zeolite beds themselves. These zeolites are classified as potassic. Major cation weight percentages are 4.32% K_2O, 0.49% Na_2O, and 2.33% CaO. CEC is 1.25 meq/gram.

The Fort LaClede zeolite deposit occurs in the vicinity of and includes the robins egg blue tuff bed, part of the Eocene Adobe Town Member in the Washakie Formation (King and Harris, 2002). The robins egg blue tuff bed is a prominent marker bed visible for several km from historic Fort LaClede, trending northeast just southeast of Iron Pipe Draw at approximately the 2140 m elevation contour. This region is covered by the Fort LaClede, Fort LaClede NE, Kinney Spring, and Manual Gap 1:24,000 USGS topographic quadrangles, and the Kinney Rim 1:100,000 USGS topographic map. Land ownership in this area is a checkerboard of private and BLM sections. This deposit is currently controlled at least in part by U.S. Zeolites, although they have ceased production and the quarry appears to be abandoned as of this writing. The quarry is located in T16N, R98W, sec. 1.

The Adobe Town Member tuff is fairly resistant and ranges in color from a pastel robins egg blue to almost white. The beds in this area are nearly completely altered to clinoptilolite, forming zones several cm to 3.7 m thick. The zone of highest purity clinoptilolite is restricted to approximately 1.2 m and is easily recognized in the wall of the quarry pit. This deposit has been estimated to contain several million tonne of high grade material (Curry and Santini, 1986).

Samples were collected from the southwest area of the quarry pit, and to the west from undisturbed outcrop just over the ridge formed by the pit wall. Both the robins egg blue and the white colored tuffs of the Adobe Town Member were sampled and found to be approximately 90% clinoptilolite with very minor heulandite. These zeolites are classified as sodic. Major cation weight percentages are 1.53% K, 4.40% Na, and 1.50% Ca. CEC is 2.04 meq/gram.

Zeolite samples were also collected from southeast Fremont County, WY (King and Harris 2002). The Green Cove area of Beaver Rim is in sections 3 and 10 of T30N R96W. The samples were collected from two tuffaceous beds 1-2 m thick near the former US highway 287. These beds occur in Unit 3 of sequences within the middle-upper Eocene Wagon Bed Formation described by Van Houten (1964). The tuff beds in the Green Cove area appear extensive and are overlain by varying thicknesses of uneroded Unit 3 as well as Units 4 and 5 at the flanks of the cove. Van Houten (1964) describes "yellowish-orange to yellowish-gray and light gray limonite-stained, well sorted fine-grained altered biotitic vitric tuffs containing quartz and feldspar grains…" Iron staining appears unrelated to zeolitization, which was confirmed by our investigation as well. XRD analyses confirm strong clinoptilolite content in the samples collected. Cation exchange capacity and exchangeable cation analyses are pending as of this writing.

For the Ca-rich Arizona zeolite (CABSORB ZS500RW) used in this study, a chemical analysis of the zeolite suggests a composition of SiO_2 (69.5%), Al_2O_3 (16.6%), TiO_2 (0.47%), Fe_2O_3 (4.33%), CaO (4.49%), Na_2O (2.40%), K_2O (1.32%) and MgO (0.89%). This product was a partially upgraded chabazite. It originated from the high Na chabazite in the Grace pit and has somewhat different thermal treatments ranging from none to high temperature activation and different upgrading ranging from none to a partial recrystallization.

X-ray Diffraction Analysis

X-ray analysis was conducted on the zeolites collected (Fig. 2 and Appendix). Samples were dried at approximately 80°C for several hours, which resulted in water loss ranging from <1% to >6%. Pulverized samples were scanned from 2-30° 2θ using Cu Kα radiation at 1.54 Å. The fewer peaks other than those of clinoptilolite in the samples suggest a higher percentage of zeolite. Typical impurities may include quartz, feldspars and/or clay minerals. Total chemical analyses were carried out on all the zeolite samples collected and are listed in the Appendix.

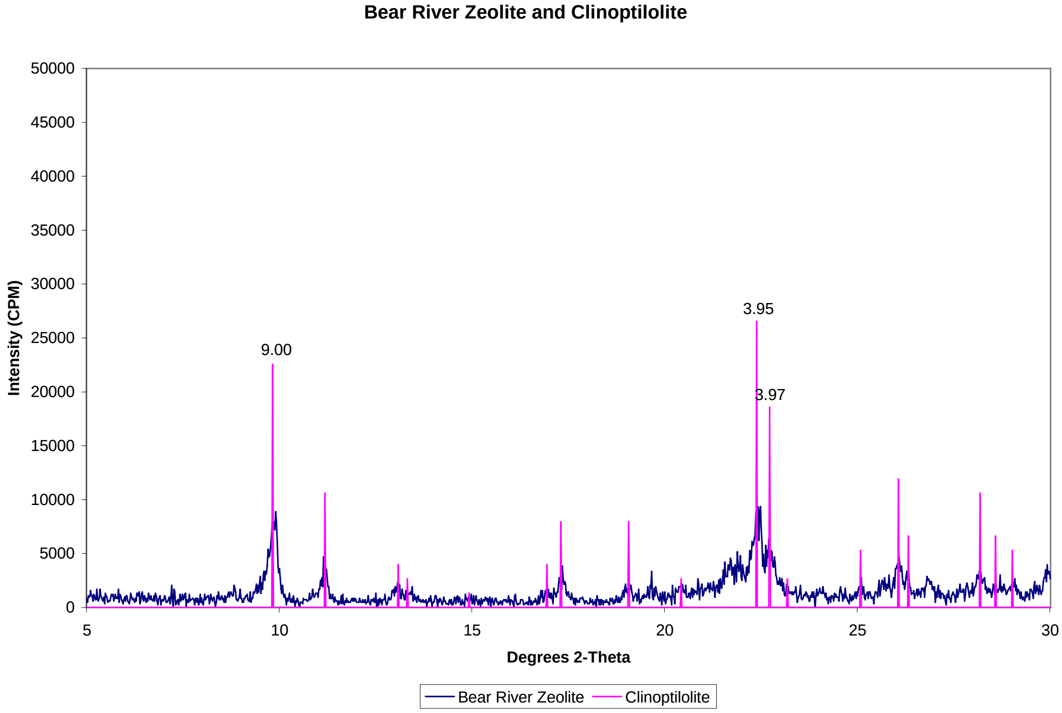


Figure 2. Representative X-Ray Diffraction Patterns (Bear River Zeolite)

Cation Exchange Capacity and Exchangeable Cation Determinations

Zeolite cation exchange capacities (CEC) and exchangeable cation concentrations were determined by a modified method of Cerri *et al.* (2002) (Table 3). For CEC measurements, the zeolites were first saturated with Na^+ that was displaced by a $(NH_4)_2SO_4$ solution to exchange NH_4^+ for Na^+. Exchangeable cations were determined using 1.0 g of zeolite sample that was reacted for 2 hours with 33 ml of 1 M ammonium acetate (NH_4Ac) at room temperature followed by centrifugation and filtration (Whatman filter #42) of the supernatant. This process was repeated two more times with the three extracts combined in a volumetric flask that was brought to total volume of 100 ml using 1 M NH_4Ac. Following the displacement of exchangeable cations from the sample with NH_4^+ acetate, Na^+, K^+, Ca^{2+} and Mg^{2+} were analyzed following the inductively coupled plasma spectrometry (Suarez 1999).

Table 3. Effective CEC and exchangeable cations (cmol kg^{-1}) of the different natural zeolite samples studied (Clinoptilolite-Dominant).

Sample	**Location**	**Na^+**	**Ca^{2+}**	**Mg^{2+}**	**K^+**	**Effective CEC**
Ash Meadows (AM)	Nevada	114	20	2	95	230
Fossil Canyon (FC1)	California	86	13	2	27	128
Fossil Canyon (FC2a)	California	149	13	1	35	198
Fossil Canyon (FC2b)	California	142	19	2	30	193
St. Cloud (SC)	New Mexico	3	61	17	7	87
Mud Hills (MH)	California	92	41	3	25	162
Bar River (BR)	Idaho	10	67	3	56	136
Fort LaClede (FL)	Wyoming	140	50	2	26	212

Adsorption Kinetics and Isotherms

Adsorption kinetics studies were carried out using 20.0 g zeolite samples diluted with surrogate CBNG water (Table 4) to 1,000 ml at ambient temperature. Aliquots of these samples (~5ml) 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 nitric acid (HNO_3) and stored until analyzed.

For Na adsorption studies, a 5.0 g zeolite sample was weighed into 50 ml polyethylene bottles containing varying amounts of NaCl. The tubes were then filled with 45 ml of sodium bicarbonate ($NaHCO_3$) solution with a concentration of 1,010 mg/L as HCO_3^-. The initial Na^+ concentrations in the tubes ranged from 0 to 8,400 mg/L. The tubes were shaken on a reciprocal shaker for 48 hours, centrifuged, and the supernatant solution filtered and acidified as described above.

The water chemistry of the surrogate CBNG water (Table 4) was chosen by compiling published data from various sources (Rice *et al.* 2002, BLM 2003, King *et al.* 2004a) and prepared using appropriate amounts of inorganic chemicals and tetraethyl orthosilicate as the silicon (Si) source.

Table 4. Water Chemistry of the Synthetic CBNG Waters (mg/L)

Element	**Na**	**Ca**	**Mg**	**K**	**Cl**	**SO_4**	**HCO_3**	**SiO_2**	**SAR**	**pH**
CNBG Water I	205	10	2.5	1.25	45.4	5	505	5	15.5	8.20
CNBG Water II	411	10	2.5	2.5	65.8	10	1,010	10	30.1	8.90
CNBG Water III	822	10	2.5	2.5	65.8	10	1,010	10	60.2	8.90

CBNG water samples were also collected from different parts of PRB region and pooled to obtain a composite sample that had an SAR of 19. In order to evaluate exchange kinetics at high Na^+ levels typically encountered in northwestern PRB, Na^+ in the composite CBNG water was increased by adding Na_2CO_3. The two CBNG waters were evaluated for ion exchange kinetics with the zeolite materials. A factorial experiment with 4 zeolite materials and 2 CBNG water qualities (SAR and EC) was conducted using the intermittent-flow columns using a mechanical vacuum extractor to keep the rate of leaching constant throughout experiment. Zeolite material was replicated 3 times and equal amount of zeolite material (50 g) was loaded into each of columns. Columns were leached with forty 50-ml volume increments of the respective CBNG waters. Leachate samples were analyzed for pH, EC, SAR, and the concentrations of soluble cations Na^+, Ca^{2+}, and Mg^{2+} with SAR calculated as:

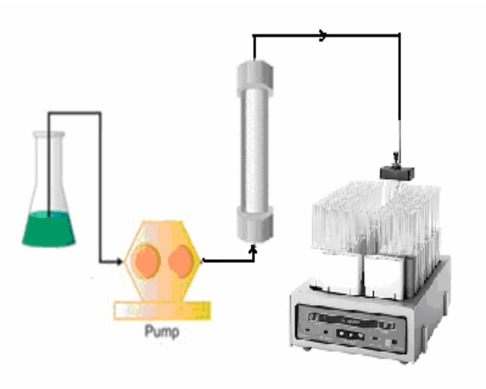
$$\text{SAR}\ (\text{mmol}^{1/2}\ \text{L}^{-1/2}) = [\text{Na}^+]/\ [\text{Ca}^{2+} + \text{Mg}^{2+}]^{1/2} \qquad \textbf{(1)}$$

where Na, Ca, and Mg represent millimolar concentrations of the respective ions (mmol L^{-1}).

The effect of sample particle size on Na^+ adsorption behavior was examined in adsorption studies using zeolites of varying particle sizes. Adsorption studies were conducted using the batch equilibration technique. A 5.0 g zeolites sample with varying particle size were weighed into 50 ml polyethylene bottles containing 45 ml of CBM water I, II, and III. The tubes were shaken on a reciprocal shaker for 48 hours, centrifuged, and the supernatant solution filtered and acidified.

Adsorption isotherms of Na-Wyoming zeolite for Ca^{2+} were also conducted using the batch equilibration technique (Zhao *et al.* 2004). A 5.0 g zeolite sample was weighed into 50 ml polyethylene bottles and spiked using stock $CaCl_2$ solution and the final volume is adjusted to 45 ml using DI water. The initial Ca^{2+} concentrations in the tubes ranged from 0 to 4,000 mg/L. The tubes were shaken on a reciprocal shaker for 48 hours, centrifuged, and the supernatant solution filtered and acidified as described above.

Packed Column Studies



Both intermittent and continuous flow-through column studies were utilized in order to predict zeolite performance under practical treatment system conditions. For the intermittent leaching studies, 50 ml columns containing zeolite were leached over a 24 hr period with 50 ml of CBNG water. This process was repeated 40 times. The continuous flow through column parameters were as follows: weight of zeolite: 132.0 g; column diameter: 25.0 mm; column length: 250 mm (for St. Cloud zeolite); 260 mm (for Bear River zeolite); flow rate: 3.0, 6.0, 16.0 ml/min; bed volume: ~125 cm^3. A smaller column with a column diameter of 15 mm, length of 400 mm was used for the WY-zeolite study at a flow rate of 5.0 ml/min. The effluents were collected using an automatic fraction collector.

For WY-zeolite, which is naturally rich in Na^+, a pretreatment was carried out using 2 L of 0.1 M $CaCl_2$ solution that was passed through the columns at a flow rate of 3.0 ml/min, followed by rinsing using DI water. Column studies were carried out as described above.

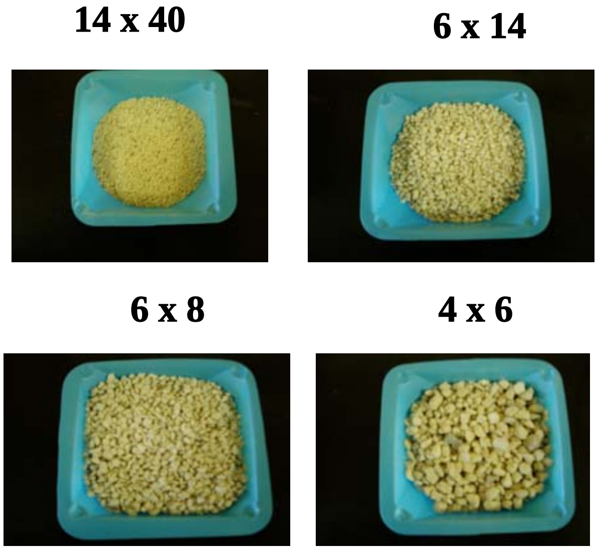
Instrumentals

The concentrations of cations (Na^+, Ca^{2+}, Mg^{2+}) in solution were analyzed using Inductively Coupled Plasma (ICP) spectrophotometry (Thermo Jarrell Ash, model P300) and K^+ was analyzed using atomic absorption spectroscopy (Perkin Elmer, model 2380). The solutions were also measured for pH and electrical conductivity (EC).

Results and Discussion

Study 1 - Evaluation of Cation Exchange Reactions between CBNG Produced Water and St. Cloud Zeolites.

St. Cloud zeolites were available in 4 commercial sizes (4x6, 6x8, 6x14, and 14x40 mesh) that were readily available and had no additional costs associated with their use. Figure 3 shows the four different size zeolite materials used for column studies with the set up for the intermittent flow column experiments illustrated in Figure 4.



14 x 40

6 x 14

6 x 8

4 x 6

Figure 3. Different St. Cloud zeolite fractions used for column studies to evaluate cation exchange kinetics with CBNG water base cations.

Figure 4. Column experiment setup used to evaluate the cation exchange kinetics between CBNG water and different sizes of St. Cloud zeolites.

Content of the St. Cloud zeolite exchangeable cations are listed in Table 5. The effective CEC of St. Cloud zeolite materials ranged from 87 to 111 cmol$_c$ kg^{-1}. Although this CEC value is less than those obtained for other deposits surveyed in this study, St. Cloud zeolite deposits were naturally enriched with Ca^{2+}, which is the key to reduce SARs in CBNG water.

Table 5. Exchangeable cations concentrations (cmol kg^{-1}) in St. Cloud Zeolite materials.

Exchangeable cation concentrations	4x6	6x8	6x14	14x40
Sodium (Na^{+})	3	4	3	4
Potassium (K^{+})	7	11	10	12
Calcium (Ca^{2+})	61	68	73	77
Magnesium (Mg^{2+})	17	15	17	18
Effective CEC (cmol$_c$ kg^{-1})	87	97	104	111

Cation exchange reactions between Zeolites and CBNG waters

St. Cloud zeolite materials performed extremely well in removing Na^+ from CBNG water samples both at low and high SAR conditions. After 50 ml of high Na^+ CBNG water was passed through the zeolites, Na^+ was reduced from 1129 to 53.4 (14x40 mesh) - 275 mg L^{-1} (4x6), Ca^{2+} from 43 (14x40) - 185 mg L^{-1} (4x6), and Mg^{2+} from 8.5 (14x40) - 19.8 mg L^{-1} (4x6). Leachates had SAR values that decreased from an initial value of 107 to 1.1 (14x40) - 9.7 (4x6) in case of high SAR CBNG water, and from 18.7 to 0.6 (14x40) - 3.4 (4x6) in case of low SAR CBNG water.

