South Dakota Water Research Institute
Annual Technical Report
FY 2005

Introduction

South Dakotas Water Resources Research Institutes program is administered through the College of Agricultural and Biological Sciences at South Dakota State University (SDSU). Dr. Van Kelley has been the Director since August 1, 2000. Dr. Kelley is also the head of the Agricultural and Biological Sciences Engineering Department. The annual base grant from the United States Geological Survey (USGS) and a legislative appropriation of $92,412 form the core of the SDWRRI budget. The core budget is supplemented by research grants from a variety of funding agencies as well as private organizations interested in specific water issues.

The mission of the South Dakota Water Resources Institute is to address the current and future water needs of people, agriculture, and industry through research, education, and service. This report is a summary of activities conducted during Fiscal Year 2005 to accomplish this important mission.

Research Program

Water is one of the most important resources in South Dakota. Together with the state’s largest industry, agriculture, it will play an important role in the economic future of the state. Enhancement of the agricultural industry and allied industries, the industrial base and, therefore, the economy of South Dakota all depend on compatible development of our water resources.

During 2005, the South Dakota Water Resources Institute (SD WRI) used its 104B Grant Program funds to conduct research of local, state, regional, and national importance addressing a variety of water problems in the state. The Advisory Committee reviews grant applications and recommends projects for funding that address research priorities, have a good chance of success, and increase our scientific knowledge. Manure management and its impact on water quality, drinking water quality, and conservation of irrigation water were emphasized in fiscal year 2005.

The subject of nutrient transport caused by runoff from manured fields has been an active research area since a literature review conducted in 2000 generated state-wide interest in transport of phosphorus from soils high in phosphorus. Information was needed to support regulations to protect the water quality of lakes and streams without placing an undue burden on livestock producers. Livestock production plays a major role in agriculture, the states number-one industry. Previous research explored the relationship between phosphorus concentration in soils and phosphorus concentrations in runoff at the plot scale using simulated rainfall. In FY2005 a project was funded to evaluate the relationship between soil phosphorus and phosphorus in runoff on a watershed scale.

Support was also provided to a project to determine the influence of manure placement on crop yields and the transport and fate of nutrients and antibiotics in manure. As the livestock industry grows and develops in South Dakota, manure management and its impact on water quality will continue to be a priority for research.

The continued availability of clean drinking water is also very important to the health of citizens of South Dakota and to future economic development. In FY2005 a study to determine the fate of disinfectants and disinfection by-products in water distribution systems was funded. South Dakota water systems use chloramine, free chlorine and chlorine dioxide as chemical disinfectants. They distribute water into systems of PVC and ductile iron pipes arranged in looped (municipal) and extensively branched (rural water) networks, containing storage tanks and booster disinfection systems. These system characteristics, along with water age and temperature, are primary factors affecting disinfectant residual decay and disinfection by-product (DBP) formation in these systems. While trihalomethanes (THMs) have been shown to increase with water age, haloacetic acids (HAAs) have been found to increase to a point in the distribution system, but then decrease, especially in areas of low disinfectant residual. Since water quality tends to have characteristics related to the hydrogeology of the water source, DBP formation in distribution systems tends to be region-specific. The objectives of this project are to more fully understand the behavior of chlorine and disinfection by-products in distribution systems in the upper Great Plains region, and develop correlations between the characteristics of distribution systems and chlorine decay and DBP production.

As the economy of South Dakota develops, increasing demands have been placed on water supplies. Irrigation is a major use of water in South Dakota and wise use of irrigation water is important if other water needs like ethanol production are to be met in the future. In FY2005, research was supported to develop methods to conserve irrigation water by using an automated irrigation management system. This technology is expected not only to conserve water but also reduce pumping costs, increase crop production, and minimize leaching of nitrates into groundwater supplies.

Some areas of South Dakota have elevated levels of arsenic, cadmium, and lead in drinking water supplies. Removal of these metals especially by small rural water system operators is a challenge. A research project to improve the efficiency of limestone-based materials for metal removal from drinking water was supported in FY2005. This is part of the effort to develop low-cost remediation technology that can be used to help small or rural water supply systems meet regulations.

Several projects from previous years were continued in 2005 to allow principal investigators to collect additional data and to meet the projects objectives. These included:

1. Evaluating Glomalin for possible use as an index in predicting the fate of organic contaminates introduced into the environment;

2. Invertebrate and aquatic plant studies of two mesotrophic lakes in South Dakota;

3. Coupled Carbon-Nitrogen Geochemistry under Reducing Conditions in a Prairie Pothole;

4. Using runoff models for estimating impacts of runoff in eastern South Dakota by validating a runoff model such as HEC and

5. Establishing the relationship between soil test phosphorus and runoff phosphorus for South Dakota soils.

The Influence of Manure Placement on Crop Yields and the Transport and Fate of Nutrient and Antibiotics

Basic Information

Title:	The Influence of Manure Placement on Crop Yields and the Transport and Fate of Nutrient and Antibiotics
Project Number:	2005SD29B
Start Date:	3/1/2005
End Date:	2/28/2006
Funding Source:	104B
Congressional District:	First
Research Category:	Water Quality
Focus Category:	Agriculture, Water Quality, None
Descriptors:	None
Principal Investigators:	Sharon Clay, C. Gregg Carlson, David E. Clay

Publication

State Water Resources Institute Program (SWRIP)
March 2005 to February 2006

Title: The influence of manure placement on crop yields and the transport and fate of nutrient and antibiotics.

Principal investigators. S.A.Clay, Professor, SDSU, Sharon.clay@sdstate.edu, 605-688-4757
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Statement of critical regional or State water problem.

While the fate of herbicides in the environment has been a major research topic for investigation, there is limited information on the fate of antibacterial chemicals in the environment and their effect on other environmental processes including pesticide persistence. This information is critical at the national scale, where total antibacterial chemical addition exceeds 8 million kg annually, and the regional level of the western Corn-Belt. The Big Sioux River and Big Sioux aquifer supply much of eastern South Dakota and small communities in western Minnesota with drinking water. Sioux Falls, the largest city in South Dakota, and other towns are highly dependent on this interconnected system. In the past 10 years, large poultry facilities have moved into Flandreau, SD, and more large dairies are located on the I-29 corridor, most upgradient of Sioux Falls. Swine production is concentrated in east central and south central regions of SD and cattle/calf production is high in the north central regions of SD (USDA SD Ag Statistics 2003). In addition, more dairies are expected to be constructed due to incentives from the state legislature and to supply milk to a large cheese plant in Lake Norden, SD. With the increase in animal production, manure and litter handling have dramatically increased and will continue to rise. In addition, biosolids from water treatment plants are being applied at agronomic rates to more agricultural land in the region. Towns and cities, especially the Sioux Falls area, are expanding and this practice will continue to increase as the population grows. The fate of antibacterial chemicals in manure is needed to assess the risk they pose to water supplies and human and environmental health.

There are several potential hazards that could occur with the application of antibacterial chemicals in manure. The first problem is the leaching and/or offsite movement of the antibacterial chemical to aquifers, lakes, rivers, streams, or terrestrial sites. Another problem could be that the antibacterial chemical interferes with the activity or controls microbes that degrade other pesticides in the environment, thereby lengthening the pesticides “normal” residence time. A longer residence time also may increase the potential for movement of the pesticide to sensitive, nontarget areas, including water or terrestrial sites.

Statement of results or benefits.

Wind and water soil erosion are processes that transports P, N, microorganisms, and antibiotics contained within manure from agricultural fields to surface waters and drainage networks. Erosion reduces land productivity and water quality. Erosion and runoff are likely to occur whenever there is excess water on a slope that cannot be absorbed or trapped in soil. Preliminary studies conducted at SDSU during 2002 showed that in eroded soils, developing a deep soil profile rich in organic matter increased yields from 50 bu/a (ranged from 25 to 75 bu/a) to 135 bu/a (ranged from 110 and 160 bu/a) and increased water infiltration 350%. Higher yields in deep tillage plots were attributed to reduced runoff, higher water infiltration rates, and more plant available water. These results suggest that by developing a deep soil structure high in organic matter, yields will be increased, the soil will absorb and hold more water, and erosion and runoff can be substantially reduced. After the deep soil profile is developed other conservation practices (no-till or strip tillage) can be adopted.

Management practices designed to solve one problem can cause other problems. For example, the deep injection of manure has the potential to increase nitrate leaching to groundwater. This problem can be minimized through site selection, proper management, and crop rotations. Site selection impacts nitrate leaching because soil parent material influences the transport and fate of P and nitrate. For example, in glacial till soils if nitrate escapes the rooting zone it's transport to ground water is slow due to: (i) low hydraulic conductivities (this is why we anticipate that deep manure injection will only be recommended for glacial till soils); (ii) organic N contained in the deep placed manure will be only slowly transformed to nitrate because nitrification requires oxygen; and (iii) due to low O2 concentrations, nitrate not taken up by the crop is likely to be denitrified.

In the fall of 2004, several replicated deep manure placement studies in 2 producer's fields were initiated. Funding for this project was provided by EPA-319. The goals of the EPA 319 funded project were to field test the impact of deep manure placement on P transport and yields in producer's fields. This project will expand the scope of this project to include the impact of precision deep manure placement on water budgets and the transport and fate of antibiotics, carbon, N, and organisms contained within the manure.

Nature, scope, and objectives of the project.

The goals of this 2-year project are to determine the impact of precision manure management/placement on the fate and transport of water, carbon, organisms, and antibiotics contained within manure to non-target areas. The hypothesis of this project is that by integrating soil and other landscape information manure can be managed such that adverse effects are minimized and profitability is increased. Fields selected for implementation have the following characteristics: (i) evidence of substantial erosion; (ii) glacial till parent materials; and (iii) have been identified as high risk by TMDL and water monitoring studies.

Objectives:

1. To determine the influence of manure placement and landscape position on tylosin and chlortetracycline transport and fate. (addition on current EPA-319 project)
2. To determine the influence of precision manure placement and landscape position on water budgets and nutrient (C, N, and P) cycling. (addition on current EPA-319 project)
3. To determine the influence of manure placement and landscape position on crop yields, runoff, and P transport (current EPA-319 project).
4. Train undergraduate and graduate students in water resources.
5. To share research findings with the general public and the scientific community.

This project requested funds to expand the scope of the current project and to conduct a more mechanistic assessment of the imposed treatments. Students (both graduate and undergraduate) assisted and conducted independent field, laboratory, simulation studies, and were trained in sampling techniques and laboratory procedures. Students had hands-on experience in water quality research and gain an understanding in land and resource stewardship when addressing environmental issues. At present, seminars, posters, and thesis projects are in preparation or have been given. Results have been presented in SDSU classes and at state and regional water quality conferences and meetings. These of the results of the first year study (2005). Continuing funding has been asked for from USGS 104 projects and were granted for 2006 to follow-up and finish the project.

Methods, procedures, and facilities.

Manure was collected from swine fed a daily diet containing no antibiotic, tylosin at 100 g kg-1, or 22 mg CTC kg-1 body weight. The feeding rates of antibiotic were labeled for nontherapeutic doses (i.e. growth promotion). The swine were held in isolation crates and manure collection started about 7 d after the diet had been imposed and continued through day 14.