Figure 5 provides information on the cation exchange kinetics with progressive additions of high and low SAR CBNG water leached through zeolite samples. The Ca-rich zeolite materials removed significant amounts of Na^+ from CBNG waters both at low and high SAR conditions. Initial leaching of high Na^+ CBNG water through the zeolites resulted in a Na^+ reduction from 1129 to 53.4 mg L^{-1}. Leachate SARs decreased from an initial value of 107 to <1.0 in the case of high SAR CBNG water, and from 18.7 to 0.6 in the case of low SAR CBNG waters. Based on column exchange reactions using high Na^+ conditions, 1 tonne of zeolite material will reduce 750 barrels of CBNG water with an SAR of 34 (typically encountered in many parts of PRB region) to an accepted level of 10. Thus the zeolite technology is an efficient, effective and affordable water treatment alternative that maximizes the beneficial use of CBNG water.

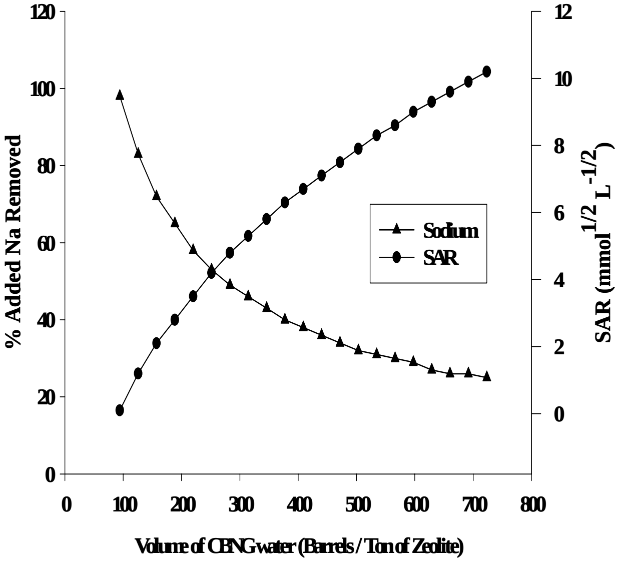


Figure 5. Reduction in cumulative CBNG water Na vs change in SAR using zeolite ion-exchange columns.

Based on the exchange kinetics obtained under high and low Na^+ conditions, 1 tonne of different particle size zeolite materials will reduce SAR of CBNG water from 34 (typically encountered in many parts of the PRB region) to accepted level of 10 is shown in Table 6.

Table 6. Volumes of CBNG water that can be treated by using 1 tonne of Zeolite to reduce SAR from 34 to a target value of 10.

Zeolite material	Liters	Gallons	Barrels
4x6	50,000	13,228	314
6x8	69,000	18,254	434
6x14	70,000	18,519	440
14x40	85,000	22,487	535

In summary, results obtained by the intermittent flow column studies indicated zeolite technology has the potential to reduce SARs to safe levels and may be used as a water treatment alternative that maximizes the beneficial use of CBNG produced water.

Study 2 - Evaluation of Exchange Reactions Between Synthetic CBNG Water and Different Ca^{2+}-Rich Natural Zeolites.

Adsorption Kinetics

Sodium adsorption rates were faster for Bear River (BR) zeolite when compared to St. Cloud (ST) zeolite (Fig. 6). In addition, BR-zeolite removed more Na^+ and released greater amounts of Ca^{2+} than that of ST-zeolite. Other major exchangeable cations (i.e., K^+ and/or Mg^{2+}) can also be replaced by Na^+ in short term experiments. The adsorption kinetics are related to many factors including particle size, pore structure, and solute diffusion.

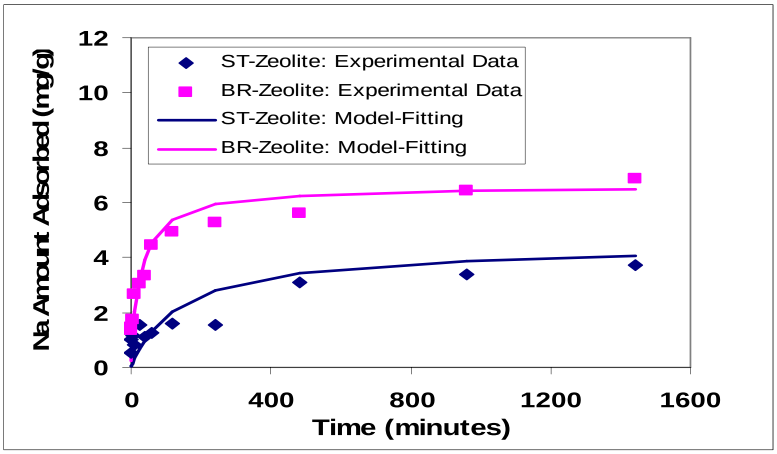


Figure 6. Na^+ adsorption kinetics and model fitting for ST-zeolite (14x40 mesh) and BR-zeolite (14x40 mesh)

Kinetics Modeling

Because adsorption kinetics is controlled by many factors, there have been many modeling approaches reported in the literature. Generally, two kinetic models of adsorption have been most frequently used: (1) active available site model and (2) chemical reaction rate model, which is based upon 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 (Reddad *et al.* 2002, Ho and Mckay 1999, 2000). The pseudo-second-order kinetic rate equation can be expressed as (Ho and McKay 1999, 2000, Reddad *et al.* 2002):

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

where Q_{eq} is the sorption capacity at equilibrium, Q_t is the solid-phase loading of Na^+ at time *t*, and *t* is time (min) and k (g/mmol∗min) is the pseudo-second-order rate constant for the kinetic model. 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:

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

and

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

where v_o (mmol/g∗min) is the initial adsorption rate. Therefore, by plotting *t* versus t/Q_t, the v_o and Q_{eq} values of kinetic study can be determined. A 24 hour equilibration period (1440 minutes) was found to be more than sufficient to establish steady state or equilibrium in sorption experiments using similar particle sizes and initial Na^+ concentrations. Results also suggested that equilibrium is obtained if the empty bed contact times (EBCT) are on the order of greater than 5 minutes.

Results were fitted using the pseudo-second-order kinetic model (Eq. 3) to estimate the rate constants, initial sorption rates, and adsorption capacities for Na^+. Relevant parameters are summarized in Table 7. The high fitting coefficients (R^2 ~0.97-0.99) indicated that the adsorption of Na^+ on the tested media could be well described using the pseudo-second-order kinetic model. Approximately 22% to 32% of the initial Na^+ in solution (about 411 ppm) was removed by the end of the 24-hr equilibration period. Rate constants and initial adsorption rates were higher for BR-Zeolite compared to ST-Zeolite. BR-Zeolite showed the highest equilibrium sorption capacity in the kinetic tests.

Differences among the zeolites are potentially attributable to differences in the physical and chemical properties of the media (i.e., composition, pore size, surface area, surface charge, sodium affinity, etc.). These adsorption kinetic parameters would be informative in predicting zeolite Na^+ removal from CBNG waters.

Table 7. Kinetic parameters for CBNG water Na^+ adsorption by zeolites using a pseudo-second-order kinetic model.

Media	R^2	k	v_o	Q_{eq} (mmol/g)	Q_{eq} (mg/g)
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.

Data Analysis for Diffusion Coefficients

_Diffusion coefficients are also an important parameter in predicting the diffusion rate of adsorbate molecules in porous media (Siegel *et al.* 2007). In order to extract 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 was proposed Ruthven (1984):

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

where ε_p is adsorbent particle porosity, q(R, t) is the adsorbed phase concentration (μg/L of adsorbate), t (s) is time, c (μg/L) is the adsorbate concentration in the supernate, D_p (cm^2/s) 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 assume to be independent of concentration in the above equation. For fractional adsorption uptake M_t/M_{max} above 70%, the solution for the equation with a 2% error is given by (Siegel *et al.* 2007):

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

where M_t (µg/L) is the mass gain of adsorbate at time t, M_{max} (µg/L) is the mass gain of adsorbate at infinite time, and D_e (cm^2/s) is the effective diffusivity defined by:

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

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

The values for effective diffusivity D_e (cm^2/s) calculated based on data points with M_t/M_{max} above 40% assuming an average particle size of 0.315 mm, are 2.01×10^{-9} (R^2=0.939) for ST-zeolite (14x40) and 7.03×10^{-9} (R^2=0.948) for BR-zeolite (14x40), respectively. BR-zeolite has a higher D_e value than that of ST-zeolite (Table 8).

Table 8. Effective Na^+ diffusivity for ST-Zeolite and BR-Zeolite samples of varying particle sizes.

Particle Size (mesh)	D_e (cm^2/s)	R^2
ST-Zeolite (14x40)	2.01×10^{-9}	0.939
BR-Zeolite (14x40)	7.03×10^{-9}	0.948

Adsorption Isotherms

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

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

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

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

Plotting $\frac{C}{q}$ *vs C*, the slope is $\frac{1}{q_{\max}}$ and the intercept is $\frac{1}{Kq_{\max}}$.

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 isotherms for ST-zeolite and BR-zeolite were 9.6 and 12.3 (mg/g) or 0.42 and 0.54 (meq/g), which accounts for approximately 38% and 39% of their measured CEC values, respectively (Table 9). 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 (K) of BR-zeolite is higher than that of ST-zeolite, indicating that Na^+ could be more strongly adsorbed by BR-zeolite. The adsorption isotherm results are consistent with the findings observed in the kinetic study.

Table 9. Langmuir adsorption parameters for the adsorption of Na^+ by ST-Zeolite (14x40) and BR-Zeolite (14x40)

Sample	q_{max} (mg/g)	K	R^2
ST-Zeolite	9.6	872	0.965
BR-Zeolite	12.3	1053	0.983

Zeolite cation adsorption behavior (i.e., adsorption capacity and selectivity) is related to a variety of factors such as mineral purity, crystallinity, media purity, cation valence/hydration degree and pre-existing cations and multiple adsorption sites with varying degree of accessibility as well as rate-limiting steps (mass transfer and diffusion) (Zhao *et al.* 2004). Although ST-zeolite contains a slightly higher exchangeable Ca^{2+} than that of BR-zeolite, the ease of which the Ca^{2+} exchanged from ST-zeolite is lower than that of the BR-zeolite, suggesting that the Ca^{2+} in ST-zeolite may occupy the stronger adsorption sites. The higher K^+ in BR-zeolite suggest that it could occupy the stronger adsorption sites thus leaving the Ca^{2+} in relatively weak adsorption sites making the Ca^{2+} in BR-zeolite more easily replaced by Na^+ than that in ST-zeolite. Overall, the adsorption results of this study suggest that both zeolites can be used to reduce the Na^+ level in CBNG waters by releasing K^+, Ca^{2+}, and Mg^{2+}, with the BR-zeolite having a higher adsorption capability than that of ST-zeolite.

Considering charge balance, the amount of Ca^{2+}, Mg^{2+} and 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. Longer term experiments may provide better evidence for the removal of Na^+ from CBNG waters as was shown for ST-zeolite in study 1.

Packed Column Study and Data Analysis

Results of the column studies at flow rate of 3.0 ml/min (Figure 7) were consistent with the tendency observed in the batch adsorption kinetic/isotherm studies (Study 2). Monitoring of the effluent solution pH indicated that, as compared to that of the 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). The BR-zeolite removed greater amounts of Na^+ from the synthetic CBNG waters and there was a longer breakthrough period for the BR-zeolite compared to the ST-zeolite. It is interesting to note that, for BR-zeolite, significant K^+ was also released, which is an important plant nutrient.

Another interesting finding relates to our studies on an Arizona (AZ) chabazite. Though Ca^{2+} is the dominant exchangeable cation, almost no Na^+ was removed in the column study, suggesting that the Ca^{2+} in the chabazite is strongly adsorbed. This may be attributed to the upgrading treatment of the raw materials with is naturally Na-rich chabazite.

If one considers CBNG water with SAR values equal to or less than 10 to be suitable for land application, using SAR breakthrough curves can estimate the efficiency of flow-through zeolite treatment systems for this purpose. The amount of the synthetic CBNG water (SAR=30 $mmol^{1/2}$ $L^{-1/2}$) that can be treated per tonne (1,000 kg) of ST-zeolite and BR-zeolite would be about 8,000 and 30,000 L, respectively. On the other hand, if CBNG water with an effluent SAR of 10 $mmol^{1/2}$ $L^{-1/2}$ were treated and collected in a large containment reservoir, CNBG waters processed initially would have very low SAR values. By integrating the area between the SAR curve and

SAR=10 cutoff line (yellow area in Figure 7), the amount of additional CNBG waters that could be treated and combined with the initially processed waters to reach a final SAR value of 10 can be estimated. Extrapolating the results suggests that one tonne (1,000 kg) of ST-zeolite and BR-zeolite can treat approximately 16,000 and 60,000 L of the synthetic CBNG water (SAR=30), respectively, to a final SAR around 10, which is considered safe for land application for agricultural use.

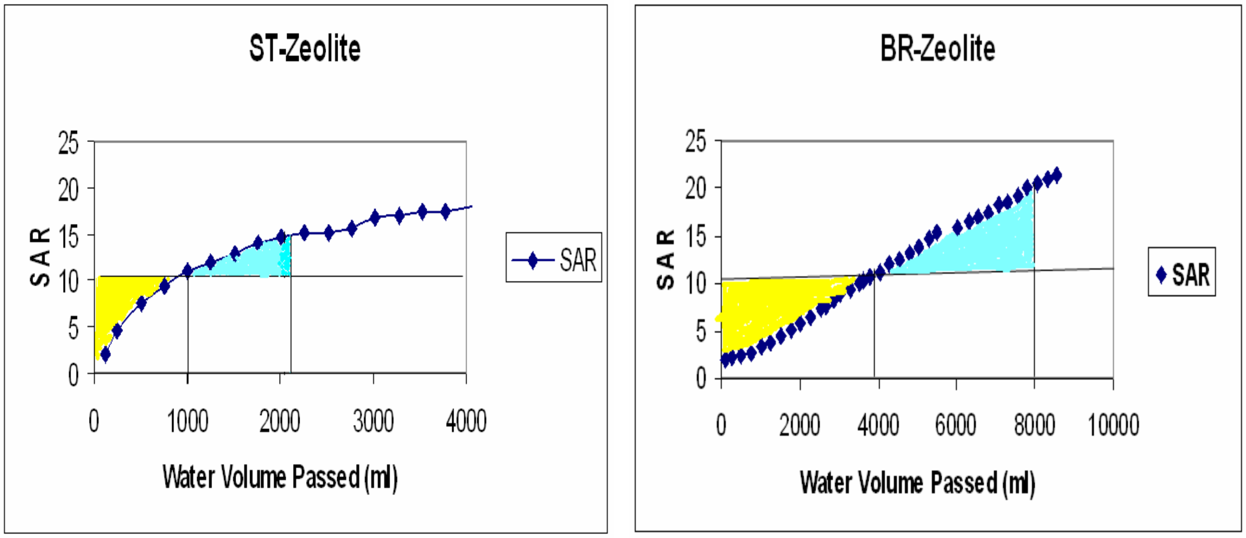


Figure 7. Estimation of cumulative treatable water volume by ST-zeolite and BR-zeolite

Regeneration Using 0.1 M $CaCl_2$ Solution

A majority (~90%) of adsorbed Na^+ by BR-zeolite can be replaced by Ca^{2+} after passing 1 L 0.1M $CaCl_2$ solution (Ca^{2+} = 4000 ppm) (Fig. 8). It is anticipated that increasing the regeneration $CaCl_2$ solution concentration could result in less $CaCl_2$ solution used as well as less spent brine generated.

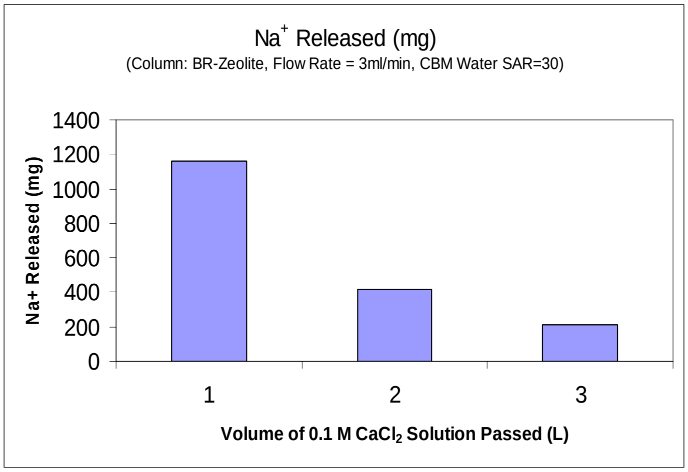


Figure 8. Regeneration of Spent BR-Zeolite Column by 0.1 M $CaCl_2$ Solution

Results from column studies will be useful for designing a scaled-up pilot project for future applications. Column performance depends upon a variety of factors that include adsorbent type, particle size, adsorption capacity, column diameter, water flow rate, adsorbent bed depth, weight of adsorbent in column, and contact time as well as water chemistry. These factors must be considered in studies evaluating the ability of zeolites to reduce Na^+ in CBNG waters.

Study 3-Natural Na-rich Zeolite (Wyoming)

Ca^{2+} Adsorption Isotherms by WY-zeolite

The Ca^{2+} adsorption isotherm curves displayed L-type adsorption on WY-Zeolite. The L-type isotherms are described well using the Langmuir equation (Eq. 3). The maximum amount of adsorption by WY-Zeolite is 10.3 mg/g, accounting for ~25% of the measured CEC value (Table 10).

Table 10. Langmuir adsorption parameters for the adsorption of Ca^{2+} by natural WY-zeolite

Sample	$q_{max\ (mg/g)}$	K	R^2
WY-Zeolite	10.3	2.2	0.999

In a previous study, Hulbert (1987) investigated Na^+, Ca^{2+}, and NH_4^+ exchange on the same zeolite materials collected from an outcrop of blue-green tuff in the Fort LaClede deposit, Sweetwater County, WY. Hulbert (1987) found that Ca^{2+} replaces Na^+ with decreasing selectivity as Ca^{2+} loading increases to about 80% at 30ºC (95% at 63ºC, above which the selectivity reverses). The standard free energy of replacement of two Na^+ ions by one Ca^{2+} ion in 0.05 M solutions was 1.2 ± 0.2 kcal/mole at 63ºC and -0.3 to -0.8 kcal/mole at 30ºC. These results suggest the Fort LaClede clinoptilolite has a moderate selectivity for Ca^{2+} over Na^+ at <80% Ca^{2+} loading and 30°C. Above this loading, the zeolite is slightly selective for Na^+. At 63ºC the zeolite has somewhat greater affinity for Ca^{2+} at all loadings than it does at 30ºC. These properties are important when considering a system for treating CBNG waters.

Figure 9 also demonstrates that a majority (~90%) of the originally adsorbed Na^+ in WY-zeolite could be replaced by Ca^{2+} after passing ~2 L 0.1M $CaCl_2$ solution (Ca^{2+}=4,000 ppm).

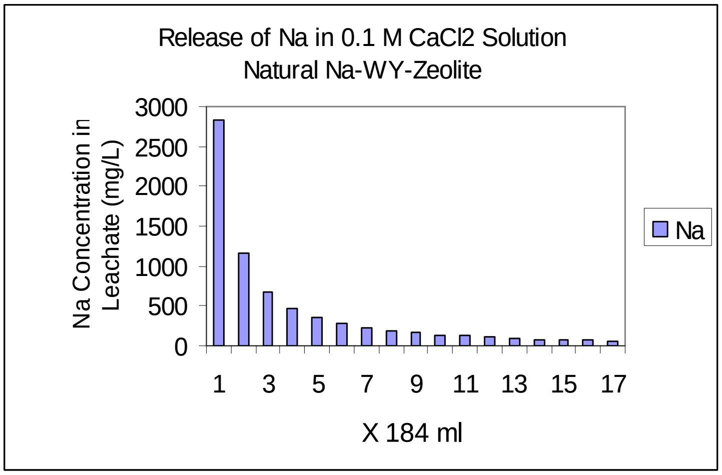


Figure 9. Pretreatment of Na-WY-Zeolite Using 0.1 M $CaCl_2$ solution in a packed column: Release of Na (x-axis: The solution volume of each collection is 184 ml)

Packed Column Studies using Ca^{2+}-Pretreated WY-zeolite

Upon pretreatment with $CaCl_2$, the Na^+ WY-zeolite was converted to a Ca-rich zeolite. It was estimated that one metric tonne (1000 kg) of the pretreated WY-zeolite can treat ~120000 L

(~32000 gallons or ~750 barrels) CBM water to reduce its SAR from 30 to acceptable 10 (Fig 10). It is interesting to note that the treatment capacity of pretreated WY-Zeolite is ~1.6 times higher than the BR-Zeolite, which is consistent with CEC measurements.

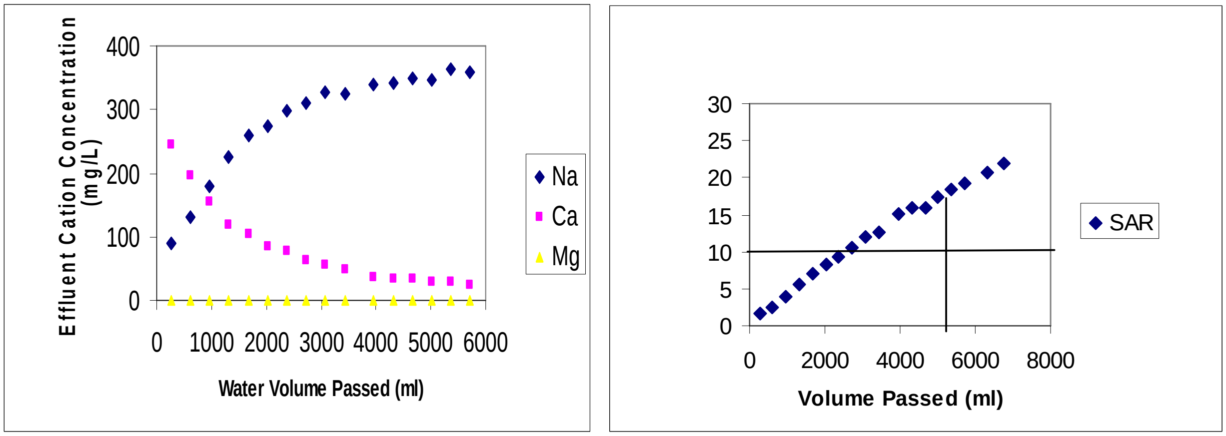


Figure 10. Column breakthrough curves for pre-modified (Ca^{2+}-treated) WY-Zeolite and corresponding water SAR upon treatment.

Technology Feasibility Analysis

The following evaluation of current CBNG water treatment technologies (Table 11) and associated operation costs (Table 12) are adapted from Chris Johnston (2006). The uses for natural zeolites can be generally categorized into different functional classifications, and within each exists a broad range of applications (Figure 11).

Prices for natural zeolite vary with zeolite content and processing. Unit values for 2005 zeolite market, obtained through the U.S. Geological Survey canvass of domestic zeolite producers, ranged from $50 to $140 per metric tonne. The bulk of the tonnage sold ranged from $80 and $140 per tonne. Eyde and Holmes (2006, p. 1058) reported that 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. Quoted prices should be used only as a guideline because actual prices depend on the terms of the contract between seller and buyer.

As might be expected, the production cost for natural clinoptilolite zeolite material varies with the size desired, amount to be purchased, and mode of transport. The average cost to produce a size fraction of 14x40 (material which will pass through a 14 mesh sieve but not through a 40 mesh sieve) is approximately $100.00 per tonne, prior to transporting. Depending on actual miles traveled, transport costs would likely run between $50.00 and $100.00 per tonne, delivered to the PRB.

Based on our results, the cost of treating CBNG water with ST-zeolite is around $0.80-1.00 per barrel, and for BR-zeolite approximately $0.20-0.40 per barrel, not including other expenses. BR-zeolite also provides K^+ which is an important plant nutrient. The locally available zeolite WY-Zeolite is naturally Na-rich, therefore, pretreatment of the samples by converting it to Ca-rich is necessary. The cost for the WY-zeolite should be around $0.10-0.20 per barrel, not including the pretreatment expenses. However, if regeneration and reuse of the media are to be considered, the treatment cost should even be lower.

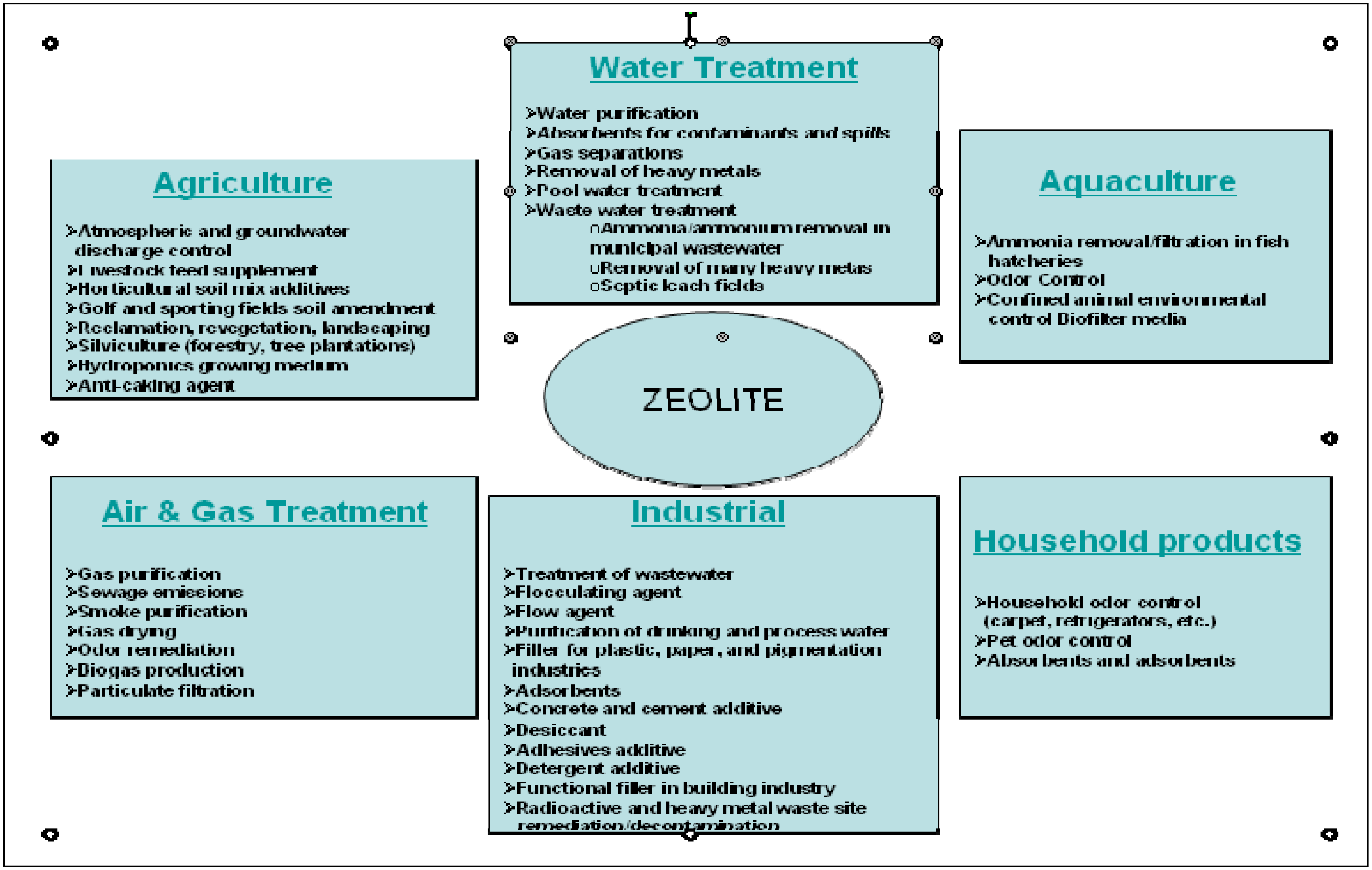
It is well know that zeolite has many applications as adsorbents in agriculture, water treatment, aquaculture, household products, industry and air/gas treatment (Figure 11). For example, zeolite is used for products such as pet litter, fish tank media, or odor control applications, with prices ranging from $0.50 to $4.50 per kilogram. Therefore, by exploring applications of the spent zeolite media for other uses, both locally or nationwide, there could be a significant reduction in the treatment cost, making the use of zeolite treatment a more feasible, cost-effective technology in CBNG water treatment.

Table 11. Costs associated with CBNG co-produced water management, US DOE, 2002).

Management Technology	Capital Costs	O & M Costs
Surface Discharge	\$300	\$0.004/bbl
Infiltration/Storage Ponds	\$10,300/well (DOE)	\$0.06/bbl (DOE)
Shallow Injection	\$6,350	\$0.045/bbl
Deep Injection	\$62,500	\$0.095/bbl
Reverse Osmosis	\$77.14/bbl	\$0.033/bbl

Table 12. Capital and O&M costs associated with managed irrigation.

Item	Capital Costs	O&M Costs
Irrigation Systems (16.2 ha)		
Center Pivot System	\$58,000	\$0.04/bbl
Side Roll Systems	\$55,000	\$0.12 - \$1.20/bbl
Automated Big Gun System	\$55,000	\$0.04 - \$0.08/bbl
Manual Big Gun System	\$20,000	\$0.20 - \$0.40/bbl
Water Treatments		
Gypsum Applicator		
175 gallon	\$2,959	\$0.02/bbl
325 gallon	\$2,870	\$0.02/bbl
525 gallon	\$3,200	\$0.02/bbl
Pump and Metering Box	\$2,000	
Sulfur Burner	\$30,000	\$0.08/bbl
Mixing Tank	\$1,500	
Pumps (2)	\$200-\$300 each	
Soil Amendments		
Gypsum and Sulfur (delivered) (1.45 Mg/ha)		\$0.12 -\$0.15/bbl



Water Treatment

- Water purification
- *Absorbents for contaminants and spills*
- Gas separations
- Removal of heavy metals
- Pool water treatment
- Waste water treatment
    - Ammonia/ammonium removal in municipal wastewater
    - Removal of many heavy metals
    - Septic leach fields

Agriculture

- Atmospheric and groundwater discharge control
- Livestock feed supplement
- Horticultural soil mix additives
- Golf and sporting fields soil amendment
- Reclamation, revegetation, landscaping
- Silviculture (forestry, tree plantations)
- Hydroponics growing medium
- Anti-caking agent

Aquaculture

- Ammonia removal/filtration in fish hatcheries
- Odor Control
- Confined animal environmental control Biofilter media

Air & Gas Treatment

- Gas purification
- Sewage emissions
- Smoke purification
- Gas drying
- Odor remediation
- Biogas production
- Particulate filtration

Industrial

- Treatment of wastewater
- Flocculating agent
- Flow agent
- Purification of drinking and process water
- Filler for plastic, paper, and pigmentation industries
- Adsorbents
- Concrete and cement additive
- Desiccant
- Adhesives additive
- Detergent additive
- Functional filler in building industry
- Radioactive and heavy metal waste site remediation/decontamination

Household products

- Household odor control (carpet, refrigerators, etc.)
- Pet odor control
- Absorbents and adsorbents

Figure 11. The various applications of zeolite products.

Conclusions

In this study, the potential utilization of Ca^{2+}-rich natural zeolites and modified Na^+-rich natural zeolites were examined for removal of Na^+ from CBNG waters. Zeolite samples examined were from New Mexico, Idaho, Arizona and Wyoming. The zeolite materials were used as received or pre-modified in adsorption kinetic/isotherm studies and column experiments. Both CBNG waters and surrogate waters that simulated the chemistry of CBNG waters were used in the various studies described herein. Results indicated that a Langmuir model fit the adsorption data well. The maximum adsorption capacities from the adsorption isotherms for ST-Zeolite and BR-Zeolite were 9.6 and 12.3 mg/g, respectively, accounting for approximately 38% and 39% of their measured CEC values. Column studies indicated that a metric tonne (1000 kg) of ST-zeolite and BR-zeolite can be used to treat 16,000 and 60,000 liters of CBNG water, respectively, in order to lower the sodium adsorption ratio (SAR, $mmol^{½} L^{-½}$) of the simulated CNNG water from 30 to an acceptable level of 10. Based on the results of this study Na^+ removal with zeolite appears to be a cost-effective water treatment technology for maximizing the beneficial use of poor-quality CBNG water. However, an upgraded Ca^{2+}-rich chabazite from Arizona shows no removal of Na^+ from CBNG waters.

Studies also included a natural Na-rich zeolite from Wyoming. The WY-zeolite was pretreated using $CaCl_2$ solution and converted to a Ca-exchanged zeolite before use. The Ca^{2+} batch adsorption isotherm curves showed L-type adsorption. The maximum amount of Na^+ adsorption by WY-Zeolite was 10.3 mg/g, accounting for ~25% of the measured CEC value. Column studies indicated that one metric tonne of the Ca-Wyoming zeolite can treat ~1.2 x 10^5 L (~3.2 x 10^4 gallons) CBNG water to reduce its sodium adsorption ratio (SAR, $mmol^{½} L^{-½}$) from 30 to an acceptable level of 10. Compared to results of the other zeolites (ST-Zeolite ~1.6 x 10^4 and BR-Zeolite ~6.0 x 10^4 L, respectively), it is suggested that water treatment with locally available Wyoming zeolite appears to be more effective and may be a promising and feasible treatment technology for maximizing the beneficial use of poor-quality CBNG in the Powder River Basin, WY. An innovative integrated system using Na-Wyoming zeolite is currently being developed.

The major accomplishments of this CBNG water treatment study include an invention disclosure, and several conference presentations and journal manuscripts (see section below). Ongoing studies are evaluating water treatment techniques involving the direct application of zeolite to CBNG waters and development of a field scale prototype.

Accomplishments

- Collected several zeolite minerals from Wyoming and the other states including California, Idaho, Nevada and New Mexico;
- Assessed feasibility of zeolite deposits in terms of mineral quality and quantity;
- Conducted numerous field studies to follow-up on research on zeolite occurrences reported in the literature;
- Eliminated several reported occurrences as potential sources for zeolite for the purposes proposed for this project;
- Characterized ten natural zeolite materials using X-Ray diffraction for mineralogical compositions and wet chemistry methods for total elemental composition, CEC and exchangeable cations;
- Extensively studied the three most promising zeolite samples to evaluate their potentials for CBNG water treatment. They were two naturally Ca^{2+} rich zeolites from New Mexico and

Idaho, and one naturally Na^+-rich zeolite from Wyoming that was subjected to pre-modification before use;
- Conducted both adsorption kinetic and isotherms studies with the data analyzed and fitted to models in order to evaluate the potential of the different zeolites for treating CBNG waters;
- Performed a series of packed column studies to determine the effect of particle size, water chemistry, and flow rate on Na^+ removal from CBNG water;
- Evaluated the possibility of direct application of zeolite to CBNG water reservoirs or ponds using a large fish tank;
- Determined that the volume of CBNG water that could be treated by the zeolites decreased in the order of: Ca-Modified-Wyoming zeolite > Idaho Bear River Ca-zeolite > New Mexico St. Cloud Ca-zeolite;
- Attributed the variation in zeolite performance for CBNG water treatment to mineralogical composition, CEC, Na^+ effective diffusivity, particle size, etc. of the zeolite samples;
- Performed an analysis on the economic feasibility of using zeolite treatment as a potential feasible, cost-effective technology in CBNG water treatment;
- Disseminated information on our findings, progress of the project as well as information on the physical and chemical nature of zeolites to conference attendees, students, general public (via inquiries, website visits, etc.);
- Began compilation of WSGS publications on zeolites and their occurrences and applications (to be published by fall, 2007);
- Continuing studies that include the design and testing of a field scale prototype.