A 240-mm diameter steel ring was pounded 75 mm into the ground and leveled. Major debris was cleared from the treatment area before pounding in the steel cylinder. One L of manure as a slurry (about 1100 g by weight) was surface applied into the ring 24-hr prior to the infiltration tests. The study was conducted on three different soils, Brandt silty clay loam at Aurora, and at a summit (Barnes series, fine-loamy, mixed Udic Haploborolls), and footslope (Buse series, fine-loamy, mixed, Udic Calciborolls) soil on an SDSU University Farm north of Brookings, SD. Each treatment was replicated three times.

Water infiltration was measured using a double ring infiltrometer (apparent saturated hydraulic conductivity) and a sprinkler infiltrometer. The sprinkler infiltrometer was also used to collect runoff. For the sprinkler infiltrometer the water-filled infiltrometer was placed on top of the steel cylinder. The initial height of the water column inside the infiltrometer was recorded. The infiltrometer used a marriotte tube to maintain constant application rate. The application rate was about 230 mm/hr, which is similar to a 50-year, 10-minute storm for eastern SD (Hershfield, 1961). Runoff samples were collected in five-minute intervals for about 45 min at each site.

Water was analyzed directly when possible for tylosin (as tylosin phosphate) or CTC using LC/MS techniques (Rabolle and Spliid, 2000). Nitrate, ammonia, and phosphate (PO4-) were also determined in each sample. Soil cores from the 0 to 60-cm depth were taken 1 d after water application from inside and outside the treatment area, divided into increments of 0- 5, 5-15, 15-30 and 30-60 cm depths and are being analyzed for chemicals of interest. Antibacterial chemicals in the manure matrix were extracted with a methanol/water mix, the methanol was evaporated off, and the aqueous phase was analyzed for tylosin or CTC with LC/MS. The limit of quantitation (LOQ) is about 0.01 mg/l for tylosin. The limit of detection was less than the LOQ; any tylosin concentration measured as less than 0.005 mg/l was considered to be zero.

Results (Year 1 - 2005)

The Cornell infiltrometer applies water by dripping from about 100 mm above the soil surface. This low elevation of water application means that water drops have little chance to gain kinetic energy due to gravity. Thus, drops strike the soil surface with relatively little energy and minimizes the formation of a crust that might seal the soil surface and reduce the infiltration rate (Mohammed and Kohl, 1987). However, the application of manure without incorporation resulted in a hydrophobic condition and sealed the soil surface in some cases. Runoff amounts averaged 3.9 L from the summit position at the Brookings location to 5.0 L at Aurora (Table 1).

The application rate of 1 L per ring was equivalent to 17500 kg of solid manure per ha. The slurry contained about 82 grams of solid fresh manure in each 1 liter of slurry applied. The total amount of CTC applied per ring averaged about 108 mg per ring whereas it was estimated that tylosin addition was < 1 mg.

Tylosin A and B were detected in the runoff samples. About 80% of the tylosin was in the tylosin B form. The average amount of tylosin collected in runoff was 0.5 mg. CTC recovery ranged from 0.9 mg to 4.2 mg and averaged about 2% of the total applied (Table 1). Slightly more CTC was found in runoff from the toeslope of the Brookings field than at the Aurora location. Due to high variability there was no difference between the amount recovered at the toeslope and summit at the same field although the trend was more CTC recovered from the toeslope than summit location. The runoff for each collection time was fairly consistent with about one-third of the runoff collected after one-third of the time (15 min). However, about 45% of the CTC was collected in this time, indicating that the first wetting timeframe was the most important for chemical runoff.

Nitrate amounts collected in runoff were extremely variable with total amounts that ranged from 0.3 to 40 mg. Ammonia, with a positive charge, had a much lower amount runoff with total amounts that ranged from 0.13 to 0.7 mg. Total phosphate amounts collected ranged from 0.2 to 1.2 mg.

These data indicate that all the compounds of interest from manure could be detected in runoff 24 hr after surface application of manure. Tylosin (in the form of tylosin B), CTC, nitrate and phosphate were present in amounts that were highly variable but at detectable levels. Analysis of soil is ongoing at the present time.

Table 1. Total water and chlortectetracycline (CTC) collected at three locations. The swine slurry was applied 24-hr previous to the runoff study. The amount of CTC collected in runoff averaged 2% of the amount applied.

Location	Total runoff	stdev	Total CTC	stdev
	(L)		(mg)	
Brookings summit	3.9	0.4	1.5	0.9
Brookings toeslope	4.7	0.4	4.2	0.9
Aurora	5.0	2.1	0.9	0.3

Temporal effects of manure on N and P concentration and water infiltration

Manure injection influenced both water infiltration rates and nutrient distributions in the soil. Manure placement generally did not influence unsaturated water infiltration but did increase ponded water infiltration. For example, seven months after the manure application ponded water infiltration was increased from 265 mm hr-1 in the conventional management to 334 mm hr-1 in the deep placement treatment of manure at the Flandreau and Volga sites.

Manure placement had a limited influence on P distribution in the soil. At Flandreau manure when compared with nutrients applied by fertilizers (conventional management) injection generally did not influence surface P levels and increased subsurface P levels. However at Volga manure placement did not influence P concentrations in the soil.

Manure placement influenced nitrate concentrations in the soil one year after application. At both sites, nitrate concentration in the deep injected manure treatments were higher in the 30-90 cm soil depths than shallow injected treatments. Nitrate concentration differences were not measured in the surface soil. These differences were attributed to deep manure injection slowing the mineralization and nitrification processes which in turn resulted more N being stored in the soil. Lower mineralization and nitrification rates can result from less O2 (deeper in the soil) and cooler temperatures. These findings suggest that deep injection of manure may also influence the degradation of any anti-bacterial compounds contained in the manure.

2006 - 2nd year study

The next study will compare runoff from surface applied manure treatments to incorporated treatments. While we expect to see no antibiotics removed in surface runoff, we hypothesize that both tylosin and CTC will be sorbed to the soil at the depth of incorporation. Tylosin will most likely be tightly sorbed or degraded to forms that are not detectable and not bioactive. Based on CTC sorption data from the literature, we suspect that CTC will not be leached during rainfall simulation but will remain in a detectable form at depth.

Related research.

Antibacterial chemicals are often fed to animals at subtherapeutic levels for growth promotion. Approximately 7.8 to 11 million kg of antibacterial chemicals are used annually in animal production; approximately 1.3 million kg are used annually in humans (Hileman, 2001).

Antibacterial chemicals that have been fed to animals can be excreted from the animal unchanged (Halling-Sorenson et al., 1998). Once in the environment, these chemicals can disrupt biogechemical cycles or become pollutants. Many public health officials are concerned that resistance can result from the wide-scale use of antibacterials in animals.

One common antibacterial chemical fed to swine is tylosin. The sorption of tylosin to soil (unpublished data) is similar to atrazine (Clay et al., 2005), making tylosin potentially mobile in the landscape.

The environmental fate of antibacterial chemicals such as tylosin, when applied in either solid or liquid animal wastes, is unknown. One potential pathway for transport of tylosin is in runoff water. If tylosin leaves agricultural fields in runoff, it may be transported to surface waters and adversely affect the aquatic ecosystem. Given the potential mobility of tylosin, the goal of this study was to determine if this commonly used antibacterial chemical can be transported in runoff water. Because runoff and infiltration rate are so closely related, the change of infiltration rate (if any) due to tylosin and manure (in which the tylosin is excreted) must also be understood.

Training.

Graduate students – 2 (M.S. Agronomy/Microbiology, 1 currently writing MS thesis)
Undergraduates – 2 (Students from Biology and Agronomy)

Literature Cited.

Clay S. A., Z. Liu, R. Thaler, and H. Kennouche. 2005. Tylosin sorption to silty clay loam soils, swine manure, and sand. J. Environ. Sci. Health *B* 40: 841-850.

Halling-Sorenson, B., S.N. Nielsen, P.F. Lanzky, F. Ingerslev, and H.C.H. Lutzhoft. 1998. Occurrence, fate and effects of pharmaceutical substances in the environment –a review. Chemosphere 36: 357-393.

Hileman, B. 2001. Furor over animal antibiotic use. In *Chemical Engineering News*, pp. 47-52.

USDA. 2003. South Dakota agricultural statistics, Bulletin No. 63. South Dakota Agricultural Association.

Water Conservation Using Automated Irrigation Water Management for Center Pivots

Basic Information

Title:	Water Conservation Using Automated Irrigation Water Management for Center Pivots
Project Number:	2005SD35B
Start Date:	3/1/2005
End Date:	2/28/2006
Funding Source:	104B
Congressional District:	First
Research Category:	Not Applicable
Focus Category:	Irrigation, Water Use, Agriculture
Descriptors:	None
Principal Investigators:	Hal D. Werner, Todd P. Trooien

Publication

1. Oswald, Jared, 2006, Automated Water Management for Center Pivot Irrigation Systems, MS Engineering Thesis, Agricultural and Biosystems Engineering Department, College of Engineering, South Dakota State University, Brookings, SD, 97 pages.
2. Oswald, Jared, Hal Werner, and Todd Trooien, 2005, Automated Water Management for Center Pivot Irrigation Systems, North Central Region ASABE Annual Conference, Brookings, SD.
3. Oswald, Jared, Hal Werner, and Todd Trooien, 2005, Automated Water Management for Center Pivot Irrigation Systems, 26th Annual International Irrigation Show and Conference, Phoenix, AZ.

State Water Resources Institute Program (SWRIP)
March 2005 to February 2006

Title: Water Conservation Using Automated Irrigation Water Management for Center Pivots

Investigators: Primary PI: Hal D. Werner
Other PIs: Todd P. Trooien

The goal of this project was to develop an automated irrigation management system for center pivot irrigation that will perform scientific irrigation scheduling. The expected outcome is that farmers will save water and energy, improve production and protect the environment. Specific objectives of this project were to:

- Develop the automated irrigation management system for center pivots using science-based irrigation scheduling principles.
- Test the system under field conditions with cooperators to determine the water conservation benefits.

Scientific irrigation scheduling uses on-site, real-time weather data together with crop and soil moisture data to conserve water, increase production, reduce pumping costs, and minimize potential nitrate leaching into the ground water caused by over irrigation.
The principle investigators and AgSense LLC, project collaborator, have developed the tools to monitor and control center pivot irrigation systems. This project combined the monitoring and control technology together with irrigation scheduling software into a center pivot automation (CPA) system.

A computer simulation model was developed to study the impact of various parameters on the operation and management of center pivots. Twenty years of weather data from seven upper Great Plains sites were used to test the model logic. The model considered three soil water holding capacities and three flow rates for a full-circle center pivot. Evapotranspiration was estimated daily during each of the twenty irrigation seasons using the Penman-Monteith method and the Jensen-Haise method. Crop coefficients for three crops (corn, soybeans and potatoes) were used along with crop-specific rooting depths and depletion allowances. Results of the model simulations indicate that center pivots can be automated to maximize water use while minimizing yield losses. Complete results of the model simulations are included in the attached report.

The CPA hardware collects data on center pivot status and position, flow rate, and weather. The management software calculates evapotranspiration (ET) and soil water balances to schedule irrigations and operate the center pivot with minimal operator intervention. The software logic controlling the automation was complex due to the operation of the center pivot machine, i.e. it may take several days for the machine to complete the irrigation cycle while, at the same time, soil moisture balances need to be maintained above prescribed levels at all parts of the field, thus forecasting ET was needed. The irrigated area may also have multiple crops that need to be managed differently. Each crop type has a distinct crop coefficient to use when calculating ET from the Penman-Monteith reference ET. Finally, the software records all of the data to maintain a record of operation including operating hours, water used, weather conditions, and soil moisture balances.