Student/Staff Support

The following individuals were involved in this project.

Kaitlin Forbotnik – Laboratory Assistant
Shannon Geslin – Laboratory Assistant
Girisha Ganjegunte - Post Doctoral Research Scientist
Robert Gregory – Geology Graduate Student
Ray Harris – Geologists (deceased)
David Micale – Research Associate
Steve Wilkins – Soil Science Graduate Student
Michael Urynowicz – Assistant Professor
Hongting Zhao – Post Doctoral Research Scientist

Additional Funding

Additional funding was received for a two year project to develop a laboratory prototype and field-scale model for treating CBNG water using the zeolite treatment technology. The principal investigators of this project are Drs. George Vance and Michael Urynowicz, Assistant Professor of Civil and Environmental Engineering, with Dr. Ron Surdam as a collaborator. We expect to provide support for a doctoral candidate from the project grant.

George Vance received a sabbatical leave grant from the USDA National Research Initiative program to support zeolite research involving the treatment of various waters. His sabbatical was funded for January to August, 2007. He has spent some of his sabbatical at New Mexico Institute of Mining and Technology working with Dr. Robert Bowman, Department Head of Earth and Environmental Sciences. Dr. Bowman has extensive experience on the use of surfactant modified zeolites for environmental protection.

Proceedings and Abstracts with Presentations

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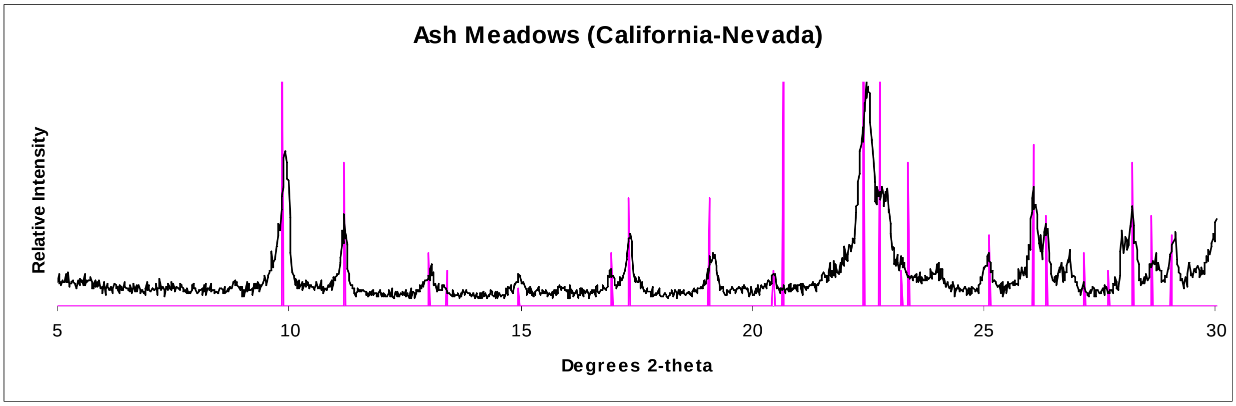
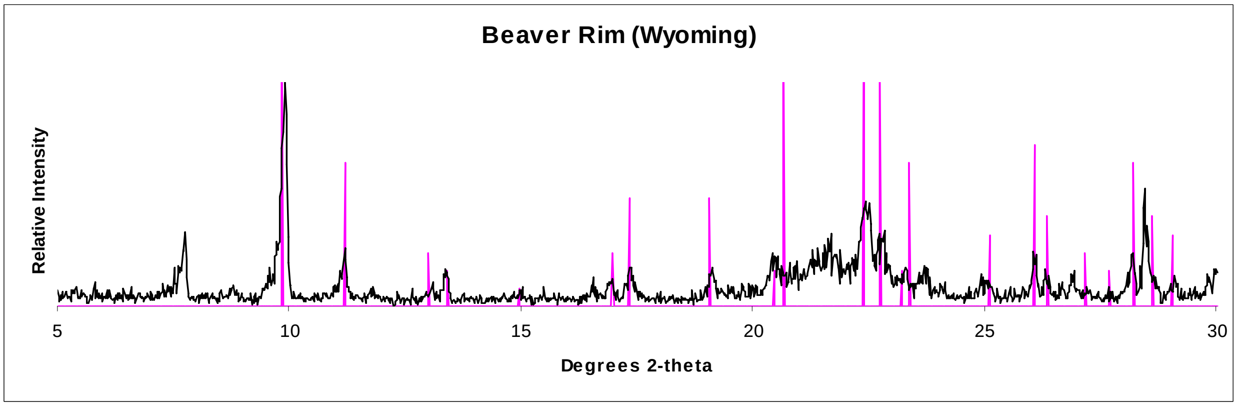
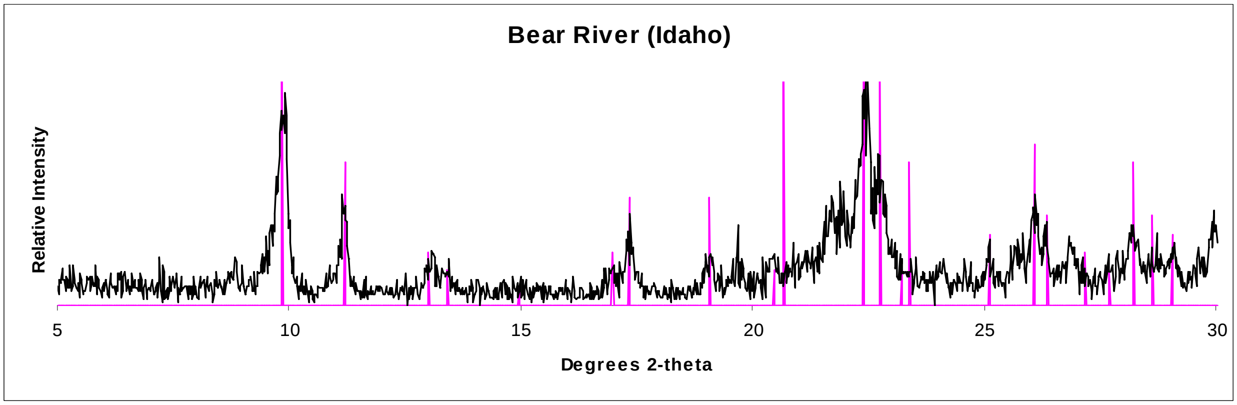
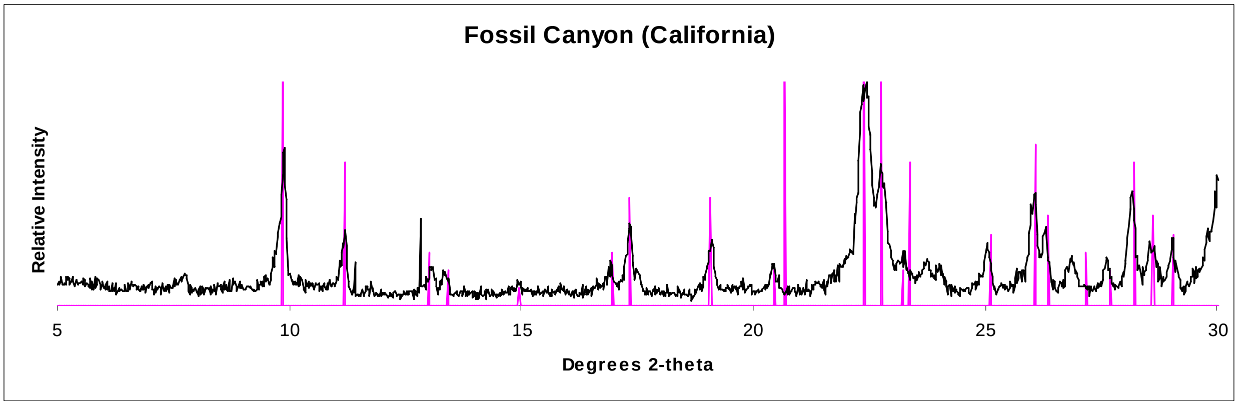
Appendix I Zeolite Diffractograms.

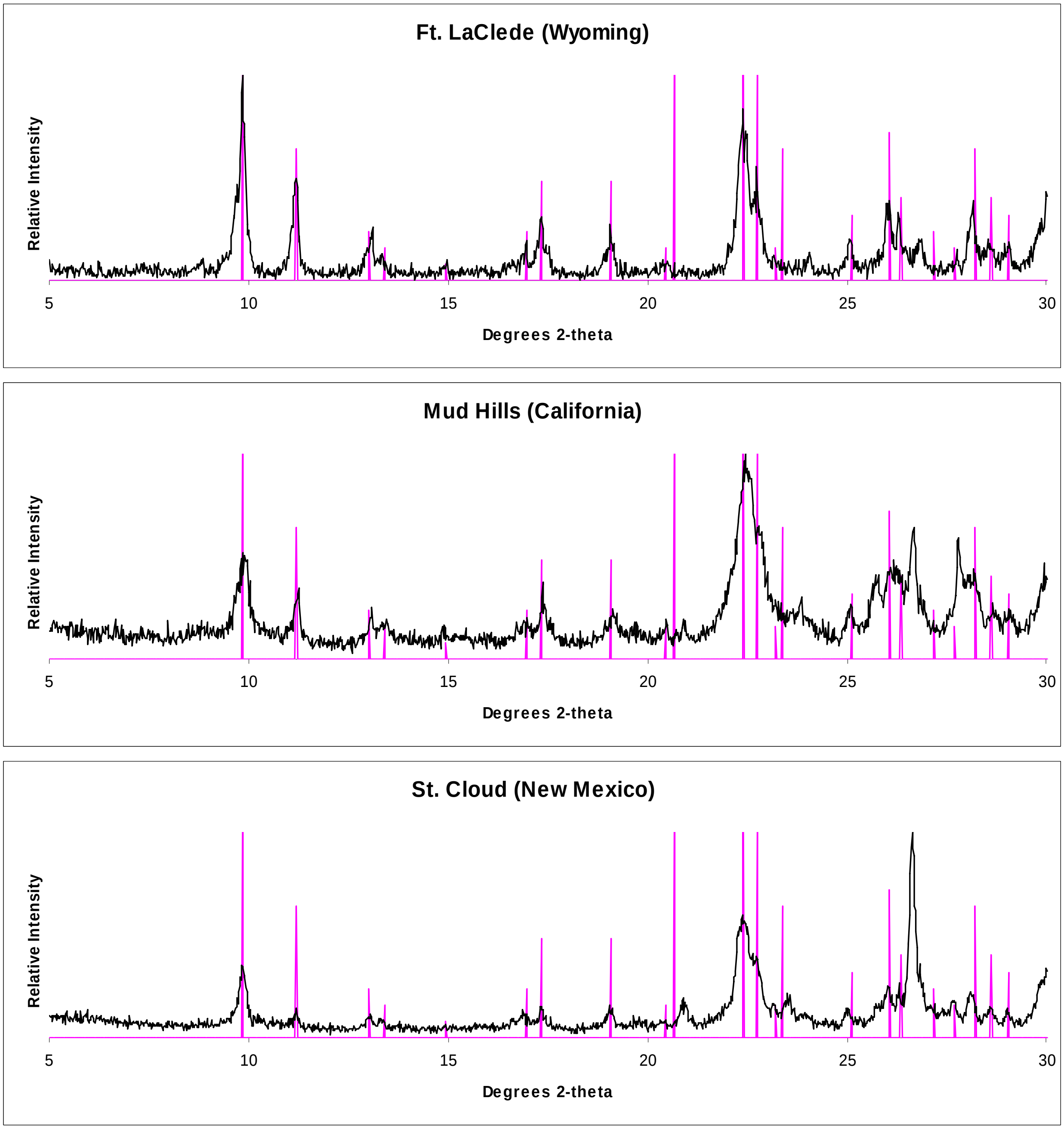

Ash Meadows (California-Nevada)


Beaver Rim (Wyoming)


Bear River (Idaho)


Fossil Canyon (California)

Appendix I Zeolite Diffractograms (continued).



APPENDIX II

Results of whole-rock analysis done by ALS-Chemex, Inc., Vancouver, B.C.

	Whole Rock Analyses										
	AM1 - 1643	**AM1 - 2035**	**AM1 - C**	**BC1-06**	**BRZ1**	**FC1**	**FC2a**	**FC2b**	**FL1-06**	**MH1**	**SC1**
Weight %											
SiO_2	65.3	65.3	65.3	60.3	66.5	61.2	61.8	61.7	62.7	64.2	66.9
Al_2O_3	10.3	10.45	10.5	11.85	10.4	12.25	11.9	12.05	12.15	11	11.95
Fe_2O_3	0.82	1.06	0.82	2.44	1.99	1.34	0.79	0.88	0.5	0.88	1.44
CaO	0.86	0.75	0.97	1.68	2.33	1.72	0.94	0.9	1.5	1.41	2.87
MgO	0.4	0.39	0.4	4.78	0.57	1.28	0.69	0.88	0.3	0.52	1.2
Na_2O	3.41	3.48	3.47	1.6	0.49	3.11	4.27	4.19	4.4	3.57	0.44
K_2O	3.6	3.66	3.73	2.91	4.32	1.78	1.74	1.55	1.53	1.63	3.44
Cr_2O_3	0.01	0.01	0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01
TiO_2	0.09	0.09	0.09	0.28	0.28	0.21	0.1	0.1	0.17	0.13	0.21
MnO	0.04	0.04	0.03	0.03	0.03	0.01	0.01	0.04	<0.01	0.04	0.07
P_2O_5	0.02	0.01	0.03	0.07	0.01	0.04	0.02	0.02	0.03	0.04	0.06
SrO	0.03	0.03	0.05	0.02	0.02	0.16	0.56	0.59	0.04	0.27	0.17
BaO	0.03	0.03	0.03	0.07	0.12	0.27	0.35	0.34	0.13	0.22	0.08
LOI	12.65	12.5	12.55	13.75	12.5	14.65	14.4	14.6	15.05	13.75	11.1
Total	97.6	97.8	98.0	99.8	99.6	98.0	97.6	97.9	98.5	97.7	99.9

Results of minor and trace element analysis done by ALS-Chemex, Inc., Vancouver, B.C.

Sample		AM1 - C	AM1 - 2035	AM1 - 1643	FC1	FC2a	FC2b	MH1	SC1	BC1-06	BRZ1	FL1-06	PB1-06
Element	units												
Ag	ppm	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
As	ppm	8	8.7	9.1	4.4	3.5	2.4	8.6	2.3	3.4	2	1	0.5
Ba	ppm	240	260	300	2280	3130	3050	1890	660	636	1020	1160	296
Bi	ppm	0.12	0.15	0.13	0.15	0.22	0.18	0.14	0.29	0.19	0.43	0.19	0.17
Ce	ppm	54	52.6	58.3	94.3	59	72	53.3	76.2	50.2	150.5	87.2	67.1
Co	ppm	0.6	0.8	0.6	2.3	0.5	0.5	0.7	2.6	2.6	1.1	1.1	3.1
Cr	ppm	42	67	22	10	<10	<10	<10	17	10	<10	<10	10
Cs	ppm	2.81	3.03	3.13	1.14	0.38	0.33	91.4	3.89	5.17	3.87	2.18	5.84
Cu	ppm	2.7	8.4	4.9	9.7	10.8	6.6	8.7	7.6	38	7	12	14
Ga	ppm	14.05	13.7	13.8	15.95	17.25	16.25	17.5	15.95	14.5	18.6	14.1	17.3
Hf	ppm	3.2	3.1	3.2	4.1	4.4	4.8	3.7	4.4	4.5	11.7	7	4.7
La	ppm	27.7	26.4	28.8	52.9	29.6	34.3	26.6	37.7	28	77.8	47.1	35.1
Mo	ppm	<2	<2	<2	<2	<2	<2	<2	<2	3	<2	<2	3
Nb	ppm	13.4	13.4	13.3	10	21.5	15	19.6	21.3	10.6	45.6	29	19.6
Ni	ppm	1.4	2.9	1.1	2.5	0.6	0.5	0.8	5.8	5	<5	<5	7
Pb	ppm	21	21.7	23.4	32.8	12.9	10.3	17.8	28	22	24	19	23
Rb	ppm	103	106.5	109	31.9	42.1	34.9	114.5	106.5	101	160	71.1	175.5
Sb	ppm	0.64	0.72	0.65	0.72	0.29	0.24	0.91	0.31	0.16	0.71	0.11	0.08
Se	ppm	1	1	2	2	1	2	1	2	<1	<1	<1	<1
Sn	ppm	1.8	1.8	1.8	2.5	2.4	2.9	2.5	2.5	2	7	3	3
Sr	ppm	387	276	285	1395	4950	5290	2280	1475	167	164	401	135
Ta	ppm	1.18	1.15	1.14	1.4	1.48	1.68	1.35	1.74	1.2	3.3	1.7	1.6
Te	ppm	<0.05	<0.05	<0.05	<0.05	0.06	0.05	<0.05	<0.05	<0.01	0.01	0.01	0.01
Th	ppm	18	17.2	18	19	18.1	23.5	13.6	22.7	19.45	27	18.1	23.7
Tl	ppm	0.52	0.55	0.6	0.23	0.05	0.04	0.3	0.57	<0.5	0.7	<0.5	0.8
U	ppm	2.6	2.5	2.6	2.2	0.2	0.2	1	2.6	5.27	6.49	5.01	6.73
V	ppm	6	7	6	15	46	43	8	13	27	<5	6	16
W	ppm	1.1	1.5	1.1	0.3	0.2	0.1	0.3	0.6	2	3	2	2
Y	ppm	11.5	12	13.8	16.4	9.1	11.6	12.3	26.6	15.1	54	22.7	21.1
Zn	ppm	24	24	23	66	56	61	52	44	34	43	40	45
Zr	ppm	79.7	78.1	77.6	83	109	110	78.7	106.5	143	398	231	131

Predicting Drought in the Green River Basin

Basic Information

Title:	Predicting Drought in the Green River Basin
Project Number:	2006WY32B
Start Date:	3/1/2006
End Date:	2/28/2008
Funding Source:	104B
Congressional District:	1
Research Category:	Climate and Hydrologic Processes
Focus Category:	Drought, Climatological Processes, Hydrology
Descriptors:	None
Principal Investigators:	Glenn Tootle

Publication

1. Tootle, G.A., T. Hunter and T.C. Piechota, 2006. Pacific Oceanic / Atmospheric Variability and the Wind River Range. Proceedings of the ASCE World Water & Environmental Resources Congress 2006, May 21-25, 2006, Omaha, NE.

Abstract

The proposed two-year research project will use proxy records derived from tree rings to examine climatic controls on Green River Basin (GRB) streamflow and assess how natural interdecadal variability might impact delivery of water from the GRB. The proposed research will review existing streamflow proxies for the GRB and assess how reconstruction methodology might affect key elements (e.g. reconstructed drought magnitude) of these records. Next, an investigation of long-term streamflow variability, focusing on extreme events such as mega-droughts, will be performed including evaluating the influence of various atmospheric – oceanic influences [e.g., El Niño-Southern Oscillation (ENSO)] on GRB streamflow. The results of the research will be used to develop probabilistic drought forecasts for the GRB. These forecasts would utilize both empirical probabilities for drought risk derived from the tree-ring record and links between streamflow and climatic drivers like ENSO and the PDO.

Statement of the Problem

From 2001 to 2003, Professor Stephen T. Jackson, Ph.D. and Stephen T. Gray, Ph.D. of the University of Wyoming's Department of Botany were funded by the Water Resources Program (WRP) on a study entitled "Combining Modern and Paleo-Climate Data to Enhance Drought Prediction and Response." Key findings of the Jackson – Gray study included: (1) Strong evidence that droughts of a greater magnitude and duration than any 20th century events have regularly occurred in western Wyoming over the past 800 year; (2) Droughts in western Wyoming show strong links to circulation patterns in the northern and tropical Pacific Ocean; (3) However, connections between western Wyoming drought and the Pacific Ocean may also be modulated by variations in other ocean basins (e.g. the North Atlantic).

The current research extends and addresses additional research needs identified in the Jackson – Gray study. In particular, the proposed research examines linkages between interannual and interdecadal ocean / atmosphere phenomena and GRB streamflow. Ultimately, the current research focuses on developing a lead-time approach where ocean / atmosphere conditions, and the resulting potential for drought, are evaluated prior to the beginning of each water year. An additional goal of the research is to develop probabilistic forecasts of drought and to perform a frequency – duration analysis of drought.

Objectives

The scientific objectives of the proposed two-year research project are to:

1. Evaluate methodologies used to reconstruct GRB streamflow.
2. Examine linkages between GRB reconstructed streamflow and large scale oceanic / atmospheric phenomena that act at interannual and interdecadal time scales.
3. Develop probabilistic forecasts of droughts, and frequency / duration analysis of droughts.
4. Supplement existing tree-ring chronologies for the Upper GRB with new collections.

Progress

The research plan is divided into four tasks, each corresponding with one of the four objectives. The following summarizes (with percent complete) the four tasks:

Task 1 – *Evaluation of Streamflow Reconstruction Methodologies* (50%). We are currently evaluating various methodologies to perform streamflow reconstructions using tree-ring chronologies. These methods include standard methods such as Step-wise Regression and new methods such as Partial Least Squares Regression, Multiple Linear Regression, Principal Component Regression and Regression applying Singular Value Decomposition. Once Task 4 (development of tree-ring chronologies) is complete we will complete Task 1.

Task 2 – *Linkages of Streamflow with Large-Scale Ocean / Atmosphere Phenomena* (50%). We have completed an evaluation of Pacific Oceanic Atmospheric Variability and Upper Green River streamflow and snowpack (01 Apr Snow Water Equivalent - SWE) for the instrumental period of record. This was published (non-peer reviewed electronic proceedings) and presented at the ASCE EWRI Conference in May 2006 (Tootle et al., 2006). This research evaluated the influence of interdecadal and interannual Pacific oceanic / atmospheric variability on the Wind River Range (WRR). Instrumental datasets were obtained for unimpaired streamflow and snow water equivalent for stations in the Green River Basin (GRB – west slope of WRR) and the Wind-Bighorn River Basin (WBRB – east slope of WRR). The phases (cold or warm) of Pacific [El Niño-Southern Oscillation (ENSO) and Pacific Decadal Oscillation (PDO)] oceanic / atmospheric phenomena were identified. Statistical significance testing of the datasets, based on the interdecadal and interannual oceanic / atmospheric phase (warm or cold), was performed applying the parametric t-test test. Once Task 4 is complete and we develop new reconstructions (Task 1) we will perform the same analysis for the reconstructed records.

Task 3 – *Probabilistic Forecasting of Droughts* (0%). The drought frequency/duration analysis will be performed upon the completion of Task(s) 4 and 1.

Task 4 – *Improvement of Streamflow Reconstructions for the Green River Basin with New Tree-ring Collections* (90%). Extensive field work was performed in Summer/Fall 2006 in the Upper Green River Basin in which new tree-rings were sampled. Typically, 20 to 30 trees (with a minimum of two samples per tree, all of the same species) must be collected to develop a single chronology. The goal of this task is to develop four to six new chronologies to supplement existing chronologies in the region. Once these chronologies are finalized (anticipate completion by June 2007), Task 4 will be complete. We will then proceed to Task 1 (developing new reconstructions). Once Task 1 is complete, we will then complete Task(s) 2 and 3.

Methodology

Task 1 – *Evaluation of Streamflow Reconstruction Methodologies* (50%). Various regression techniques (Step-wise Regression, Partial Least Squares Regression, Multiple Linear Regression, Principal Component Regression and Regression applying Singular Value Decomposition) are being evaluated to perform the streamflow reconstructions.

Task 2 – *Linkages of Streamflow with Large-Scale Ocean / Atmosphere Phenomena* (50%). First, spatial and temporal streamflow variability for the GRB and WBRB was evaluated by applying a 5-year filter to standardized water-year streamflow volumes for the two GRB stations and the three WBRB stations. Next, spatial and temporal snowfall (SWE) variability for the GRB and WBRB was evaluated by applying a 5-year filter to standardized 01 April SWE values for the four GRB stations and the three WBRB stations.

Finally, the impacts of the interdecadal (PDO) and interannual (ENSO) oceanic / atmospheric influences on WRR streamflow and snowfall were evaluated by testing of water-year (or 01 April) means for the individual and coupled oceanic / atmospheric influences.

The current water-year (October through September) was the period selected for streamflow and the 01 April date was selected for SWE. The previous year (or season) was selected to define the phase (e.g., warm or cold) of the PDO and ENSO. This analysis evaluated the current water-year streamflow (or 01 April SWE) response (e.g., positive or negative shifts in means) to the previous year (or season) of the oceanic / atmospheric (PDO, ENSO) phase (cold or warm). The testing performed here was for both the individual and coupled oceanic / atmospheric indices with streamflow (or SWE).

The parametric two-sample t-test (Maidment, 1993) was performed on the response of streamflow means to changes in oceanic / atmospheric phase, including coupling. The t-test compares two independent data sets and determines if one data set has significantly larger values than the other data set (Maidment, 1993). The t-test assumes that the two data sets are normal with equal variances (Maidment, 1993). A detailed discussion of this method is provided in Maidment (1993) and is also provided in most statistical textbooks. Recent applications of the t-test include Harshburger et al. (2002) evaluation of Idaho spring streamflow response to Pacific Ocean influences, Rogers and Coleman (2003) evaluation of continental U.S. streamflow response to Pacific and Atlantic Ocean influences, Tootle and Piechota (2006) evaluation of continental U.S. streamflow response to atmospheric – oceanic influences and Hunter et al. (2006) evaluation of atmospheric – oceanic influences and western U.S. snowfall. An example is hereby provided.

The PDO is an atmospheric – oceanic phenomena associated with persistent, bimodal climate patterns in the northern Pacific Ocean (poleward of 20^o north) that oscillate with a characteristic period on the order of 50 years (a particular warm or cold phase of the PDO will typically persist for about 25 years) (Mantua, et al., 1997, Mantua and Hare, 2002). Below is an example of applying the Two-sample t-test to determine if a significance difference in water year streamflow occurs for the Salt River when comparing PDO Cold and PDO Warm years. The streamflow response to PDO Cold years is assumed to be 1951 to 1977 while PDO Warm years is assumed to be 1978 to 2002.

Step 1 is to segregate the data (PDO Cold and PDO Warm years):

Year	**Q (AF)**	**Year**	**Q (AF)**
1951	196014	1978	1100369
1952	1178437	1979	1901620
1953	242529	1980	1361963
1954	346840	1981	315227
1955	217069	1982	601737
1956	203248	1983	1330350
1957	350370	1984	765836
1958	725958	1985	1399247

1959	239193	1986	582914
1960	850360	1987	755821
1961	170796	1988	642460
1962	726923	1989	257612
1963	383660	1990	205848
1964	275349	1991	1052467
1965	737240	1992	882214
1966	1059405	1993	2287736
1967	278607	1994	387564
1968	917749	1995	1063326
1969	522342	1996	171399
1970	300688	1997	396191
1971	202650	1998	669428
1972	425693	1999	254655
1973	1877065	2000	138097
1974	199212	2001	449523
1975	609882	2002	148872
1976	337731		
1977	193842		

Step 2 is to compute the mean (PDO Cold years $\bar{x}$ = 509957, PDO Warm years $\bar{y}$ = 764899) and standard deviation (PDO Cold years s_x = 399123, PDO Warm years s_y = 562976) of each data set. The spooled degrees of freedom (*df*) = 27 PDO Cold years + 25 PDO Warm years – 2 = 50.

Step 3 is to compute the test statistic, *t*.

$$t = \frac{\bar{x} - \bar{y}}{\sqrt{\frac{s^2{}_x}{n} + \frac{s^2{}_y}{m}}}$$

t = -1.89 which corresponds to a significance level of 90% (Fisher and Yates, 1938).

Task 3 – *Probabilistic Forecasting of Droughts* (0%). The Weibull method and the Compound Renewal Method (Loaiciga, 2005) will be utilized to determine drought frequency / duration of streams in the Upper Green River basin.

Task 4 - *Improvement of Streamflow Reconstructions for the Green River Basin with New Tree-ring Collections* (90%).

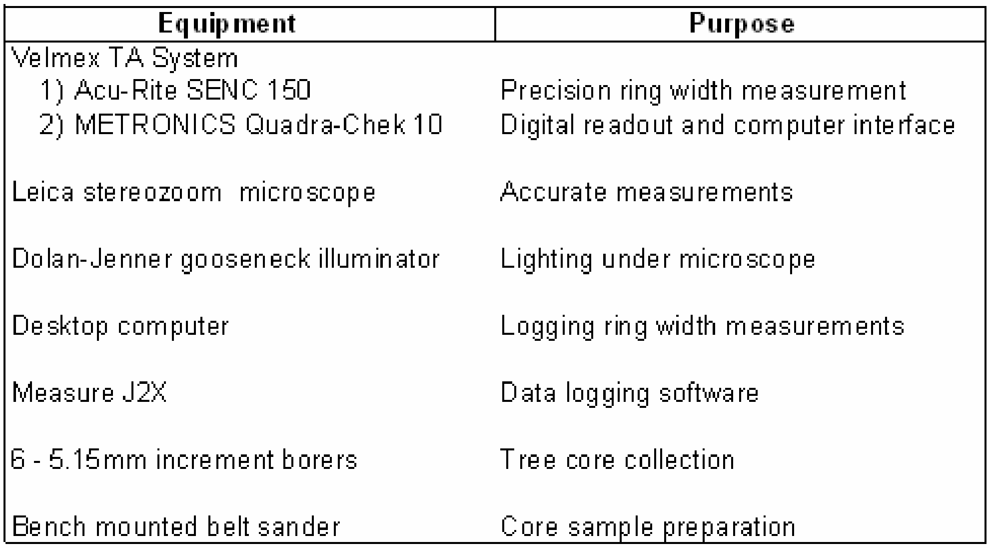
Training and Equipment.

Tree-ring research was initiated in March, 2006. Prior to field work, students were trained on the methods of dendrohydrology. In May, a group from the University of Wyoming attended a dendrochronology workshop in Boulder, CO put on by Connie Woodhouse (NOAA Paleoclimatology Pogram) and Jeff Lukas (Institute of Arctic and Alpine Research). The workshop was designed to teach procedures of field collection and to give a brief overview of site selection, lab setup, lab analysis, and basic reconstruction techniques.

Following the workshop, Jeff Lukas provided instruction on the setup of a new tree-ring lab at the University of Wyoming and the equipment that is required to conduct field sampling. The new lab is necessary since other tree-ring analysis equipment on campus is older and the equipment needs to be located in an area that is accessible to students. The new lab (see figure and table below) was completed in the fall of 2006 and will provide the necessary tools for streamflow reconstructions.

Civil Engineering tree-ring lab.

Major equipment used in field and laboratory work.



Equipment	Purpose
Velmex TA System	
1) Acu-Rite SENC 150	Precision ring width measurement
2) METRONICS Quadra-Chek 10	Digital readout and computer interface
Leica stereozoom microscope	Accurate measurements
Dolan-Jenner gooseneck illuminator	Lighting under microscope
Desktop computer	Logging ring width measurements
Measure J2X	Data logging software
6 - 5.15mm increment borers	Tree core collection
Bench mounted belt sander	Core sample preparation

Site Selection and Sampling

Dr. Steve Gray assisted students with the identification of appropriate sites around the Green River Basin and Wind River Mountains. A prospective site has one of two moisture sensitive species of tree. The two most prevalent species of moisture sensitive trees in northwestern Wyoming are Douglas Fir and Limber Pine. It is preferred for the trees in a site to be growing on a south facing slope in rocky soil that will not hold moisture for a long period after a precipitation event. When a promising site was located, spot samples were taken from trees and the cores were used to determine the approximate age of the trees by roughly counting visible rings (see figure below).

Spot sampling a site to determine approximate age of trees before sampling the full site.

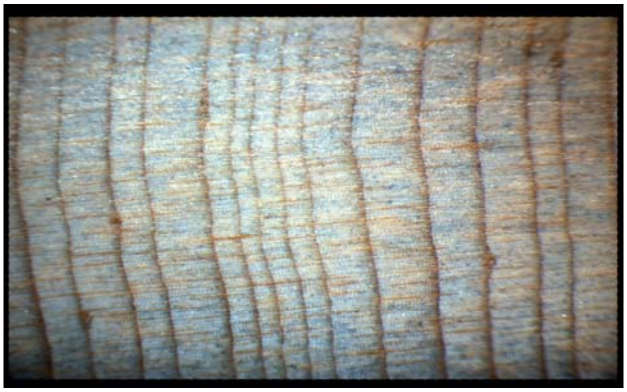
In August 2006, ten sites around the Wind River Mountains were sampled. Douglas Fir were much easier to sample, work with in the lab, and often show a stronger moisture signal. However, it is necessary to sample Limber Pine since they may be the only moisture sensitive species in the area and can provide more detail on regional climate. Three of the sites sampled were Douglas Fir and seven were Limber Pine. Thirty to Fifty trees were sampled per site with a minimum of two 5.15mm core samples (see figure below) per tree. All core samples taken were placed in paper straws and labeled for transportation back to the lab.

Sampling a nearly 1000 year old Limber Pine.

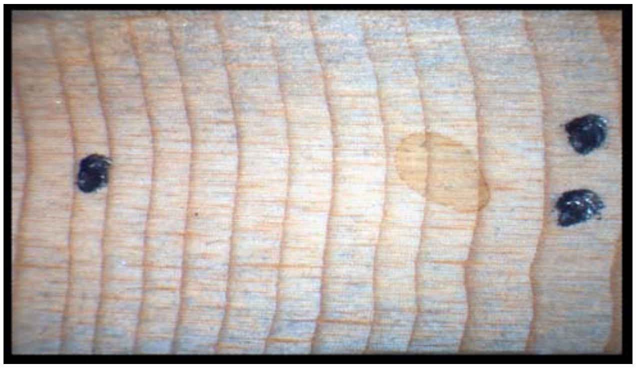
Lab Analysis

The first step (when returning to the lab) involves removing the core samples from straws and gluing the cores to a mounting block (wood trim with a quarter inch groove cut into the top). Once the core is mounted each core is given a flat surface using a bench mounted belt sander with 180 grit sand paper. The first round of sanding is completed by re-sanding the surface with 320 grit sandpaper to remove the grooves caused by the rough sandpaper used to create the flat surface. The second round of sanding is completed just before analysis under the microscope and consists of hand sanding using 400, 600, and if a sample has fine enough rings, 1200 grit sand paper.