Field testing of the CPA system was anticipated during summer 2005. The computer model along with the scientific irrigation scheduling logic was transferred to the internet server at AgSense. Monitoring and control hardware was installed on a cooperator’s center pivot during late summer and the sensors delivered field data to the internet-based management software. However, timely rainfall precluded any further irrigation late in the season. Field testing was not completed but will be conducted during summer 2006.

Evaluating Phosphorus Loss on a Watershed Scale

Basic Information

Title:	Evaluating Phosphorus Loss on a Watershed Scale
Project Number:	2005SD36B
Start Date:	3/1/2005
End Date:	2/28/2006
Funding Source:	104B
Congressional District:	First
Research Category:	Not Applicable
Focus Category:	Groundwater, Water Quality, Solute Transport
Descriptors:	
Principal Investigators:	Frank V. Schindler, Ronald H. Gelderman, David R. German

Publication

1. German, D. 2006. Soil P and Runoff P Relationships: Implications for Lake and Watershed Management. 18th Annual Environmental and Ground Water Quality Conference Mar 14 16, 2006. Pierre SD.
2. Nonpoint Source 319(h) Progress report. 2006. South Dakota Department of Environment and Natural Resources.
3. Guidry, A.R., F.V. Schindler, D. R. German, R. H. Gelderman, and J.R. Gerwing. 2005. Evaluating Phosphorus Loss Potential of Dominant Agricultural Soils in South Dakota. Annual Meeting of Professional Soil Science Association of South Dakota. Huron, South Dakota. March 11, 2005.

Final Report

State Water Resources Institute Program (SWRIP)
March 2005 to February 2006

PART I.

Title: Evaluating Phosphorus Loss on a Watershed Scale

Investigators: Dr. Ronald H. Gelderman, Plant Science Department
Dr. Frank V. Schindler, Dept. of Chemistry and Biochemistry
Mr. David R. German, Water Resources Institute

The following report discusses the results of the research project titled ” Evaluating Phosphorus Loss on a Watershed Scale” during the funding period of March 2005 through February 2006. This project is part of an ongoing phosphorus (P) study to evaluate the P loss potential of South Dakota soils, and has been conducted in cooperation with a project funded, in part, by the South Dakota Department of Environment and Natural Resources (SD DENR). The information gathered from this project provides the SD DENR sound scientific data in which to base their regulations of manure and fertilizer P application to agricultural land.

This project has been funded, in part, by the SD DENR (319 funds) for two years. The USGS-SWRIP contributions were to provide funding not covered by the SD DENR 319 grant, which included costs of a Masters level graduate student, and the analyses and travel costs of a third watershed. By evaluating an additional watershed (for a total of three), we will be better able to statistically assess plot scale versus watershed scale P loss. The third watershed will also double the number of watershed treatment effects that can be analyzed starting in year three when the project begins its paired watershed evaluation phase. The specific objectives of this project were:

Objective 1: Evaluate the relationship that exists between total P loss from micro-plot field areas and total P loss on a watershed scale.

Objective 2: Provide field demonstrations and P loss education to livestock producers, extension educators, water quality experts, state regulators, and various environmental stakeholders.

Methodology and Accomplishments:

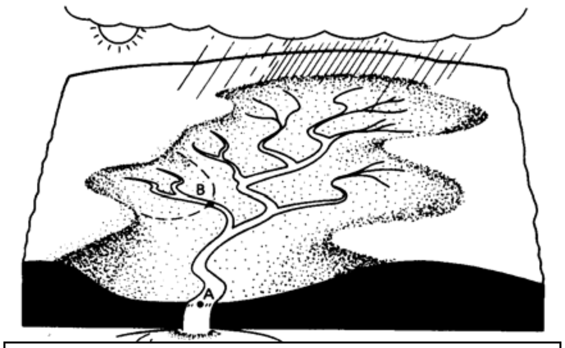

Figure 1. Delineation of a watershed boundary.

Identification and characterization of two areas on university owned land that possess the physical and drainage character of typical watersheds in South Dakota have commenced. Three watershed areas of approximately 5.5 acres in size were located on university owned land. Each watershed possesses the physical and drainage properties of typical South Dakota watershed as defined by NRCS specialists. Each watershed area contains a similar drainage area (Point A in Fig. 1), length, slope, and shape, and are established with similar land cover and use, surface roughness, and soil characteristics. The identification of watershed areas were accomplished through the help of

NRCS personnel, Water Resources Institute, and SDSU staff having watershed and natural resource expertise.

Watershed identification has been completed. Figure 2 shows the three watersheds as delineated using a Global Positioning Receiver (GPS) and a Handheld Geographical Information System. The red box in Fig. 2 represents the discharge area of the three watersheds and corresponds to point A of Fig. 1.

Figures 3 and 4 show the front view of the flumes for the three watershed areas, and a rear view of the flumes with the wing walls and established burms, respectively. Burms were plowed around the entire watershed area and between individual watershed areas to isolate surface flows.

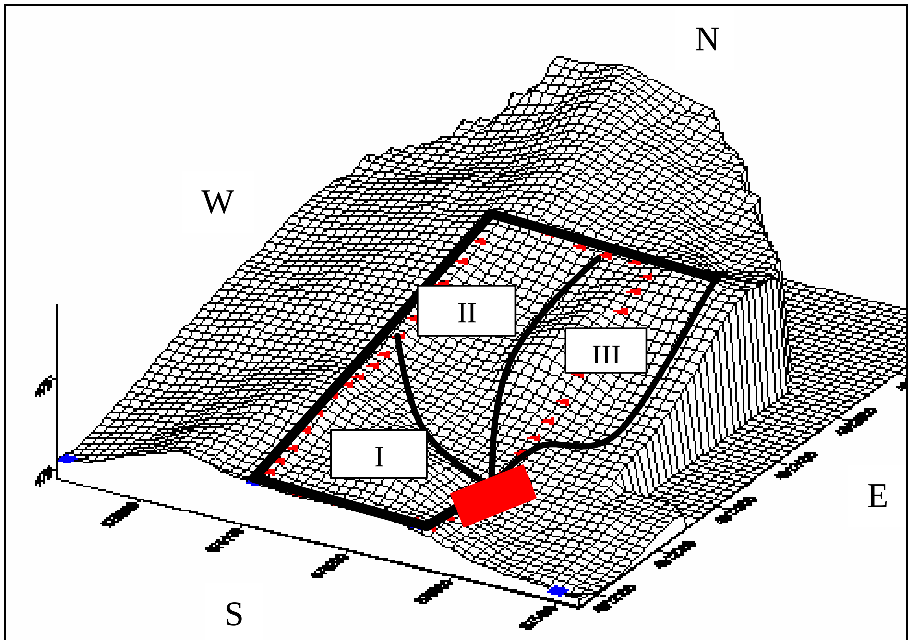

Figure 2. Delineated watershed areas showing discharge and sample location (i.e., red boxed area).

Figure 3. Front view of watershed flumes at the runoff discharge site.

Figure 4. Rear view of flumes showing wing walls and burms.

Samples will be collected from 0-2 and 0-6 inch depth intervals in April 2006 to establish initial characteristics. A composite soil sample at each depth increment will be obtained through an intensive grid sampling scheme. This will be used to establish the average soil P-value of the watershed. During the grid sampling, 10 discrete soil samples at each depth increment will be obtained and used to determine the degree of watershed heterogeneity, and also used for composite value comparisons. These samples will be analyzed by SDSU Soil and Plant Testing Laboratory and will include values for pH, Olsen extractable P, nitrate-N, potassium, organic matter, and soluble salts.

P loss in surface water runoff at the microplot scale will be evaluated. To facilitate microplot assessments and minimize plot and watershed disturbance, two additional rainfall simulators were obtained from the University of Illinois. Microplot establishment and rainfall simulator set-ups will occur immediately following spring 2006 planting, and all runoff evaluations will be conducted according to the protocol for the National Research Project for Simulated Rainfall-Surface Runoff Studies (NPRP, 2001).

Assessment of runoff volumes and total P loss from watershed areas began in March 2006. Two light rainfall events in March 2006 that generated flow at the flume discharge sites. Runoff samples and flow measurements were taken manually. Automatic flow recorders and samplers are going to be installed once a protective housing is build over the flumes. The automation will allow remote access to all flow data. The sampling automation includes and SIC dataloggers, solar power kit, telephone surge and lightening protection, and tipping bucket rain gage. NexSens iChart Software was purchased with USGS-SWRRI funds that will be used to interface all samples and flow meters. A computer/electronics expert from the Agricultural Engineering Dept, will help install and hard wire all electronic recording devices. All materials needed to build the protective housing over the flumes have been acquired, and building is scheduled to begin on April 11, 2006. Total runoff and P loss data collection will be completed by 10/06 and 8/07 for the first and second year of the overall project, respectively.

Objective two of the study was to provide field demonstrations and P loss education to livestock producers, extension educators, water quality experts, state regulators, and various environmental stakeholders. Educational brochures, fact sheets, and handouts are all types of media that will be used to explain the field results produced and will be distributed to the appropriate end users. Information in these educational media will explain the total runoff and potential P loading to water resources as related to field plot and watershed scales. Since little data has been collected at this point, no informational media has been devised. Also, information dissemination will coincide with the Soil Extension Specialist's annual manure training seminars, workshops, and fertility update meetings across South Dakota, which are typically conducted in the late fall and winter months

Preparation of P manure management project reports describing runoff volumes, water quality, and total P loss relationship between the micro-plot and watershed scales will be accomplished as part of the established milestones for the SD DENR. Semi-annual reports will continue in April 2006, 2007, and annual reports will be prepared in September 2006, & 2007. Ten copies of a final report will be submitted to the SD DENR by December 31, 2007. A manuscript will be prepared and submitted for publication in a refereed, scientific journal.

Principal Findings and Significance:

Olsen-P values for the gridded watershed areas ranged from 27 to 163 mg P kg^{-1}. The nitrate-N and potassium ranged from 2 to 83, 213 to 6581 mg kg^{-1}, respectively, and the pH and soluble salts ranged from 7.0 to 8.3 and from 0.3 to 2.0 mmoh cm^{-1}, respectively. Three watershed areas have been established, and flumes at each discharge area have been installed. Several runoff events have been recorded and the associated samples collected. Enough runoff data should amass by the early summer months to begin developing educational brochures. All milestones to date have been adequately met, and project remains on schedule.

All runoff collection and monitoring will be conducted electronically and data from the three watershed flumes will be accessed remotely. A student is currently setting up all electronics necessary to remotely access data generated from depth gauges, Isco autosamplers, discrete flow measurements from a Montedoro Whitney Model PVM-2A flowmeter, and a tipping bucket recording rain gauge. Runoff samples will be collected by use of automatic samplers at each watershed and analyzed for their total phosphorus and total dissolved phosphorus levels have remote access. Limited runoff data has been generated to date.

References:

National Phosphorus Research Project, 2001. National research project for simulated rainfall surface runoff studies protocol [Online]. Available at http://www.sera17.ext.vt.edu/Documents/National_P_protocol.pdf (verified March 17, 2006). North Caroline State University, Raleigh.