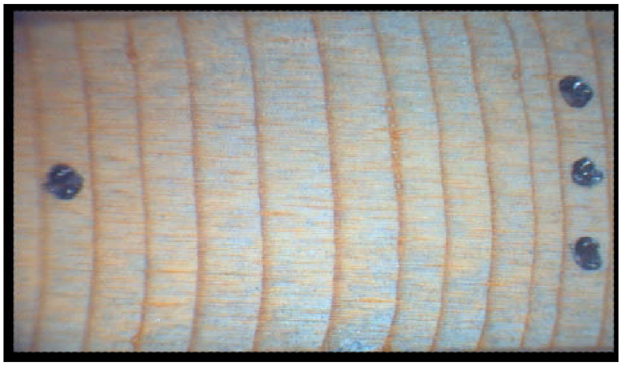
After sanding each sample, the rings are counted under the microscope and marks are place every decade, half century, and century (see figures below). This gives a reference to check when measuring the sample. The reference system also allows for accurate data collection of the rings and may identify false rings or areas where a missing ring may exist. Ring measurement is measured down to thousandths of a millimeter and logged by a computer connected to measurement slide. Once the samples are measured, they are dated using the last ring, the total number of rings, and patterns of ring growth within the sample. The logged and dated data is compiled and verified using two software programs COFECHA (Grissino-Mayer, 2001) and DPL (Dendro Program Library). Both programs are widely used in the creation of tree-ring chronologies.



Ring width variability.



Decade and half century markings.

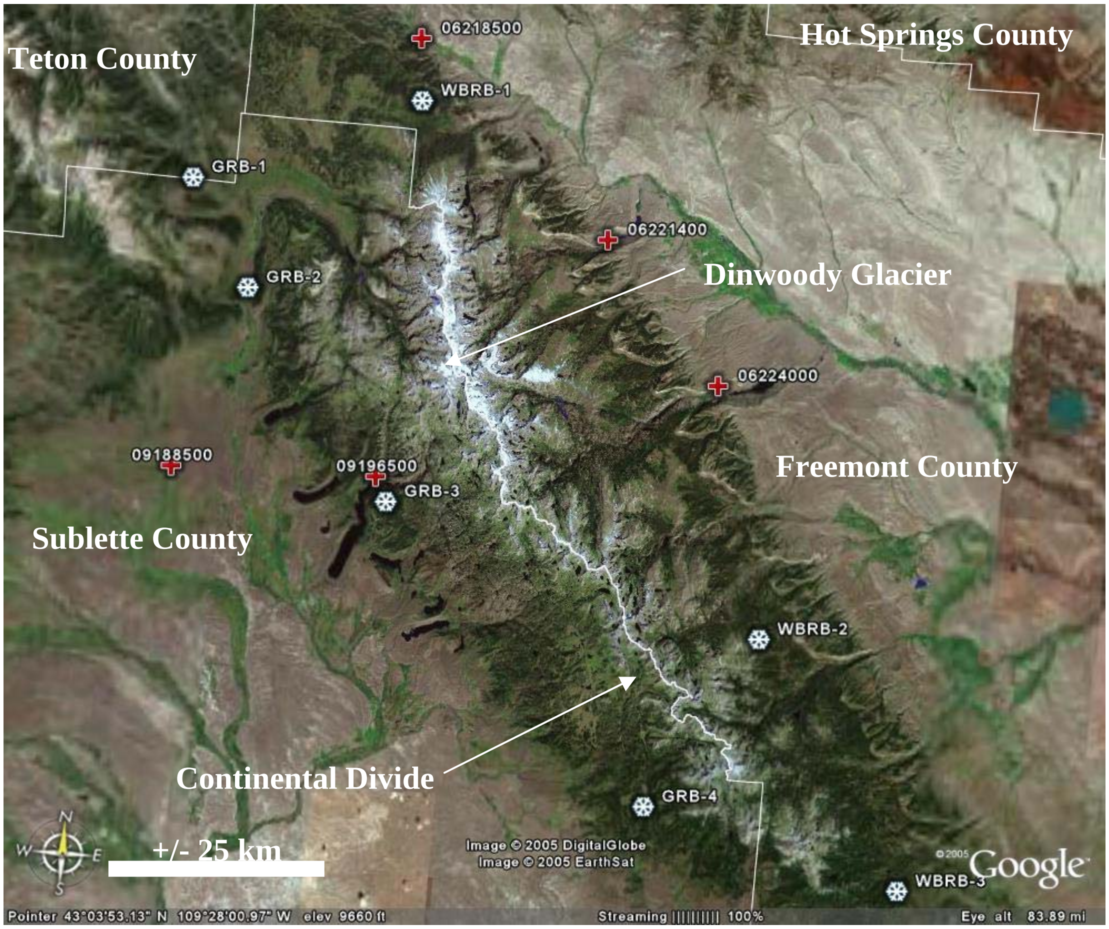


Decade and century markings.

Principal Findings and Significance

Task 1 – No report.

Task 2 – The 5-year filter analysis resulted in stations (both GRB and WBRB) having similar spatial and temporal relationships (see figure and table below).

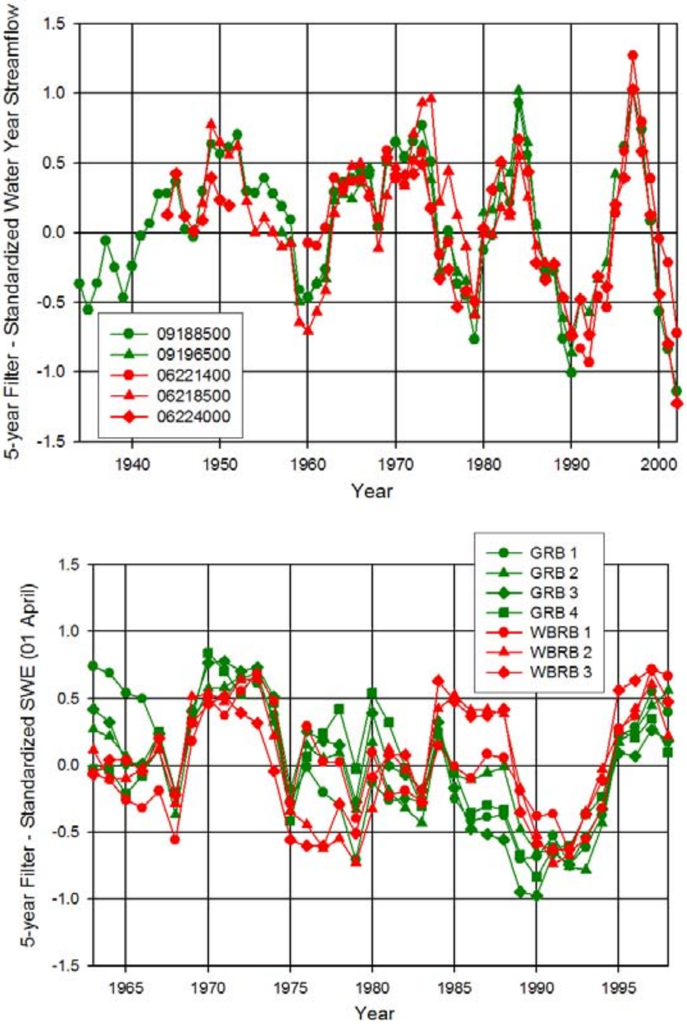


Locations of unimpaired USGS streamflow stations and NRCS SNOTEL stations in the Wind River Range.

List of unimpaired USGS streamflow stations and NRCS SNOTEL stations in the Wind River Range.

River Basin	Site Name	USGS or NRCS Site #	Latitude / Longitude
Green	Green River, Near Daniel, WY	09188500	43.02/-110.12
Green	Pine Creek Above Fremont Lake, WY	09196500	43.03/-109.77
Wind-Bighorn	Wind River Near Dubois, WY	06218500	43.58/-109.76
Wind-Bighorn	Dinwoody Creek, Near Burris, WY	06221400	43.35/-109.41
Wind-Bighorn	Bull Lake Creek Above Bull Lake, WY	06224000	43.18/-109.20
Green	Gros Ventre Summit, WY	506 (GRB-1)	43.39/-110.13
Green	Kendall R.S., WY	555 (GRB-2)	43.25/-110.02
Green	Elkhart Park G.S., WY	468 (GRB-3)	43.01/-109.76
Green	Big Sandy Opening, WY	342 (GRB-4)	42.65/-109.26
Wind-Bighorn	Little Warm, WY	585 (WBRB-1)	43.50/-109.75
Wind-Bighorn	Hobbs Park, WY	525 (WBRB-2)	42.87/-109.09
Wind-Bighorn	South Pass, WY	775 (WBRB-3)	42.57/-108.84

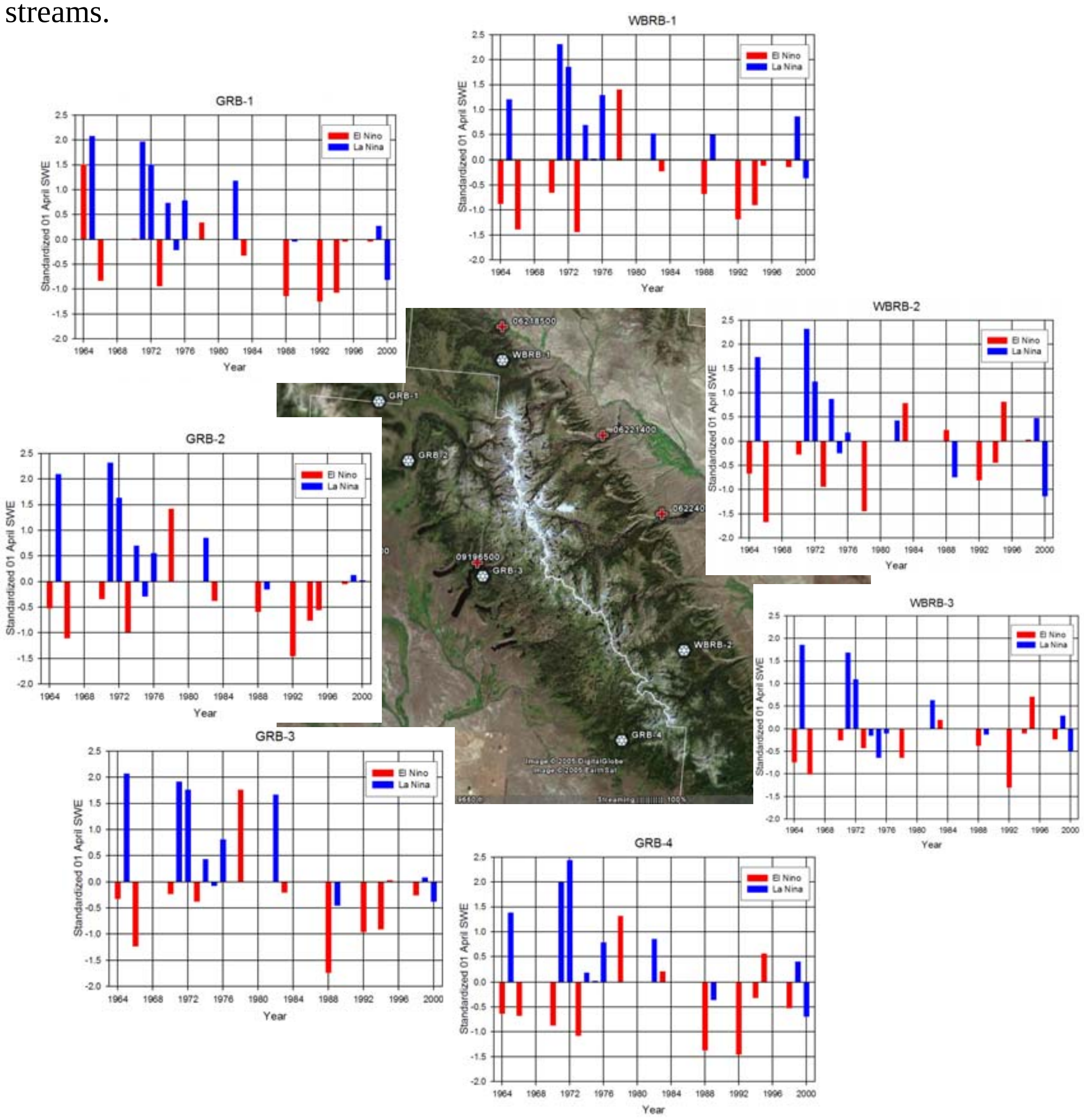
The period of record varied for the streamflow stations while a common period of record (1961 – 2000) was identified for the SNOTEL stations. Interestingly, for the 40 year period of record (1961-2000), the average 01 April SWE for the four GRB SNOTEL stations was 14.4 inches with a standard deviation of 4.7 inches. The average 01 April SWE for the three WBRB SNOTEL stations was 14.4 inches with a standard deviation of 4.2 inches. Therefore, snowfall amounts were virtually identical on each side of the continental divide.



5-year filter applied to Standardized Water-year Streamflow and 01 April SWE.

Initially, the phases (cold and warm) were evaluated for the PDO and ENSO (individually) such that significant (greater than 95%) differences in streamflow (and SWE) means were reported. Next, the coupled impacts of the interdecadal PDO phases on La Niña (and El Niño) on streamflow (and SWE) means were evaluated.

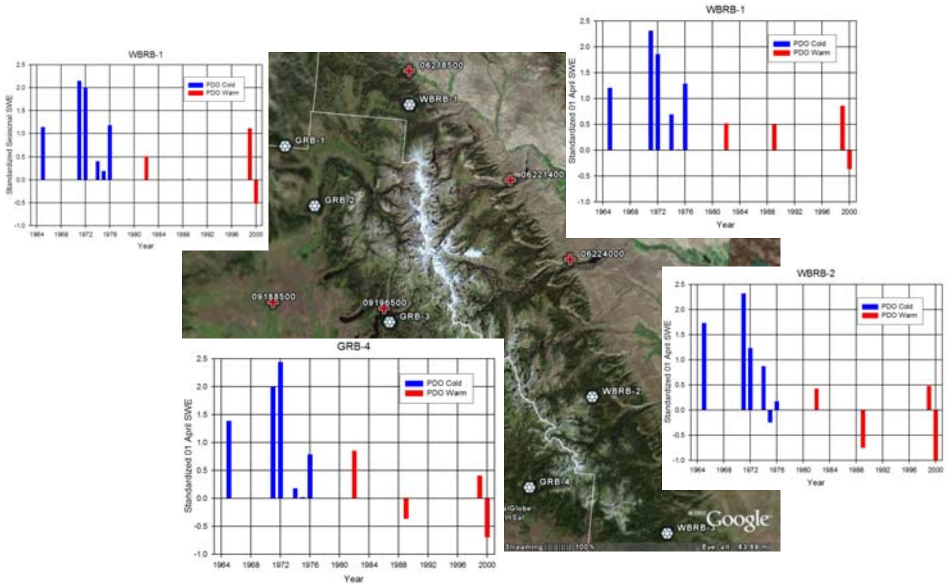
The PDO signal (at 95% significance) was not detected in either streamflow or SWE. However, a significant ENSO signal was detected in three of five streamflow stations and all seven SWE stations. Figure 4 presents standardized 01 April SWE for La Niña and El Niño years. For all the SWE stations, the average standardized 01 April SWE after a previous summer season La Niña (El Niño) was +0.69 (-0.43). Neutral previous year summers resulted in average standardized 01 April SWE of -0.12. Therefore, a previous year summer La Niña (El Niño) results in increased (decreased) snowfall. Interestingly, the two streamflow stations (Dinwoody Creek – 06221400 and Bull Lake Creek – 06224000) that failed to show an ENSO signal appear to have high contributions of glacial meltwater. This may explain why the ENSO signal was not identified in these streams.



Standardized 01 April SWE for La Niña (blue) and El Niño (red) years.

Finally, an evaluation of the PDO's influence on ENSO was performed. For example, given the occurrence of a La Niña (or El Niño), how does the phase (cold or warm) of the PDO enhance (or dampen) the influence of La Niña (or El Niño) on streamflow (or SWE). The testing of PDO Cold – El Niño and PDO Warm – El Niño and, the testing of PDO Cold – La Niña and PDO Warm – La Niña for the streamflow stations resulted in no stations having a statistically significant difference in water-year streamflow.