PART II:

Information Transfer Program: Information transfer will begin when sufficient runoff data has been collected and summarized. This is expected to begin during the summer months 2006. Mr. Jim Gerwing, South Dakota Soil Extension Specialist, will present the P runoff information generated from this project at his annual manure training and meetings/workshops. Meetings conducted include soil testing workshops for ag consultants and fertilizer dealers, manure application training workshops for people applying for state CAFO permits, and Certified Crop Advisor CEU workshops.

Field demonstrations within the watershed area may coincide with the SDSU Plant Science Agronomy tours (field days) scheduled in June 2006

Student Support: This project was originally budgeted to fund a graduate student. Because a qualified student was not found, and since no runoff was generated during the March 2005 to February 2006 time frame, the budget needed to be revised to insure efficient use of funds. We requested that the remaining funds from this project be used for student labor, professional salaries, and equipment. Dr. Van Kelley approved the revised budget. This project will be completed using EPA 319 funds.

Publications/presentations:

German, D. 2006. “Soil P and Runoff P Relationships: Implications for Lake and Watershed Management.” 18th Annual Environmental and Ground Water Quality Conference Mar 14 –16, 2006. Pierre SD.

Nonpoint Source 319(h) Progress report. 2006. South Dakota Department of Environment and Natural Resources.

Due to limited data to date, no manuscripts have been written.

Development of an Agglomeration Process to Increase the Efficiency of Limestone-Based Material to Remove Metals from Drinking Water

Basic Information

Title:	Development of an Agglomeration Process to Increase the Efficiency of Limestone-Based Material to Remove Metals from Drinking Water
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Descriptors:	None
Principal Investigators:	Arden D Davis, David J. Dixon

Publication

1. Webb, C.J., Davis, A.D., Dixon, D.J., Sorensen, J.L., and Dawadi, S., 2005, Limestone-based material for arsenic removal from drinking water (abstract): Geological Society of America, Abstract No. 95792.
2. Webb, C.J., Davis, A.D., Dixon, D.J., Sorensen, J.L., Berryman, G., and Williamson, T.E., Arsenic remediation of drinking water using limestone: characterization of limestone and dolomite: Submitted for publication, Environmental Science and Technology.
3. Webb, C.J., Campbell, C., Davis, A.D., Dawadi, S., Dixon, D.J., and Sorensen, J.L., 2006, Arsenic remediation of drinking water using limestone-based material: American Chemical Society, Division of Environmental Chemistry, Symposia Paper (paper submitted in 2005).
4. Davis, A.D., Webb, C.J., Dixon, D.J., Sorensen, J.L., and Dawadi, S., 2006, Arsenic removal from drinking water by limestone-based material: SME Paper TP-05-025, Society for Mining, Metallurgy, and Exploration, Littleton, Colorado, 4 p. [Paper submitted in 2005.]
5. Sorensen, J.L., Davis, A.D., Webb, C.J., and Dixon, D.J., 2005, Engineering design considerations for using limestone-based material to remove arsenic from drinking water: Presented at 17th Annual South Dakota Ground-Water Quality Conference, March, 2005, Pierre, South Dakota.

6. Webb, C.J., Davis, A.D., and Dawadi, S., 2005, Investigation of the formation of arsenic-containing minerals on a limestone base: Presented at Geological Society of America, Annual Meeting, Division of Geochemistry, Denver, Colorado.
7. Webb, C.J., and Davis, A.D., 2005, Arsenic remediation of drinking water using modified limestone: American Chemical Society, Anaheim, California.
8. Sorensen, J.L., Davis, A.D., Dixon, D.J., Webb, C.J., and Hocking, C.M., 2005, Arsenic removal demonstration project at Keystone, South Dakota: Presented at Western South Dakota Hydrology Conference, Rapid City, South Dakota, April, 2005.
9. Webb, C.J., Campbell, C., Davis, A.D., Dawadi, S., Dixon, D.J., and Sorensen, J.L., 2006, Arsenic remediation of drinking water using limestone-based material: American Chemical Society, Division of Environmental Chemistry, Symposium on Current Status of Research on Arsenic Remediation (submitted in 2005).

Annual Progress Report
State Water Resources Institute Program (SWRIP)
March 2005 to February 2006

Title: *Development of an Agglomeration Process to Increase the Efficiency of Limestone-Based Material to Remove Metals from Drinking Water*

Investigators: Arden D. Davis, Department of Geology and Geological Engineering; David J. Dixon, Department of Chemistry and Chemical Engineering; Jenifer L. Sorensen, Department of Geology and Geological Engineering, South Dakota School of Mines and Technology, Rapid City, South Dakota 57701

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ABSTRACT

Metals contamination of drinking water is a major problem facing many areas of the United States and the world. There is a need for an inexpensive remediation technology for the removal of metals in drinking water that can be applied to small rural water systems. The metals in drinking water considered for this research included arsenic, cadmium, and lead. All three are toxic in the environment and cause both acute and chronic toxicity in humans at elevated concentrations.

Limestone-based material has demonstrated the potential to reduce select metals in drinking water. Earlier research by the principal investigators of this grant and others has demonstrated arsenic removal of greater than 95 percent by limestone. The purpose of this study was to develop a technique to agglomerate powdered limestone into granules and characterize the ability of the manufactured granules to remove metals from solution using both batch and column adsorption experiments. Limestone is readily available and its use for metals removal is relatively inexpensive.

Three specific objectives were achieved during this research: 1) development and testing of a bench-scale agglomeration process for granulating limestone-based material as a filter media for metals adsorption, 2) development of a mixture formula for the limestone-based granules and a manufacturing protocol, and 3) investigation of the adsorption capacity of manufactured granules to remove metals from solution using batch and column experiments.

This project investigated the technique of agglomeration as a method to improve the metals removal efficiency of limestone-based material. Agglomeration is the process of taking fine materials and forming them into spherical granules. Magnesium carbonate powder was tested as an additive to enhance metals removal and was found to be effective. Portland cement was added as an insoluble binder to the limestone mix to bond the individual particles together and to strengthen the granules. Agglomeration increased material surface area as compared to crushed limestone without compromising water flow through rates.

Using batch and column experiments, it was shown that limestone-based granules effectively remove arsenic, cadmium, and lead from water. The adsorption of arsenic by limestone follows the Langmuir isotherm model and arsenic removal by limestone does not show pH dependence in the pH range from 4 to 10. Arsenic adsorption capacity of 1-2 mm sized manufactured granules at a starting concentration of 100 ppb arsenic was 5.4 ug arsenic per gram granules. In comparison, an equal mass of limestone powder has an arsenic capacity of 5.9 ug/gram and 1-2 mm crushed limestone chips have a capacity of 4.2 ug/gram. Column experiments showed that 1-2 mm limestone-based granules had an adsorption capacity about four times greater than crushed limestone chips of the same diameter. Arsenic adsorption capacity by the granules dropped from 22 to 9.8 ug/gram when naturally occurring groundwater with arsenic at 50 ppb was tested as the influent solution.

Limestone-based granules also showed a very high adsorption capacity for both cadmium and lead. At concentrations from 5 to 50 ppm, greater than 99 percent of the cadmium was removed by the granules in batch experiments. Lead was removed to below detection limits for all concentrations measured (up to 3 ppm).

INTRODUCTION

Metals contamination of drinking water is a major problem facing many areas of the United States and the world. The problem has been highlighted by the U.S. EPA's decision to mandate the reduction of the maximum contaminant level of arsenic from 50 to 10 parts per billion (ppb) in January 2006. There is a need for an inexpensive remediation technology for the removal of metals in drinking water that can be applied to small rural water systems. There are at least five benefits to the drinking water community by which an effective rural water treatment method can be evaluated: 1) reasonable removal efficiency as compared to material and operation costs, 2) broad geographic and water system applicability, 3) compatibility with other water treatment processes, 4) ease of technical use, and 5) low-cost disposal in ordinary landfills. This research focused on the removal of three inorganic metal contaminants from drinking water: arsenic (in the arsenate form), cadmium (Cd(II)), and lead ((Pb(II)).

Mineral surfaces such as carbonates, which include limestone, dolomite, and aragonite (another form of calcium carbonate), regulate the concentrations of dissolved trace metals in natural aqueous environments. Concentrations of trace metals are usually less than the solubilities of the pure solid phases which contain the metal ion. Processes such as adsorption and ion exchange are used to explain this discrepancy (Drever, 1982). The mineral calcite (calcium carbonate) is the main constituent of limestone and is the mineral surface considered when discussing metals adsorption mechanisms by limestone.

The purpose of this study was to develop a technique to agglomerate powdered limestone and additives into granules and characterize the ability of the manufactured granules to remove metals from solution using adsorption studies. These macroscopic adsorption studies were carried out in both stirred reactors (batch experiments) and flow-through column studies. Batch and column experiments place an aqueous solution of the metal of interest (the adsorbate) in contact with the adsorbent, in this case limestone-based media. Batch and column experiments monitor changes in solution chemistry and provide indirect information on the nature of the adsorption process. However, they do not provide enough information to characterize the identity and stoichiometry of the adsorbed species (Brown et al., 1995). To better understand the molecular-level interactions between the aqueous metals and the limestone-based material, microscopic studies of adsorption processes previously published by other researchers were reviewed and summarized.

Chemistry of Arsenic

Arsenic is a persistent, bio-accumulative toxin. The maximum contaminant level for arsenic, formerly 50 parts per billion (ppb), will be lowered to 10 ppb in 2006 because of links to cancer. In South Dakota alone, about 30 (8.6 percent) of the state's public water supply systems will not be in compliance with this mandate. Lowering of the standard will cause economic pressures for rural communities with high levels of arsenic in their drinking water supplies. Current removal technologies are expensive and their implementation will cause economic pressures for rural communities. The American Water Works Association has estimated the cost of decreasing the arsenic standard to 10 ppb in South Dakota at $8.25 million, and has estimated a cost of $550 million per year to meet the new standard nationally (Frost et al., 2002).

An example of the impact of elevated arsenic levels on a small rural drinking water system is the Grass Mountain area on the Rosebud Reservation of South Dakota. Elevated arsenic levels (greater than 80 ppb) were first observed in 1990 at two production wells, and local residents were supplied with an alternate water supply in 1993. A study by the United States Geological Survey (Carter et al., 1998) characterized the extent of arsenic in the study area and attributed the primary source of arsenic to arsenic-rich volcanic ash, which is abundant in the Arikaree Formation and White River Group.

Arsenic in the aquatic environment has very complex chemistry that is dependent on a number of factors, including pH, redox potential, ions present, and adsorbing surfaces. The speciation of arsenic governs its availability, accumulation, and toxicity to living organisms as well as its mobility in the environment. Inorganic arsenic has two oxidation states – arsenate (As(V)) and arsenite (As(III)). Arsenate forms four different oxyanions in water, depending on pH. At pH less than two, the dominant form is H_3AsO_4. For the pH range from 3 to 6, the dominant form is $H_2AsO_4^-$. For the pH range from 8 to 10 dominant form is $HAsO_4^{2-}$. For pH values greater than 12, arsenate takes the form AsO_4^{3-}. Arsenite forms three different oxyanions, depending on pH. For the pH range from 7 to 8, the dominant form is H_3AsO_3. For the pH range from 10 to 11, the dominant form is $H_2AsO_3^-$. For the pH range from 12 to 13, the dominant form is $HAsO_3^{2-}$. The arsenite form of arsenic is about sixty times more toxic than arsenate. Arsenate is the most stable form in oxidized environments, although significant amounts of arsenite can also exist in oxidizing environments (Seyler and Marin, 1989). Arsenate is the form of arsenic examined during this research.