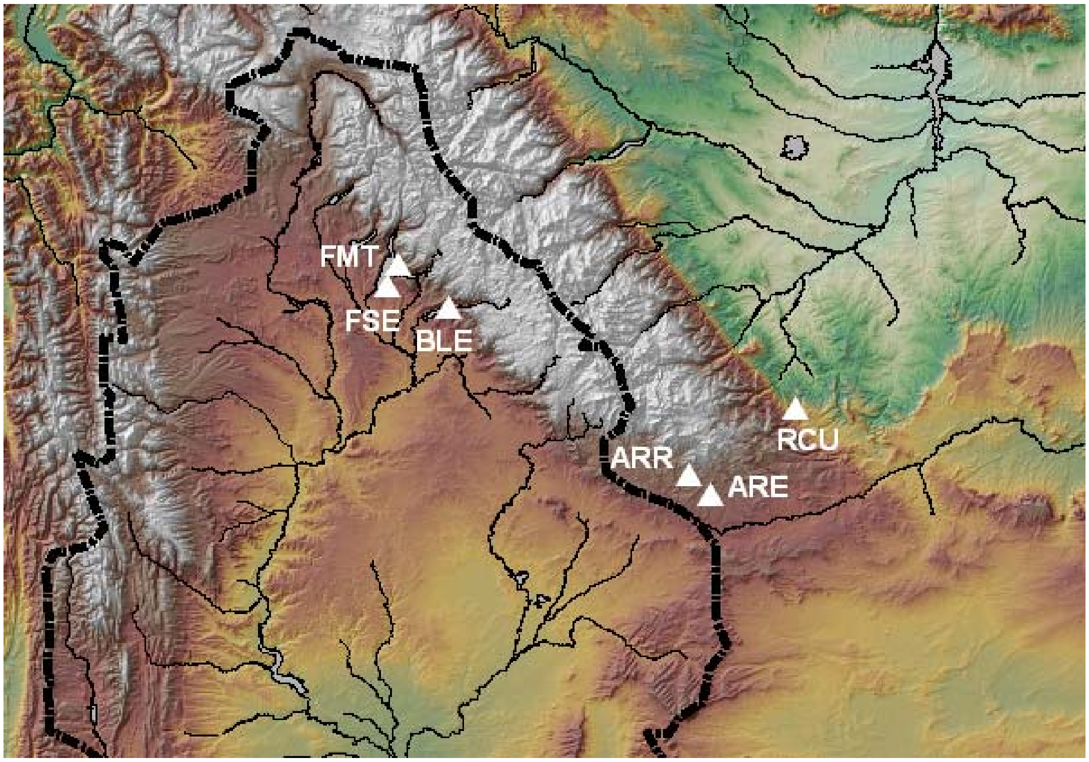
The testing of PDO Cold – El Niño and PDO Warm – El Niño for the SWE stations resulted in no stations having a statistically significant (greater than 90%) difference in 01 April SWE. However, when testing PDO Cold – La Niña and PDO Warm – La Niña, three of the seven SWE stations were identified as having statistically significant (greater than 90%) differences in means (Figure 5). For all seven stations, the average standardized 01 April SWE, given a previous summer season La Niña during a PDO Cold phase, was +1.07 while the average standardized 01 April SWE, given a previous summer season La Niña during a PDO Warm phase, was +0.12. Given that La Niña (i.e., ENSO cold phase) results in increased SWE, the PDO Cold phase enhances La Niña in this region. This is consistent with the findings of Harshburger et al. (2002) that ENSO (El Niño or La Niña) is strongest during the similar PDO (warm or cold) phase.



Standardized 01 April SWE for PDO Cold (blue) and PDO Warm (red) for La Niña years.

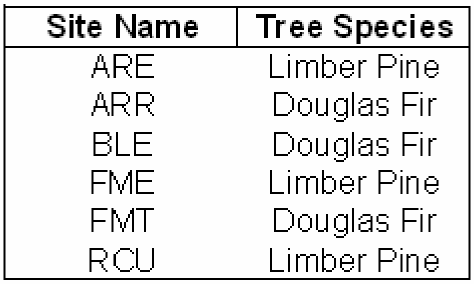
Task 3 – No report.

Task 4 – The ten sample sites collected in August were narrowed down to useable samples after the first round of sanding. Two of the sites were immediately eliminated due to their spatial location with respect to sites that had longer record and cleaner samples. One site had samples with rot pockets (in the same time period) that limited the number of usable cores such that it would require re-sampling. Two Limber Pine sites with good sample size were combined into one large site due to their close spatial proximity. After reducing the number of sites, this resulted in three Douglas Fir sites and three Limber Pine sites (see figure and table below).



6 sites sampled that are being analyzed in lab.

Site name and species.



Site Name	Tree Species
ARE	Limber Pine
ARR	Douglas Fir
BLE	Douglas Fir
FME	Limber Pine
FMT	Douglas Fir
RCU	Limber Pine

Presentations

Tootle, G.A., T. Hunter and T.C. Piechota, 2006. Pacific Oceanic / Atmospheric Variability and the Wind River Range. Presentation at ASCE World Water & Environmental Resources Congress 2006, May 21-25, 2006, Omaha, NE.

Hunter, T. and G.A. Tootle, 2006. Oceanic-Atmospheric Variability and Western Snowfall. American Geophysical Union (AGU) Hydrology Days, March 20-22, 2006, Fort Collins, Colorado.

Cheesbrough, K., Watson, T. and G.A. Tootle, 2006. Pacific Oceanic / Atmospheric Variability and the Wind River Range. American Geophysical Union (AGU) Hydrology Days, March 20-22, 2006, Fort Collins, Colorado.

Barnett, F.A. Climate History of the Upper Green River Basin. University of Wyoming Stook Forum, November 2006, Laramie, Wyoming.

Barnett, F.A. Upper Green River Basin Drought Analysis. November 2006, USGS/WRP Annual Meeting, Cheyenne, Wyoming.

Student Support Information

The USGS / WRP research grant is currently supporting three graduate students: Anthony Barnett, Kyle Cheesbrough and Tom Watson. Tom is scheduled to graduate (Master's in Civil Engineering) in Summer 2007 while Anthony and Kyle are scheduled to graduate (Master's in Civil Engineering) in Fall 2007.

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Precipitation Measurement and Growth Mechanisms in Orographic Wyoming Snowstorms

Basic Information

Title:	Precipitation Measurement and Growth Mechanisms in Orographic Wyoming Snowstorms
Project Number:	2006WY33B
Start Date:	3/1/2006
End Date:	2/28/2009
Funding Source:	104B
Congressional District:	1
Research Category:	Climate and Hydrologic Processes
Focus Category:	Water Quantity, Climatological Processes, Hydrology
Descriptors:	None
Principal Investigators:	Jefferson Snider, Bart Geerts

Publication

Abstract

Much of Wyoming's water supply originates as winter snow, mainly over the state's numerous mountain ranges. Snowrate and snow accumulation measurements are complicated by strong winds. A consequence is that springtime runoff estimates have limited accuracy and this uncertainty impacts our ability to assess the efficacy of water management practices. This work, sponsored by WWDC and the USGS has two related objectives: (a) to advance techniques for measuring regional snowrates based on a newly developed hotplate snowrate sensor and operational weather radar data; and (b) to conduct airborne investigations with a view toward advancing understanding of atmospheric processes leading to snow generated in clouds forming over the Wyoming high country. Such research is fundamental to snow measurement and to its augmentation by artificial means (i.e., cloud seeding).

The first objective was addressed using data acquired at a surface site 25 km northwest of Cheyenne, WY; data was collected in winter orographic snowstorms between January and March 2006. The study recognizes the advantages of using radar to monitor region-wide snowfall amounts, but also recognizes the need for robust parameterizations which relate snowrate (S) to what a radar measures (backscattered microwave energy or Z). This work focused on the development of a Z-to-S parameterization for the National Weather Service radar operated in Cheyenne, WY. Since temperature can influence both Z and S, a surface temperature-dependent, and a cloud temperature-dependent, Z-S parameterization were developed.

The airborne studies were performed using the University of Wyoming King Air equipped with a millimeter-wavelength radar, the Wyoming Cloud Radar (WCR; acronyms are defined in the Appendix). The WCR was used to measure snow above and below the aircraft as well as the associated air motion fields. Funding from WWDC/USGS supported seven additional flight hours, supplementing an allotment of 23 flight hours procured with support from NASA. We acquired data by conducting flight transects across the Laramie Range and Snowy Range; the data set is now being used to investigate how cloud depth, horizontal and vertical wind speed, thermal stability and properties of the aerosol ingested by winter orographic storms influence snow formation. The surface and the airborne investigations, plus the ongoing data analyses, are being conducted in close coordination with the State of Wyoming Weather Modification Program.

To date, one MS student has graduated with support from the WWDC/USGS project (Jonathon Wolfe); a second MS student is currently supported (Bujidmaa Borkhuu). In addition, two related awards, from NASA and DEPSECoR, are being used to support two students who are conducting analyses of the WWDC/USGS data set as part of their MS thesis research.

Year- 1 Progress Report -

We conducted both airborne- and ground-based studies in Year-1. The former benefited from work previously planned by the University of Wyoming Department of Atmospheric Science through a grant from NASA (acronyms are defined in the Appendix). In total we flew 13 missions in January and February 2006; six of these were conducted on the same day as missions flown by the Weather Modification Inc. (WMI) aircraft. Flight operations are summarized in Table 1. In addition, surface measurements of snowrate were made in coordination with the Cheyenne, WY National Weather Service Weather Surveillance Radar (WSR) between January and March 2006.

In year-1 our overarching objective was to conduct airborne and surface measurements with a view toward our broader objectives of studying how cloud depth, horizontal and vertical wind speed, atmospheric stability and properties of the aerosol ingested by winter orographic storms influence snow formation. A further objective was to derive a reflectivity-to-snowrate relationship using data collected near Cheyenne. As we discuss below, the Year-1 objectives were met. We now look forward to continuing support from WWDC/USGS, so we can continue our data analysis, to assist graduate students as they complete their theses, and to report findings in peer-reviewed journals.

Table 1 - Wyoming King Air Flights Sponsored by NASA and WWDD/USGS

Date, YYYYMMDD	HHMMSS to HHMMSS, UTC	Duration, hr	WMI Flight?
20060210	1919-2131	2.3	
20060209	2152-0019	2.6	Yes
20060205	1321-1600	3.1	
20060202	1854-2207	3.3	Yes
20060131	1310-1630	3.4	Yes
20060127	2358-0302	3.2	Yes
20060127	2133-2300	1.5	
20060126	1902-2215	3.4	Yes
20060124	2025-2123	1.1	
20060118	1957-2258	3.1	Yes
20060113	2109-2214	1.2	
20060110	2224-2328	1.1	
20060110	2108-2244	0.7	

Year-1 Findings –

Measurements made with the Wyoming King Air and its Wyoming Cloud Radar (WCR) during January and February 2006 provide us with unprecedented views of the structure of winter orographic clouds, the motion fields embedded within them and the interplay among the spatial distribution of the snow, velocities and the underlying terrain. Four specific avenues of investigation were pursued:

1) A variety of cloud and precipitation structures were observed in orographic clouds that formed over the Snowy and Sierra Madre ranges. An important finding obtained from the WCR vertical-plane measurements of reflectivity and Doppler velocity is that turbulent motions are evident through a substantial depth of the cloud section. These motions are evident even when the atmospheric stability is relatively large. Vertical velocities associated with this turbulence, and with the cumulus convection that was observed on a few of the study days, are typically larger than the orographically-forced ascent rate. We believe that the turbulent and convective motion fields are key to understanding snow particle growth and snowfall rates. Quantification of the importance the turbulent and convective motions, compared to the orographically-driven ascent, is an area of investigation for Professor Bart Geerts and MS student Heather McIntyre. Heather is supported by our NASA grant.

2) Laboratory characterizations of a hotplate snowrate sensor (YES Inc.), and field studies of the reflectivity (Z) versus snowrate (S) relationship for the Cheyenne Wyoming WSR, were conducted by Jon Wolfe. Jon's analyses of these data reveal a temperature dependence in the Z/S relationship. This result is compelling for two reasons: 1) It squares well with previous results showing that crystal concentration in Wyoming wintertime orographic clouds are related inversely to temperature, and 2) the derived Z/S relationship should improve the accuracy of snowrate estimates derived from WSR measurements of radar reflectivity. Jon was supported by the WWDC/USGS grant during 2006 and graduated with a MS in Atmospheric Science in May 2007. A new MS-level student, Bujidmaa Borkhuu, is now supported by our WWDC/USGS grant.

3) Aerosol particle measurements made upwind and downwind of the Snowy Range show evidence for particle removal during transport through the orographic clouds probed by the King Air. How this removal is related to the cloud macroscopic structure, e.g. cloud depth, and to snowrate, is a MS research topic for Binod Pokharel. Binod is supported by an award from DEPSCoR.

4) Two proposals have been submitted and awarded in the past year; neither could have been written without the King Air and WCR data collected over the Snowy Range in Jan-Feb 2006, in a project partly funded by our Year 1 WWDC-USGS grant. Firstly, our colleague Gabor Vali investigated the production of ice crystals originating from processes other than nucleation. His analysis of the King Air and WCR data reveals that ice crystals can enter orographic clouds from a source at the terrain/atmosphere interface. This crystal source process is not yet characterized but testable hypotheses were articulated in a proposal submitted by Vali to NSF. Vali's NSF proposal was successful and his initiative is expected to have important implications for cloud seeding efficacy in Wyoming.

Secondly, co-PI Bart Geerts submitted a proposal to the WWDC/USGS to use the WCR and King Air particle probes to describe the signature of cloud seeding in orographic snowstorms in Wyoming. That research is directly relevant to the 5-year Cloud Seeding Pilot Program awarded to NCAR/RAL, and involves close collaboration with the PI of that program, Dan Breed at NCAR/RAL. Our understanding of the efficacy of cloud seeding has been plagued by lack of direct observations of physical processes; rather, the approach has been statistical, and the causality of the relationship between seeding and snowfall has remained veiled in a black box. The purpose of this successful proposal is to observe changes in ice crystal shape within volumes of the atmosphere treated with ice nucleating AgI aerosol. The AgI plumes will be tracked by the WCR as long as possible, possibly until they reach the ground. If successful, this initiative would be the most physically explicit test of cloud seeding efficacy ever conducted.

Plans for Year-2 -

In our WWDC/USGS proposal we proposed two activities for Year-2: 1) Intercomparison of two hotplate sensors at the NCAR Marshall Field Site in Colorado, and 2) Intercomparison of hotplate versus SNOTEL snowrate measurements made in the Snowy Range. We now propose to change the first of these activities; however, the approach now proposed will not depart from our Year-2 objective of improving the accuracy of surface snowrate measurements.

During Year-2 we plan to focus our efforts on measurements of snowrate made at the Glacier Lakes Ecosystem Experimental Site (GLEES) located near the summit of the Snowy Range. Specifically, we plan to make intercomparisons of five nearly collocated snowrate systems: 1) a hotplate located above the forest canopy on the 30 m AMERIFLUX tower, 2) a SNOTEL system (site number 367), 3) a NADP gauge system (site number WY95), 4) a NADP sample bucket system, and 5) a Vaisala VRG precipitation gauge. All of these sensors will be positioned within a circle of radius 2 km.

The activities now proposed have developed from our growing confidence in measurements of snowrate made with our hotplate sensor, particularly our understanding of its performance in strong wind conditions. Another factor influencing the modification of our research is an analysis of snowrate measurements made at the GLEES site. The latter is shown in Figure 1 where we present data from the two NADP precipitation measurement systems at GLEES (gauge and sample bucket, see previous paragraph), stratified by time of year. Week-averaged precipitation measurements from the months June/July/August and December/January/February are shown in the left- and right-hand panels, respectively. It is evident that precipitation measured with the gauge and sample bucket are in reasonable agreement during the summer months. However, during the winter months very different values are reported by these two measurement systems. We attribute the wintertime disparity to blowing snow captured by the gauge, but not by the sample bucket, and to loss of collected precipitation (stored in the sample bucket) that occurs during windy precipitation events. Given the degree of the mismatch during winter, about a factor of seven, and that GLEES is located in a region targeted by the cloud seeding planned for winter 2006/2007 and future years, we feel justified in focusing our Year-2 research at the GLEES site. As discussed above, we will not conduct the proposed Marshall Site intercomparisons in 2006/2007 (Year-2).

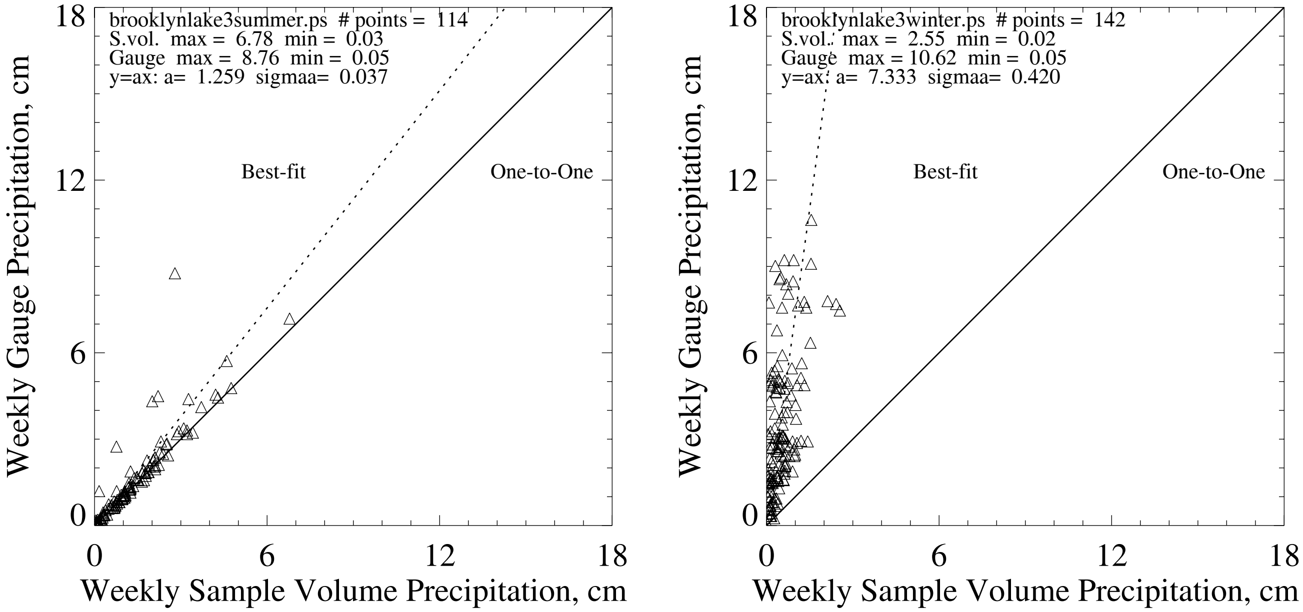

Figure 1 – Weekly precipitation from two sensors operated at the Brooklyn Lake National Atmospheric Deposition Program site. The two NADP sensors are referred to as “gauge” and “sample volume.” Twenty years of data is analyzed (1985 to 2005). Weekly samples collected in June/July/August (left-hand panel) and into December/January/February (right-hand panel) were selected for this presentation. Precipitation was detected in 114 weeks out of 261 (June/July/August; left-hand panel) and in 142 weeks out of 261 (December/January/February; right-hand panel).

Specific Objective for Year-2-

1) From the above- and below-canopy measurements of precipitation rate we intend to investigate if snow falling into the forest canopy can be distinguished from blowing snow generated within the canopy. Preliminary results from our Year-2 field season, including temperature, wind speed, precipitation rate, relative humidity, barometric pressure and wind direction, can be viewed in the directory http://www-das.uwyo.edu/~jsnider/snow/preliminary/. These data were acquired using the hotplate and a Vaisala WXT510 surface observing station operated on the AMERIFLUX tower at GLEES.

2) We are also plan to analyze two-way comparisons of the five snowrate measurements planned for GLEES in 2006/2007. One strategy will be to stratify these comparisons by wind speed and time since the beginning of a snow event.

3) From these analyses we should be able to advise on the relative merits of the five snowrate measurement systems, to specify conditions that they can be relied on, and to also specify conditions when the data quality is suspect.

4) We will also continue our analysis of data collected by the WCR, King Air and WSR during 2006. The first step in this direction is the successful completion of Wolfe's MS thesis work in May 2007. On going is the thesis work of three more MS students who are either supported by the WWDC/USGS award (Borkhuu) or are analyzing data collected with support from WWDC/USGS (Pokharel and McIntire). Theses and peer-reviewed publications are forthcoming.

Student Involvement

Wolfe, J.P., Radar-estimated Upslope Snowfall Rates in Southeastern Wyoming, MS thesis, Dept. of Atmospheric Science, University of Wyoming, May 2007

Casey, G., A comparison of observed vs. predicted snowfall amounts over the mountains of Southeastern Wyoming in Jan-Feb 2006. An undergraduate research term paper, Dept. of Atmospheric Science, University of Wyoming, 2006

Presentations with Abstracts

Pokharel, B., J.R.Snider and D.Leon, Freshly-formed Aerosol Particles: Connections to Precipitation, accepted for presentation at the 17th International Conference Nucleation and Atmospheric Aerosols, Galway, Ireland, August, 2007

Geerts, B., Detailed vertical structure of orographic precipitation development in cold clouds. Oral presentation at the 16th Conf. on Mountain Meteorology, American Meteorological Society, Santa Fe, NM, 28 Aug-1 Sept. 2006

Presentations without Abstracts

Snider,J.R., Precipitation Measurement and Growth Mechanisms in Orographic Wyoming Snowstorms, Wyoming Weather Modification Technical Advisory Board, January 18, 2007

Snider,J.R. (for B.Geerts), Detecting the Signature of Cloud Seeding with the Wyoming Cloud Radar, Wyoming Weather Modification Technical Advisory Board, January 18, 2007

McIntyre, H., NASA06 observations of orographic precipitation types over the Snowy Range under different stability and flow regimes, UW-NCAR RAL workshop in Boulder, CO, September 6, 2006

Snider, J.R., Aerosol scavenging in winter orographic clouds, presented at the Wyoming-NCAR RAL workshop in Boulder, CO, September 6, 2006

Wolfe, J., Temperature dependence of the Z-S relationship for upslope snowfall, presented at the Wyoming-NCAR RAL workshop in Boulder, CO, September 6, 2006

Appendix –

AgI – Silver Iodide
DEPSCoR – Defense Experimental Program to Stimulate Competitive Research
NADP – National Atmospheric Deposition Program (http://nadp.sws.uiuc.edu/)
NASA – National Aeronautic and Space Administration
NCAR – National Center for Atmospheric Research (http://www.ncar.ucar.edu/)
NSF – National Science Foundation
SNOTEL – SNOpack TELemetry (http://www.wcc.nrcs.usda.gov/snotel/)
NWS – National Weather Service (http://www.crh.noaa.gov/cys/)
WCR – Wyoming Cloud Radar (http://www-das.uwyo.edu/wcr/)
WMI – Weather Modification, Inc. (http://www.weathermod.com/index.php)
WSR – Weather Surveillance Radar (http://weather.noaa.gov/radar/radinfo/radinfo.html)

Information Transfer Program

During FY06, information dissemination efforts included reports and presentations by the Director to State and Federal entities, Conservation Districts, and the Private sector. The Director reports annually to the Wyoming Water Development Commission and to the Select Water Committee (of the Wyoming Legislature). Presentations were given throughout the state concerning the research program and project results. The Director serves as the University of Wyoming Advisor to the Wyoming Water Development Commission and attends their monthly meetings. This provides a means of coordinating between University researchers and Agency personnel. The Director serves as an advisor to the Wyoming Water Association.

Publications and other information dissemination efforts were reported by the PIs of the projects funded under this program. The project PIs report to the Institute's Advisory Committee on an annual basis. Presentations discussing final results are made by PIs of projects which were completed during the year at the Committee's July meeting. Presentations discussing interim results are made by PIs of continuing projects at the Committee's winter meeting. All PIs are encouraged to publish in peer reviewed journals as well as participate in state-wide water related meetings and conferences. Publications are listed elsewhere in this report.

Director information dissemination activities include the following:

Director Service: UW Advisor to the Wyoming Water Development Commission. Advisor to the Wyoming Water Association. Member of the Governors Drought Task Force. UW representative to Wyoming Water Forum. Member of the Wyoming Weather Modification Advisory Team. Wyoming State Engineer Office, work with office to provide stream gage recorders. Cheyenne, WY., February, 2006. Co-Sponsor Produced Waters Workshop. Fort Collins, CO., April 4-6, 2006. Sponsored UW Research Team for Dendro-Cronology Workshop at NCAR. Boulder, CO., May 16-17, 2006. Sponsored trip to Wind River Indian Reservation for UW Magazine on Wind River Glaciers and Isotope Water Sampling for article. Crow Heart, WY., May 24, 2006. Sponsored State of Wyoming Agency Priority Meeting. Cheyenne, WY., June 29, 2006. UW Water Research Program Meeting. WRP Priority and Selection Committee to select research priorities. Cheyenne, WY., July 25, 2006. Co-Sponsor, Water Drought and Climate Workshop, University of Wyoming. Laramie, WY., October 5, 2006. Wyoming Water Development Commission, Wyoming Framework Water Plan Meeting. Cheyenne, WY., October 18, 2006.

Director Presentations: Office of Water Programs and Wyoming Water Research Program. Wyoming Water Development Commission. Cheyenne, WY., January 12, 2006. Office of Water Programs and Wyoming Water Research Program. Legislative-Select Water Committee. Cheyenne, WY., January 13, 2006. Legislative Meeting Presentation on the UW Office of Water Programs, to the Wyoming Water Association. Cheyenne, WY., February 14, 2006. Water Research Program, Thorbardin Ranch Group. Laramie, WY., January 26, 2006. Office of Water Programs. Presentation on program and Glacier Project Wyoming Weather Modification Advisory Group. Casper, WY., April 12, 2006. Office of Water Programs and Wyoming Water Research Program, Presentation on programs to University of Wyoming Faculty Water Meeting. Laramie, WY., April 26, 2006. Office of Water Programs, Wyoming Water Research Program and Wind River Glaciers. Presentation to the Laramie Rotary Club. Laramie, WY., June 22, 2006. Office of Water Programs and Wyoming Water Research Program, Wyoming Water Association-Board summer meeting and tour. Lander, WY., July 13-14, 2006. Wyoming Water

Development Commission/Select Water Committee Meetings and Tour. Cody, WY., August 23-25, 2006. Office of Water Programs and Wyoming Water Research Program, Presentation on Office of Water Programs and the Water Research Program to Department of Applied & Computational Math, University of Wyoming. Laramie, WY., September 15, 2006. Wyoming Water Development Commission/Select Water Committee Meetings. Presentation on Office of Water Programs, Wyoming Water Research Program and Wind River Glaciers Study. Casper, WY., November 8-10, 2006.

Information Exchange Meetings Attended by Director: Wyoming Water Association Board Meeting, Cheyenne, WY., January 14, 2006. Wyoming Water Development Commission Meetings. Cheyenne, WY., February 9-10, 2006. Legislative Review-Advisor to the Wyoming Water Association. Cheyenne, WY., February 22, 2006. NIWR meetings. Washington, DC., February 27 - March 1, 2006. Wyoming Water Development Commission Meeting. Cheyenne, WY., May 12, 2006. Wyoming Water Development Commission Workshop. Cheyenne, WY., June 7, 2006. Wyoming Water Development Commission/Select Water Committee Meetings. Cheyenne, WY., June 8, 2006. Wyoming Water Association-Board summer meeting and tour. Lander, WY., July 13-14, 2006. Wyoming Water Development Commission/Select Water Committee Meetings and Tour. Cody, WY., August 23-25, 2006. Wyoming Water Development Commission, Wyoming Framework Water Plan Meeting. Cheyenne, WY., October 18, 2006. Wyoming Water Association, Annual Meetings. Casper, WY., November 1-3, 2006.

Information dissemination activities reported by research project PIs include the following:

Project: Land Use Impacts on Nitrogen Fixation in Jackson Hole Streams. Lisa Kunza (Neerhof), a Ph.D. student, presented a talk in June 2006 at the national meeting of the North American Benthological Society entitled High Nitrogen Fixation in Wyoming Streams. She will present another talk entitled The Contribution of Nitrogen Fixation to Nitrogen Cycling in Ditch Creek, WY throughout the Summer Season at the national meeting of the North American Benthological Society in June 2007. Two manuscripts are currently in preparation. A third manuscript and Lisa's dissertation will be completed by 2008.

Project: Real-Time Monitoring of E. Coli Contamination in Wyoming Surface Waters. Two invited papers presented at the 2006 Cytometry Development Workshop, Asilomar, California: High-Throughput-Axial Imaging Flow Cytometry with LED illumination and Imaging Flow Cytometry. A presentation at a 2006 Select Water Committee Meeting of the Wyoming State Senate: Detection of Pathogenic Organisms in Wyoming Surface Water

Project: Innovative Technology Development to Maximize Beneficial Use of Produced Water from Coalbed Natural Gas Operations in the Powder River Basin,Wyoming. Disseminated information on project findings, progress of the project as well as information on the physical and chemical nature of zeolites to conference attendees, students, general public (via inquiries, website visits, etc.). Proceedings and Abstracts with Presentations: Johnston, C,R., S. Jin, G.F. Vance and G. Ganjegunte. 2006. Impacts of coalbed natural gas co-produced water on cropland irrigated soils in the Powder River Basin, Wyoming. To be presented at the 23nd National American Society of Mining and Reclamation Symposium/Billings Land reclamation Meetings, Billings, MT. In: R. Barnhisel (ed.) Reclamation: Supporting Future Generations, Lexington, KY. Vance, G.F., Ganjegunte, G.K., R.W. Gregory, and R.C. Surdam. 2006. Removal of sodium from saline-sodic coalbed natural gas waters using natural zeolites. To be presented at the 7th International Conference on the Occurrence, Properties and Utilization of Natural Zeolites, Socorro, NM. ICOPUNZ Abstracts. Vance, G.F. 2006. Innovative Technology Development to Maximize

Beneficial Use of Produced Water from Coalbed Natural Gas Operations in the PRB, WY. Wyoming Water Development Commission, Cheyenne, WY. Vance, G.F. 2006. Management of saline-sodic waters from coalbed natural gas production. Special Symposium Management and Use of Waters of Altered and Impaired Quality at the Soil Science Society of America Annual Meetings, Indianapolis, IN. Agronomy Abstracts CD-ROM 103-5. Vance, G.F., H.T. Zhao, M.A. Urynowicz, G.K. Ganjegunte and R.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. 8 pp.

Project: Predicting Drought in the Green River Basin. Presentations with Abstracts: Tootle, G.A., T. Hunter and T.C. Piechota, 2006. Pacific Oceanic / Atmospheric Variability and the Wind River Range. ASCE World Water & Environmental Resources Congress 2006, May 21-25, 2006, Omaha, NE. Hunter, T. and G.A. Tootle, 2006. Oceanic-Atmospheric Variability and Western Snowfall. American Geophysical Union (AGU) Hydrology Days, March 20-22, 2006, Fort Collins, Colorado. Cheesbrough, K., Watson, T. and G.A. Tootle, 2006. Pacific Oceanic / Atmospheric Variability and the Wind River Range. American Geophysical Union (AGU) Hydrology Days, March 20-22, 2006, Fort Collins, Colorado. Presentations without Abstracts: Barnett, F.A. Climate History of the Upper Green River Basin. University of Wyoming Stook Forum, November 2006, Laramie, Wyoming. Barnett, F.A. Upper Green River Basin Drought Analysis. November 2006, USGS/WRP Annual Meeting, Cheyenne, Wyoming. Conference Proceedings: Tootle, G.A., T. Hunter and T.C. Piechota, 2006. Pacific Oceanic / Atmospheric Variability and the Wind River Range. Proceedings of the ASCE World Water & Environmental Resources Congress 2006, May 21-25, 2006, Omaha, NE.

Project: Precipitation Measurement and Growth Mechanisms in Orographic Wyoming Snowstorms. Presentations with Abstracts: Pokharel, B., J.R.Snider and D.Leon, Freshly-formed Aerosol Particles: Connections to Precipitation, accepted for presentation at the 17th International Conference Nucleation and Atmospheric Aerosols, Galway, Ireland, August, 2007. Geerts, B., Detailed vertical structure of orographic precipitation development in cold clouds. Oral presentation at the 16th Conf. on Mountain Meteorology, American Meteorological Society, Santa Fe, NM, 28 Aug-1 Sept. 2006. Presentations without Abstracts: Snider,J.R., Precipitation Measurement and Growth Mechanisms in Orographic Wyoming Snowstorms, Wyoming Weather Modification Technical Advisory Board, January 18, 2007. Snider,J.R. (for B.Geerts), Detecting the Signature of Cloud Seeding with the Wyoming Cloud Radar, Wyoming Weather Modification Technical Advisory Board, January 18, 2007. McIntyre, H., NASA06 observations of orographic precipitation types over the Snowy Range under different stability and flow regimes, UW-NCAR RAL workshop in Boulder, CO, September 6, 2006. Snider, J.R., Aerosol scavenging in winter orographic clouds, presented at the Wyoming-NCAR RAL workshop in Boulder, CO, September 6, 2006. Wolfe, J., Temperature dependence of the Z-S relationship for upslope snowfall, presented at the Wyoming-NCAR RAL workshop in Boulder, CO, September 6, 2006

Previous Project: Geochemistry of CBM Retention Ponds Across the Powder River Basin, Wyoming. Jackson, R.E., and K.J. Reddy. 2006. Geochemical changes of coalbed natural gas produced water in the Powder River Basin: Salinity, sodicity, and trace metals. Basin Advisory Group Meetings, Wyoming Water Development Commission, New Castle, Wyoming. Reddy, K.J. and R.E. Jackson. 2007. (Invited) Coalbed natural gas produced water quality across the Powder River Basin, Wyoming: Beneficial Uses. Wyoming Water Law Conference, Cheyenne, Wyoming. M. Raisbeck, K.J. Reddy, M. Smith, R.E. Jackson. 2007. (Invited) Critical review of the scientific literature review relating to water quality for

Wyoming livestock and wildlife. Environmental Quality Council, Wyoming Department of Environmental Quality, Cheyenne, Wyoming. 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. Reddy, K.J. R. E. Jackson, C. L. Milligan. 2007. (Invited) Energy from Coalbed natural gas (CBNG). Energy and Environment, Research Experience for Undergraduates. Department of Chemistry, University of Wyoming, Laramie, Wyoming. Jackson, R.E., and K.J. Reddy. 2007. (Invited) 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.

Student Support

Student Support					
Category	**Section 104 Base Grant**	**Section 104 NCGP Award**	**NIWR-USGS Internship**	**Supplemental Awards**	**Total**
Undergraduate	6	0	0	0	6
Masters	7	0	0	0	7
Ph.D.	1	0	0	0	1
Post-Doc.	2	0	0	0	2
Total	16	0	0	0	16

Notable Awards and Achievements

Publications from Prior Projects

1. 2003WY10B ("Geochemistry of CBM Retention Ponds Across the Powder River Basin, Wyoming") - Articles in Refereed Scientific Journals - 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.
2. 2003WY10B ("Geochemistry of CBM Retention Ponds Across the Powder River Basin, Wyoming") - Conference Proceedings - Jackson, R.E., and K.J. Reddy. 2007. (Invited) Coalbed Natural Gas (CBNG) Produced Water: Geochemical Processes and Beneficial Uses in Semi-Arid Environments. In Proceedings of 9th International Conference on Biogeochemistry of Trace Elements, Beijing, China. 2pp. (in press)
3. 2002WY7B ("Drought prediction model development and dissemination in Wyoming") - Other Publications - Smith, Michael A., 2007. Recognizing and Responding to Drought on Rangelands. WYO Range Facts, University of Wyoming Cooperative Extension Service MP-111.09, April, 2pp.