The current technologies most commonly considered for reduction or removal of arsenic in drinking water are iron-based media, activated alumina, coagulation-filtration (Han et al., 2003; Karcher et al., 1999), and ion exchange (Clifford et al., 2003; Kim et al., 2003). These technologies have been shown to reduce arsenic to 2 to 5 ppb. They are more effective when arsenic is in the form of As(V). If As(III) is present, it must be oxidized to As(V), necessitating pretreatment and adding to the overall treatment cost. Coagulation-filtration is most efficient at mid-range pH, and the efficiency of the process depends on the type of coagulant, residence time, and dosage range (Scott et al., 1995).

Additionally, disposal of sludge is a cost factor. The efficiency of ion exchange treatment is affected by competition with sulfate, selenium, fluoride, nitrate, and total dissolved solids. Although this technology is considered appropriate for small ground water systems (less than 10,000 users), it is still too costly for water supply systems in rural areas. Other processes that are generally less effective than coagulation-filtration and ion exchange are reverse osmosis, activated alumina, and lime softening.

Chemistry of Cadmium and Lead

Cadmium is a persistent and bio-accumulative toxic metal. Long-term exposure has the potential to cause kidney, liver, bone, and blood damage. The maximum contaminant level for cadmium is set at 5 ppb because of health concerns and links to cancer. Cadmium in the environment is the result of both natural and anthropogenic sources. Anthropogenic sources are the greater environmental threat, and include industrial activities such as smelting operations, urban and industrial wastes, and fertilizer production and application. About one percent of cadmium ingestion is via drinking water; most cadmium intake is related to the food supply. On average, carbonate rocks contain about 48 ppb cadmium, while shales and igneous rocks contain about 200 ppb cadmium (Hem, 1978)

Cadmium in the aquatic environment has a +2 oxidation state. The solubility and partitioning of cadmium depends on a number of factors including pH, cations present, organic carbon present, and adsorbing surfaces (Davis et al., 1987; Filius et al., 1998; Fuller and Davis, 1987; Johnson, 1990; Seco et al., 1999). Cadmium carbonate ($CdCO_3$) has a very low solubility, with a solubility product (K_{SP}) equal to $10^{-13.7}$. Observations of $CdCO_3$ (otavite) and $CaCO_3$ solid solution formation on calcareous aquifer material show that cadmium is initially adsorbed during a fast adsorption stage and then forms a regular solid solution where Cd^{2+} is incorporated into calcium carbonate by direct growth of a $(Cd,Ca)CO_3$ solid solution (Davis et al., 1987).

Lead is a well-known toxin that causes delays in the physical and mental development of children that are exposed to elevated levels. Lead poisoning causes anemia, damage to the central nervous system, mental deterioration, and can impact all major body systems (Mohd et al., 1998). The action limit for lead is 15 ppb. Lead was historically widely used in plumbing, and older plumbing systems provide the opportunity for lead to dissolve into drinking water, especially by waters with low pH (Hem, 1978). Lead is used in a number of products including lead crystal and flint glass, paint pigment, lead-acid storage batteries (PbO_2), insecticide ($Pb_3(AsO_4)_2$), fireworks, ammunition, and building construction materials.

The oxidation state of lead in water is +2. Lead concentrations in natural oxidized waters are mainly controlled by the formation of lead carbonate (cerussite) (Hem, 1978). Lead carbonate ($PbCO_3$) has a very low solubility, with a solubility product (K_{SP}) equal to 7.4×10^{-14}.

REVIEW OF RELATED RESEARCH

Arsenic Literature Review

Limited research has been completed examining arsenic adsorption by calcite, lime, and limestone. Bothe and Brown (1999) studied the types of hydrated calcium arsenates that form when high concentrations of arsenic are exposed to lime for extended time periods. Non-hydrated forms of calcium arsenate were not observed. Their efforts focused on the immobilization of arsenic in lime as a treatment method for solutions containing high arsenic concentrations. Cheng et al. (1999) studied the incorporation of arsenite at the calcite surface using microscopic techniques. Their study showed that arsenite is incorporated at carbonate sites, although the exact speciation of the arsenite was not determined. Arsenite is incorporated into calcite in a dissolution/reprecipitation mechanism similar to that for the otavite/calcite solid solution, and surface dissolution or precipitation of one monolayer of calcite is estimated to take only several seconds. Other studies (House and Donaldson, 1986; Karaca et al., 2004) have examined the nature of phosphate adsorption on calcite and dolomite, which is significant in that the chemistry of phosphate is similar in nature to the chemistry of arsenate.

A study by Ongley et al., (2001) examined the used of untreated, crushed limestone as a simple method of arsenic water treatment in Mexico, and demonstrated the material's efficacy. Maeda et al. (1992) used iron(III) hydroxide-loaded coral limestone and Ohki et al. (1996) used aluminum-loaded coral limestone to adsorb arsenic. While both materials improved removal efficiency over untreated limestone, the iron-treated material performed significantly better. Reardon and Wang (2000) have tested limestone as a removal agent for fluoride from wastewaters, and Wang and Reardon (2001) used siderite (iron carbonate) in a column to elevate the low initial pH of an influent arsenic solution and simultaneously dissolve the siderite material. Iron-arsenic compounds precipitated out of solution onto the surface of the siderite, removing the arsenic in solution. Mackintosh et al. (2002), using a limestone contactor to harden soft water, observed that metals concentrations in the water stream were also removed by the limestone. This was an unintended benefit of the water softening treatment.

Surface complexation modeling of dissolved metals on oxide surfaces has been extensively studied and used as a template for predicting surface complexation reactions on carbonate surfaces. Although calcium and magnesium carbonates make up about 20 percent of sedimentary rocks and the reactivity of these minerals (adsorption, dissolution/precipitation) plays an important role at the solid/water interface in soils and aquifers, the exact surface species that control the reactivity of carbonates in water are not established (Pokrovsky et al., 2000). Van Cappellen et al. (1993) developed a surface complexation model for the reactivity of the carbonate-water interface. Surface complexation theory is based on the concept that water molecules and dissolved species (such as metals) form chemical bonds with ions at the mineral lattice surface. A series of reactions were proposed to model surface speciation in the metal ion – carbonate - water system. The metal ions considered were Ca^{2+}, Mn^{2+}, and Fe^{2+}, which combine with the carbonate ion (CO_3^{2-}) to form carbonate minerals. Surface complexation models for dolomite (calcium-magnesium carbonate) (Pokrovsky et al., 1999a) and magnesite (pure magnesium carbonate mineral) (Pokrovsky et al., 1999b) have also been developed.

Surface adsorption of arsenic to iron oxides, iron hydroxides, and clay minerals has been extensively characterized (Goldberg, 1986; Goldberg, 2002; Holm, 2002; Manning and Goldberg, 1996; Pierce and Moore, 1982). Other iron-based media that adsorb arsenic include granulated ferric hydroxide (Driehaus et al., 1998; Thirumavukkarasu et al., 2003), red mud (bauxsol) (Genc et al., 2003; Genc-Fuhrman et al., 2004), ferrihydrite (Jain and Loeppert, 2000; Raven et al., 1998), goethite (Fendorf et al., 1997; Gao and Mucci, 2001; Grossel et al., 1997), iron-treated activated carbon (Huang and Vane, 1989), and zero-valent iron (Farrell et al., 2001; Melitas et al., 2002; Nikolaidis et al., 2003). Aluminum-based adsorbents, such as aluminum hydroxides and oxides (Anderson et al., 1976; Arai et al., 2001, Ladeira et al., 2001), activated alumina (Lin and Wu, 2001), and aluminum-loaded zeolites (Xu et al., 1998) are also shown to remove arsenic. Other, more novel arsenic adsorbents include hardened Portland cement (Kundu et al., 2004), manganese-dioxide coated sand (Bajpai and Chaudhuri, 1999), titanium dioxide (Dutta et al., 2004), and ettringite (Myneni et al., 1997). Although extensive, the above list is only a portion of the literature available on the chemistry of arsenic adsorption.

Cadmium Literature Review

Zachara et al (1991) examined the uptake of cations, including cadmium, onto calcite, and proposed the following order of cation affinity for calcite: cadmium > zinc ≥ manganese > cobalt > nickel >> barium = strontium. Several possible mechanisms have been proposed for the uptake of cadmium by calcite: ionic radius and the solubility product of the cadmium carbonate solid (Zachara et al, 1991), ion exhange of Cd^{2+} for Ca^{2+} at the mineral-water interface (McBride, 1980; Davis et al., 1987), defect-enhanced diffusion into the calcite lattice (Stipp et al., 1992), and co-precipitation (Zachara et al., 1991). The formation of $CaCO_3$-$CdCO_3$ solid solutions and the crystal growth of $CdCO_3$ (otavite) on calcite during cadmium uptake from solution has been confirmed through spectroscopic studies (Chiarello and Sturchio, 1994; Stipp et al., 1992).

Cadmium uptake has been shown to occur in two steps: 1) fast adsorption of dissolved cadmium onto the calcite surface, and 2) slower solid phase incorporation (Davis et al., 1987; Martin-Garin et al., 2003; Stipp et al., 1992). The rate of solid phase incorporation was found to be independent of the amount of adsorbed cadmium (Davis et al., 1987) and initial migration of the cadmium ions into the calcite lattice is limited to a few angstroms (Martin-Garin et al., 2003). Stipp et al (1992) showed that solid phase incorporation sequestered the cadmium in the calcite permanently and surface uptake ranged from the equivalent of about one to four monolayers. Martin-Garin et al. (2003) found that adsorption of cadmium ions inhibits the dissolution of calcite and the degree of inhibition increases with the surface density of adsorbed cadmium and reaches a maximum of about 75 percent when maximum cadmium adsorption is reached. Ion interference by increasing phosphate and sulfate concentrations was shown to decrease cadmium adsorption by calcite and also affected the sorption reversibility of cadmium (Van der Weijden et al., 1997). Wang and Reardon (2001) showed that crushed limestone is effective at removing dissolved cadmium, while siderite (iron carbonate) has no influence on cadmium concentrations.

A number of studies have been completed examining cadmium uptake by a variety of adsorbents other than calcium carbonate. Commonly known adsorbents that also adsorb cadmium include but are not limited to: activated carbon (Leyva-Ramos et al., 1997; Marzal el al., 1996; Rangel-Mendez et al., 2002; Seco et al., 1999), iron oxide (Cowan et al., 1991), aluminum oxide (Floroiu et al., 2001), goethite (Johnson, 1990; Venema et al., 1996), hematite (Davis and Bhatnagar, 1995; Pivovarov, 2001), red mud (Apak et al., 1998), gibbsite (Weerasooriya et al., 2002), and clays, including kaolinite (Angove et al., 1997; Suraj et al., 1998) and montmorillonite (Barbier et al., 2000). Also, articles have been published examining cadmium adsorption onto calcium-rich materials, including calcareous soils and sands (Fuller and Davis, 1987; Martin-Garin et al., 2002).

Lead Literature Review

Although it is well known that lead is a common, toxic, heavy metal contaminant in the environment, there are limited atomic-scale studies of the adsorption of lead onto minerals such as calcium carbonate (calcite). An investigation using synchrotron X-ray standing wave, X-ray reflectivity techniques, and atomic force microscopy showed that most (60 percent) of the lead adsorbed on the calcite occupied the calcium (Ca^{2+}) site in the calcite surface (40 percent of the adsorbed lead was disordered). There was a total of 0.08 equivalent monolayers of adsorbed lead at the calcite-water interface, and 70 percent of the ordered lead found in the calcium sites in the calcite lattice was in the surface atomic layer (Sturchio et al., 1997). This is interesting since divalent metals strongly sorbed by calcite (Mn, Co, Ni, Zn, and Cd) tend to have ionic radii less than or about equal to the calcium ion (0.99 Å). In contrast, the ionic radius of lead is 1.20 Å, indicating more complex reasons for this observation than ionic radius alone (Davis et al., 1987; Lorens, 1981; McBride, 1980; Zachara et al., 1991).

Additional recent studies have furthered the understanding of lead adsorption onto calcite at the atomic level. Godelitsas et al. (2003) have shown that the lead sorption process by calcite is mainly surface precipitation leading to overgrowth of lead carbonate (cerrusite) and hydrated lead carbonate (hydrocerrusite, $Pb_3(CO_3)_2(OH)_2$). The resulting calcite surface with the adsorbed lead may have an aragonite-type character. At low lead concentrations (1 uM) using X-ray absorption fine structure instrumentation, Rouff et al. (2004) observed that lead forms mononuclear inner-sphere complexes at the surface. At higher lead concentrations (20 and 60 uM), precipitation of hydrocerussite and cerussite was observed. A study comparing lead and cadmium uptake by calcite determined that the uptake of cadmium was greater than lead under similar experimental conditions (Chada et al., 2005). A study examining the effects of interference ions and pH on lead adsorption by calcite (Rouff et al., 2005) showed that nitrate and chloride interference ions showed no significant effect on lead adsorption. Lead adsorption increased from pH 7.3 to 8.5, with a decrease from 8.5 to pH 9.4.

A number of studies have been completed examining lead uptake by a variety of adsorbents other than calcium carbonate. Well-known adsorbents found in the literature to adsorb lead include but are not limited to: activated carbon (Gomez-Serrano et al., 1998; Reed et al., 1996), zeolite (Al-Haj-Ali and El-Bishtawi, 1997; Scott et al., 2002), clay materials such as montmorillonite (Barbier et al., 2000), bentonite (Naseem and Tahir, 2001), and kaolinite (Orumwense-Faraday, 1996), and slag materials such as activated slag (Srivastava et al., 1997), electric furnace slag (Curkovic et al., 2001), and granulated blast-furnace slag (Dimitrova and Mehandgiev, 1998). Adsorbents such as ferrihydrite (Scheinost et al., 2001), manganese and iron hydroxides (Yarrow et al., 2002), red mud (Gupta et al., 2001), and oxide surfaces (Strawn et al., 1998) are also effective lead adsorbents. Other more novel lead adsorbent materials described in the literature include manganese oxyhydroxide (Matocha et al., 2001), diatomite (Al-Degs et al., 2001), mackinawite ($(Fe,Ni)_9S_8$) (Coles et al., 2000), hydroxyapatite (Ma, 1996), and peat (Ho and McKay, 1999).

Adsorption of lead onto oxide surfaces has been modeled by Davis and Kent (1990) using a surface complexation approach. X-ray adsorption fine structure (XAFS) studies of oxides and hydrous oxides have shown that lead generally forms monodentate or bidentate inner-sphere complexes with oxide surfaces at low surface coverage (submonolayer) and may form multinuclear lead complexes at higher surface coverage (near monolayer) (Chisholm-Brause et al., 1990; Manceau et al., 1992; Roe et al., 1991)

Agglomeration Process Literature Review

The science of agglomeration has been described extensively by Pietsch (2001). McClellan et al. (2002) have researched the granulation of limestone fines for purposes of producing a concrete aggregate from quarry waste materials. In their study, three insoluble granule binders were tested and the manufactured granules were tested for strength. The manufactured material was incorporated into concrete and observed by scanning electron microscopy to see how the material changed the quality of concrete when it was incorporated in the mix.

Previous Work by This Research Group Using Limestone-Based Material

Previous research completed by the principal investigators of this grant and others during Phase I and Phase II U.S. EPA Small Business Innovation Research (SBIR) grants and other grants demonstrate arsenic removal of greater than 95 percent by limestone. Some of the research completed so far is presented in Fivecoate (2004), a M.S. thesis in Geological Engineering from the South Dakota School of Mines and Technology.

Research completed used arsenate as the primary form of arsenic tested. Past experiments using arsenite and limestone have shown that limestone does not significantly remove arsenite. An experiment was completed using arsenite that was oxidized prior to contact with limestone in batch experiments and percent arsenic removal was comparable to that seen when arsenate is used.

Materials used for testing arsenic removal (numerous limestone rock types and reagent grade calcium and magnesium carbonates) were characterized using BET specific surface area measurements, particle size analysis, and X-ray diffraction analysis (to determine material composition). Research has shown that as the particle size is reduced, the efficiency and capacity of arsenic removal are improved significantly.

Toxicity Characteristic Leaching Procedure (TCLP) tests of arsenic-treated material have shown that final arsenic concentration of the extraction fluid was 24 ppb, well within the standards set for disposal in ordinary landfills. Also, thermal stability tests of arsenic-treated limestone have shown that the product is thermally stable and can be used as a raw material in cement kilns for manufacturing cement.

Batch experiments were used to examine the impacts of interference ions on arsenic removal. Both chloride and nitrate ions showed interference with arsenic removal. Sulfate did not show much impact to arsenic removal, even at concentrations greater than 1000 ppm. Batch experiments were also completed, using additives to the limestone powder, including magnesium carbonate, iron oxide, titanium oxide, and activated alumina. Iron oxide was found to improve removal significantly, but addition of the material to batch experiments iron-stained the effluent water. Magnesium carbonate was also an effective additive, improving arsenic removal. One drawback to adding magnesium carbonate is that it increases the effluent pH to about 10.

The proposed mechanism for the removal of arsenic by limestone is the adsorption/precipitation of hydrated calcium arsenates, $Ca_3(AsO_4)_2 \bullet xH_2O$, or hydrated magnesium arsenates, $Mg_3(AsO_4)_2 \bullet xH_2O$, onto the heterogeneous surface of the limestone. The solubility product of calcium arsenate, $Ca_3(AsO_4)_2$, is 6.8×10^{-19} and the solubility product of magnesium arsenate, $Mg_3(AsO_4)_2$, is 2.0×10^{-20}. The removal of arsenic, and the subsequent stability of the waste product, is facilitated by the alkaline surface pH of the limestone (pH 9-10). Calcium-rich arsenic compounds have been observed with scanning electron microscopy when samples were prepared with about 1,000 to 8,000 ppm arsenic.

RESEARCH OBJECTIVES

The purpose of this research was to develop a granular adsorbent product that removes dissolved metals and that can be manufactured and sold for use at the drinking water source, at point-of-use, or point-of-entry. This technology has been designed for use by small, rural water supply systems. The major benefit of this research is the development of a low-cost treatment technology for source reduction that will reduce select metals to below drinking water standards. Limestone agglomeration efforts built on the work described in McClellan et al. (2002), in which limestone was granulated for purposes of producing an aggregate for incorporation into concrete. The manufacturing of limestone-based granules was completed on a bench-scale level and did not require specialized equipment.

During earlier phases of this on-going project, laboratory research has indicated improvements in metals removal with finer grain sizes of limestone and the addition of magnesium carbonate. Agglomeration has provided a means to utilize the increase in surface area of powdered material while not compromising filter flow through rates.

The specific objectives, tasks, and criteria for success of this research included:

Objective 1: Development and testing of an agglomeration process for granulating limestone-based material as a filter media for metals adsorption.

Tasks:

- Determine optimum granule grain size, binder, and manufacturing method.

Criteria for Success:

- Development of a bench-scale agglomeration process for granulating powdered limestone mixed with enhancing additives and binder to produce a granulated water filter media.

Objective 2: Development of a mixture formula and manufacturing process for granulation, and production of sufficient quantities for use in batch and column experiments.

Tasks:

- Test the granule mixture formula at different percentages of limestone, additive, and binder to determine the optimum formula for metals removal while still maintaining granule strength and material surface area.
- Perform batch experiments to compare the performance of the different granule mixture formulas.

Criteria for Success:

- Successful production of agglomerated granules with sufficient strength to withstand use in batch and column experiments.
- At a minimum, metals removal efficiency of the manufactured granules will be comparable in efficiency to an equal mass of powdered limestone.

Objective 3: Investigation of the efficiency of the manufactured granules to remove select metals (arsenic, cadmium, and lead) using batch and column experiments.

Tasks:

- Perform batch experiments with granules and varying concentrations of arsenic, cadmium, and lead.
- Develop isotherm models to determine if the metals removal follows an adsorption type model.
- Determine mass of metals removal per gram of material at different metals concentrations.
- Perform column experiments to compare the rate of metals removal by granules versus crushed native limestone of similar size.

Criteria for Success:

- Isotherm models will be developed and mass of metal removed per gram of granule material will be determined.

MATERIALS CHARACTERIZATION AND METHODS

Materials Characterization

Minnekahta Limestone from the Pete Lien and Sons Quarry in Rapid City, South Dakota, was used as the limestone source for this research. Limestone fines were collected from the quarry and sieved to a size of less than 74 microns (sieve mesh #200). Based on X-ray diffraction analysis, Minnekahta Limestone is composed of about 95 percent calcite, 4 percent quartz, and 1 percent microcline. Surface area of the powdered Minnekahta Limestone used in manufacturing the granules was about 1 m^2/gram (although this measurement is for ball-milled limestone, as measurements for the sieved powder are not available). Reagent-grade magnesium carbonate, $MgCO_3$, (source: Fisher Scientific), used as an additive in the granules to enhance arsenic removal, has a specific surface area of about 22 m^2/gram. The surface area of the Portand cement used as an insoluble binder in the granules is about 1 m^2/g. Portand cement is a hydraulic cement that sets and hardens by reacting chemically with water, a process called hydration. Portland cement is composed of tricalcium and dicalcium silicates, tricalcium aluminoferrite, tricalcium aluminate, and calcium sulfate.

Figure 1 is a photo of manufactured granules after drying. Granules in the red circle are about 1-2 mm in diameter. Table 1 lists specific surface area measurements for three of the granule formulations tested during this research. Overall, granules appear to have a surface area of 4 to 6 m^2/gram. In comparison, the surface area of crushed limestone chips of the same diameter (1-2 mm) is about 0.3 m^2/gram. Some of the increase in surface area of the granules is likely due to the nature of the granule surface itself – the granules abrade easily, forming powder.

Figure 1. Photo of manufactured limestone-based granules. Granules in the red circle are about 1-2 mm in diameter.

Sample Description	BET Surface Area (m^2/g)
Manufactured granules composed of 10% Portland cement and 90% Minnekahta Limestone	5.3
Manufactured granules composed of 15% Portland cement and 85% Minnekahta Limestone	6.4
Manufactured granules composed of 10% Portland cement, 87% Minnekahta Limestone, and 3% reagent grade $MgCO_3$	4.4

Table 1. BET surface area measurements of three formulas of manufactured limestone-based granules.

Scanning electron micrograph (SEM) images of the surfaces of manufactured limestone-based granules were taken to visually characterize the granule surfaces. Figure 2 shows the surface of a manufactured granule of limestone with 10 percent Portland cement binder. Surface area appears to be increased over that of limestone chips, but the granules also seem to be coated, perhaps with the binder. Figure 3 shows the surface of a limestone granule with 15 percent Portland cement binder. In this portion of the granule, it appears that nanometer-sized crystals formed on the surface of the granules. X-ray florescence indicated that these crystals are composed of calcium carbonate. This type of crystallization was not observed on all the granules and was not widespread.

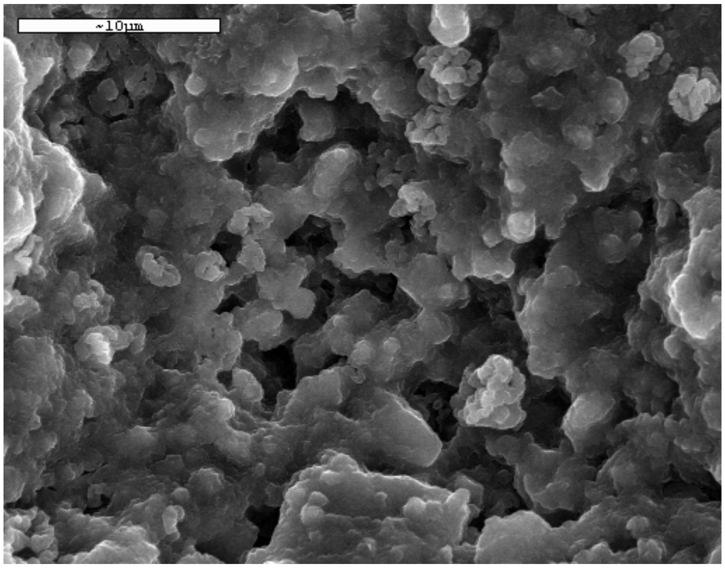

Figure 2. Limestone granule with 10 percent Portland cement binder, taken at 3,500x magnification.

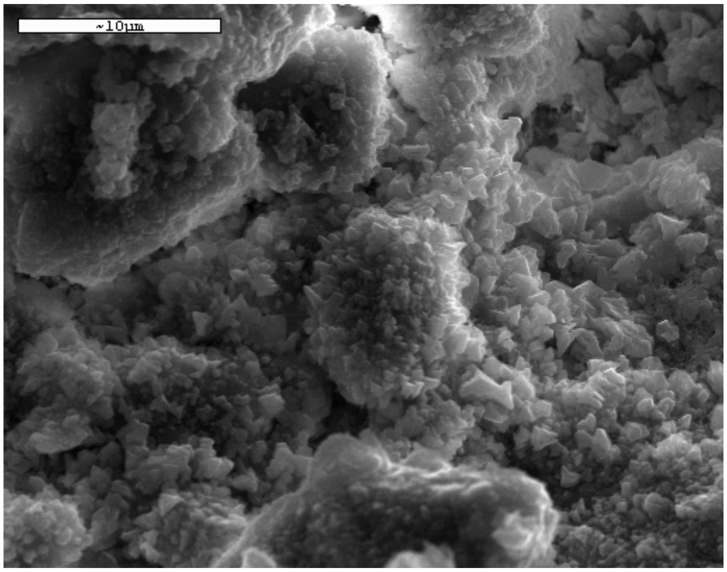

Figure 3. Limestone granule with 15 percent Portland cement binder, taken at 3,500x magnification.

Batch Experiment Methodology

Weighed samples of the limestone-based material are placed in labeled round-bottomed flasks. One-hundred millileters of metals solution (concentrations vary depending on the experiment and the metal being examined) is added to each flask. The metals solutions are pH-balanced to a pH of 8 ± 2 prior to mixing with the adsorbent using either concentrated nitric acid (HNO_3) or sodium hydroxide (NaOH). The flasks are secured to the wrist shaker (Figure 4) are and agitated for 48 hours (or two hours in the case of limestone-based granules). After mixing, the samples are filtered with a 0.45 µm filter. The pH and conductivity of the effluent solution are measured. The samples were analyzed by MidContinent Testing in Rapid City, South Dakota for metals concentration.

Figure 4. Photo of a batch experiment on the wrist shaker.

Column Experiment Methodology

The columns are constructed of PVC pipe of varying diameters and lengths, depending on the column design. Influent metals solution is mixed to varying concentrations, depending on the experiment and the metal being examined. Metals solutions are pH balanced to a pH of 8 ± 2 prior to use. The influent solution is pumped into the column from the bottom up and a constant flow rate out of the column is set using valves at the flow outlet at the top of the column. Samples of effluent are collected regularly and the pH and conductivity of the effluent are measured. Samples are filtered with a 0.45 μm filter and are then analyzed by MidContinent Testing for metals concentration. Figure 5 shows a typical column set up.

Figure 5. Photo of column experiments being run.

Development of the Agglomeration Process

An investigation of methods for agglomerating powdered limestone into granules was completed for this research. The purpose of agglomeration is to increase the limestone surface area relative to the size of the limestone particles. Since fine limestone material cannot be used as a filter media in a flow-through column filter system (due to reduced flow-through capacity of the material at grain sizes less than the diameter of sand), efforts were made to granulate powdered limestone, in order to maintain high surface area but allow flow through of water.

Agglomeration takes fine materials and forms them into spherical granules. A binder is added to the material mix to bond the individual particles together and to strengthen the granules. One advantage of the agglomeration process is that it allows the addition of additives to the limestone that improve removal efficiency. Magnesium carbonate was added to the limestone/binder mix to enhance metals removal efficiency. Limestone agglomeration techniques were derived from the work of McClellan et al. (2002), in which limestone powder was granulated for purposes of producing an aggregate for incorporation in concrete.

The agglomeration was done at bench-scale using a metal coffee can with three paddles attached on the inside as the granulator. Mixed powdered materials were placed in the can and the can was rotated on a bottle roller at about 50 revolutions per minute (rpm). As the can rotated around, water was sprayed into the can using a spray bottle. The process of rotating the can while adding water allowed for the agglomeration to occur and the formation of a wide size range of granules. The granules were wet sieved, spread out on screens, and set in a cement curing room with elevated levels of humidity for several days to promote further hydration of the cement binder. The granules were then air-dried and sieved for use in experiments. After drying, the granules are firm enough to hold their shape in a column and do not disintegrate when exposed to water because the binder is insoluble. Over time (several weeks), the cement continues to cure and the granules become harder.

RESEARCH RESULTS

Preliminary Batch Experiments to Determine Granule Formulation

Manufactured granules of limestone with Portland cement binder and two different additives (magnesium carbonate and calcium carbonate) were manufactured. Batch experiments using arsenic solution as the dissolved metal were performed to compare arsenic removal by granules with five percent, 10 percent, and 15 percent binder. Batch experiments were also done with one percent and three percent of each additive added to see how this improved arsenic removal efficiency. Each batch experiment with the granules used 1.5 grams of granules as the adsorbent and 100 mL of 100 ppb arsenic solution. The granules used were 2 to 4 mm in size and were made using ball-milled Minnekahta Limestone. Figure 6 shows final arsenic concentrations of each batch experiment. Batch experiments were also completed with 1.5 grams of ball-milled limestone (not granulated) and 90 percent limestone/10 percent binder (not granulated) as a performance comparison for the manufactured granules.

The batch experiment that showed the highest removal efficiency (lowest final arsenic concentration) was the ungranulated mixture of Minnekahta Limestone powder (90 percent by weight) Portland cement powder (10 percent by weight). Powdered cement performs well as an arsenic removal agent, but causes the pH and conductivity of the final solution to be significantly elevated. Final pH values were about 11.5 and conductivity values about 1,800 µmhos/cm for this powdered mixture.

As the percent Portland cement binder was increased in the manufactured granules, final arsenic concentration increased. With 5 percent binder, final arsenic concentration averaged 58 ppb. With 10 percent binder, final concentration increased to 60 ppb and with 15 percent binder, final arsenic concentration was 68 ppb. Research by Kundu et al (2004) shows that at pH values above 7, arsenic removal by hardened cement decreases. Optimum pH for arsenic removal by hardened cement is 4 to 5. Final pH of the batch experiments using limestone granules was about 10. With more binder added to the granules, the Portland cement could also be coating more of the surface area of the powdered limestone and reducing its effectiveness as an arsenic removal agent. Also, as additional binder is added to the mixture, there is less limestone in the mix, which may also reduce arsenic removal.

Manufactured granules with reagent-grade magnesium carbonate as an additive showed promise as an arsenic removal agent. Final arsenic concentration of the batch experiment with one percent $MgCO_3$ averaged 43 ppb, while the batch experiment with three percent $MgCO_3$ averaged 32 ppb. This final concentration is similar to the batch experiment of an equal mass of ball-milled limestone (not granulated), which had a final arsenic concentration of 33 ppb. Thus, using granulation and three percent by weight of

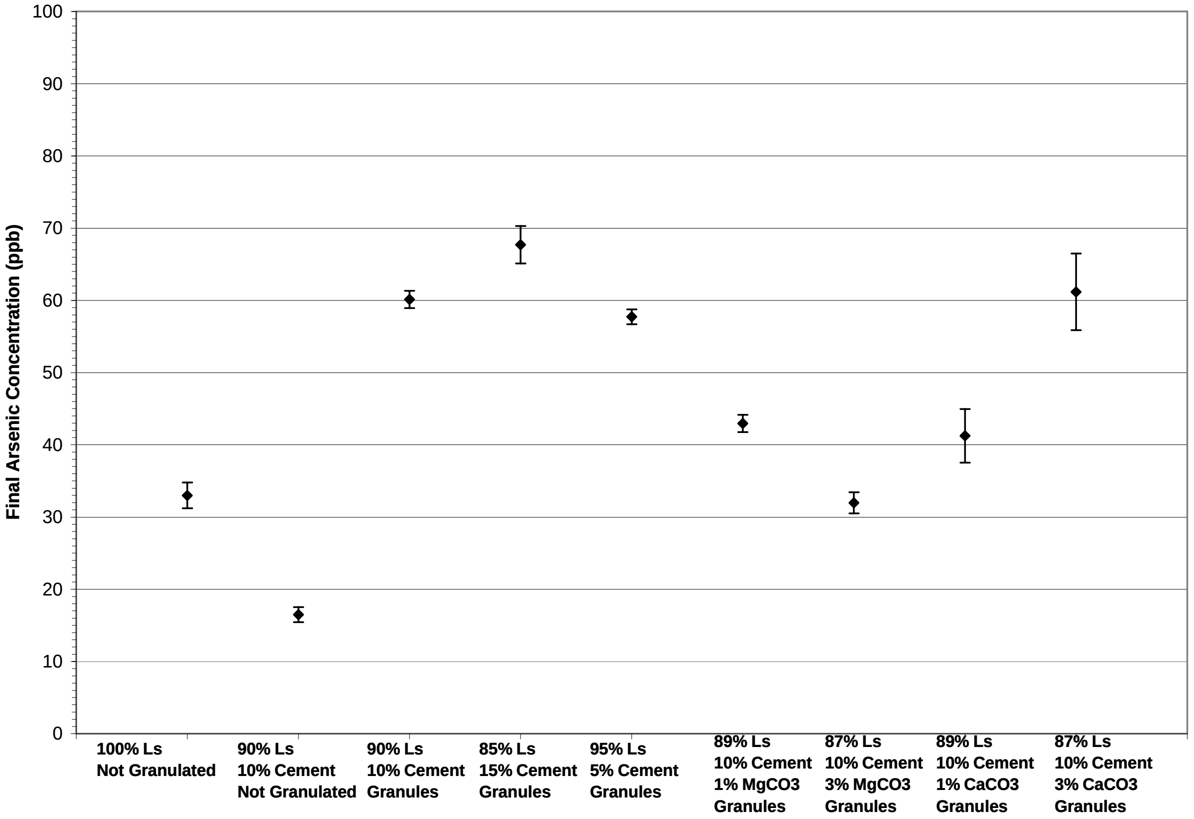

Figure 6. Arsenic removal by different limestone-based granule formulations. Initial batch experiment conditions: 1.5 grams of 2-4 mm sized manufactured granules or powdered limestone-based media in 100 mL 100 ppb arsenic solution, initial solution pH 8 ± 0.2 pH units, room temperature, duration 2 hours.

magnesium carbonate as an additive achieved the same level of arsenic removal as powdered limestone, with the added benefit of being in a form that can be readily used as a filter media. The final pH of solutions treated with granules containing magnesium carbonate ranged from about 10 to 10.5 and conductivity ranged from 100 to 125 µmhos/cm. The final pH of solutions treated with limestone powder was 9.6 and had a conductivity of about 60 µmhos/cm.

Reagent-grade calcium carbonate, $CaCO_3$, as an additive in granules did not perform as well as magnesium carbonate. The batch experiment with one percent $CaCO_3$ had a final arsenic concentration of 41 ppb, while the batch experiment with three percent $CaCO_3$ had a final concentration of 67 ppb. The reason for this increase in final arsenic concentration is unclear, although batch experiments with $CaCO_3$ completed previously have shown that arsenic removal using this additive varies unpredictably and is consistently a poorer performer than magnesium carbonate.

Granule Attrition Resistance Test

The granule attrition resistance test completed for this investigation is based on a method described by Brady and McKay (1996). The purpose of the test is to measure the amount of fines generated during batch experiments using limestone-based granules due to sample agitation. Two sizes of limestone granules were tested: 1 – 2 mm and 0.5 – 1 mm. The tests used 100 mL of deionized water pH-adjusted to 8.0 ± 0.2 pH units and 1.0 gram of limestone-based granules (87 % limestone sieved to < 74 microns, 3 % magnesium carbonate, and 10 % Portland cement binder). Each test was repeated in triplicate and results averaged. The experiments were completed in 500 mL round bottomed flasks placed on a wrist shaker. The flasks were shaken for two hours. Following agitation, the granules and fines (material < 0.2 mm) were sieved, dried, and weighed. Attrition resistance was then determined as percent granule loss due to production of fines using the equation:

$$\frac{\text{weight of fines (grams)}}{\text{weight of starting granules (grams)}} \times 100 \text{ percent}$$

For the 1-2 mm granules, attrition resistance averaged about 35 percent. For the 0.5 – 1 mm granules, attrition resistance averaged about 42 percent. The smaller granules (0.5 – 1 mm) abraded about six percent more than the 1 – 2 mm granules. For both sizes of granules tested, at least half of the granules remaining after agitation sieved to the starting size range. However, the level of attrition resistance observed for granule testing under batch experiment conditions is significant. This information must be taken into consideration when evaluating data results from batch experiments using granules.

Effect of Granule Size on Arsenic Removal

Batch experiments were completed to compare the effect of the size of the limestone-based granules on arsenic adsorption capacity at three initial arsenic concentrations (50, 100, and 500 ppb). Granules composed of 87 percent Minnekahta Limestone, three percent reagent grade magnesium carbonate, and 10 percent Portland cement as binder were tested at two different granule sizes: 1-2 mm and 0.5-1 mm. The results of this study are shown in Figure 7. It is clear that as initial arsenic concentration increases, adsorption capacity increases for both granule sizes. For 1-2 mm size granules, the increase in adsorption capacity from 100 to 500 ppb arsenic is from 5.4 to 20 ug arsenic per gram limestone-based granules, whereas the increase for 0.5-1 mm size granules is from 8.6 to 37 ug arsenic per gram granules, At an initial concentration of 50 ppb arsenic, there was a difference of 1.1 ug/g between the adsorption capacities of the two granule sizes, with 0.5-1 mm size granules having the greater adsorption capacity. However, because the 1-2 mm size granules are more durable during batch experiments, this granule size was chosen for subsequent batch experiments.

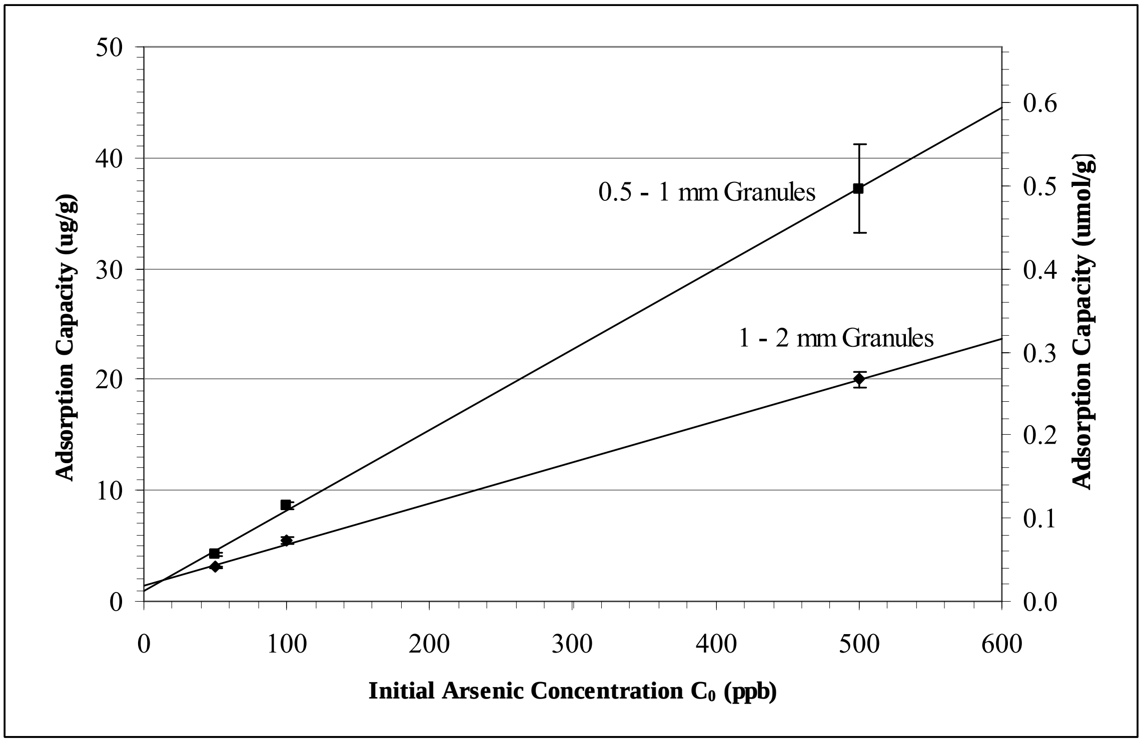

Figure 7. Adsorption capacity of two limestone-based granule sizes at three arsenic concentrations. Initial batch experiment conditions: 1.0 gram of granules (either 0.5-1 or 1-2 mm in size) in 100 mL arsenic solution of three concentrations (50, 100, and 500 ppb), initial solution pH 8 ± 0.2 pH units, room temperature, duration 2 hours.

Adsorption Isotherm Study Using Limestone Powder

There are three main processes by which an aqueous metal solute (such as arsenic, cadmium, or lead) reacts with the surface of a solid phase such as limestone: adsorption, absorption, and surface precipitation (Sposito, 1986). Absorption refers to the diffusion of an aqueous solute into a solid phase to form a solid solution (Sposito, 1986). The bonding mechanisms of adsorption and surface precipitation are similar – adsorption is two-dimensional and surface precipitation is three-dimensional (Corey, 1981). In order for surface precipitation to occur, the aqueous solution must be supersaturated with respect to the solubility of the solid phase. In systems which are undersaturated, either adsorption or absorption will control the concentration of solute. Surface precipitation means that a solid phase grows by the propagation of a molecular unit that repeats itself in three dimensions (Sposito, 1986). The time scale of metal adsorption onto mineral surfaces has typically been found to be in the range of minutes (Davis et al., 1987; McBride, 1980), and is followed by a slow removal step on the time scale of hours to days. This slow step may be due to surface precipitation, co-precipitation, or diffusion of previously adsorbed ions into the existing solid (Martin-Garin et al., 2003).

An adsorption isotherm consists of batch equilibrium experiments that provide data relating the amount of adsorbate adsorbed per unit weight of adsorbent to the amount of adsorbate remaining in solution. Factors that affect an isotherm model include adsorbent preparation and dosage, pH, temperature, and contact time (Bernardin, 1985).

When examining an isotherm plot, slope provides a visual estimation of the affinity of the adsorbate for the adsorbent. An isotherm with a steeper slope indicates that the adsorbent in that experiment has a greater affinity for the adsorbate than an isotherm with a shallower slope (Deutsch, 1997). A linear (straight line) adsorption isotherm implies that the process of adsorption is not affected by adsorbate concentration in solution and that the surface of the solid has unlimited capacity for adsorption. Such adsorption isotherms are appropriate at low concentrations of adsorbate, but are not appropriate at higher concentrations when the surface sites for adsorption become filled (Deutsch, 1997). Also, isotherm models should be developed for the concentration range likely to be encountered in practice, because the extrapolation of isotherm data can lead to errors and may overestimate adsorption (Kinniburgh, 1986).

The Langmuir isotherm is a commonly used adsorption isotherm for assessing the potential use of an adsorbent material for removal of metals such as arsenic, cadmium, and lead. Based on the results of adsorption studies done for this research, limestone powder as an adsorbent obeys the Langmuir isotherm model and the results show high correlation coefficients with the model.

For adsorption by solid adsorbents from solution, the Langmuir adsorption isotherm is expressed as:

$$q_e = \frac{Q_0 b C_e}{1 + bC_e}$$

This equation indicates that q_e approaches Q_0 asymptotically as C_e approaches infinity (Faust and Aly, 1987). The linearized form of this equation is:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0}$$

where:

q_e = adsorption capacity (amount of solute adsorbed per unit weight of adsorbent), umol/g

C_e = equilibrium concentration, umol/L
Q_0 = adsorption capacity required for surface monolayer coverage, umol/g

b = adsorption constant related to the enthalpy of adsorption [$b \infty (\exp(-\Delta H/RT))$], 1/umol

When C_e/q_e is plotted against C_e, a straight line, having a slope $1/Q_0$ and an intercept $1/bQ_0$ is obtained. Obtaining slope and intercept values graphically, the constant b can be determined. The monolayer adsorption capacity, Q_0, defines the total capacity of the adsorbent for a specific adsorbate. However, reliable Q_0 values can only be obtained if the system exhibits the Type 1 isotherm of the Brunauer's classification (Faust and Aly, 1987).

Linearized isotherms with respect to the Langmuir model are shown in Figure 8 and the calculated Langmuir isotherm constants are tabulated in Table 2. These Langmuir isotherm plots were derived from a series of batch experiments with initial arsenic concentrations varying from 100 to 1000 ppb and amounts of Minnekahta Limestone powder varying from 0.5 to 6.0 grams. Results show that adsorption of arsenic on Minnekahta Limestone conforms to the Langmuir isotherm model at concentrations from 100 to 1000 ppb arsenic.

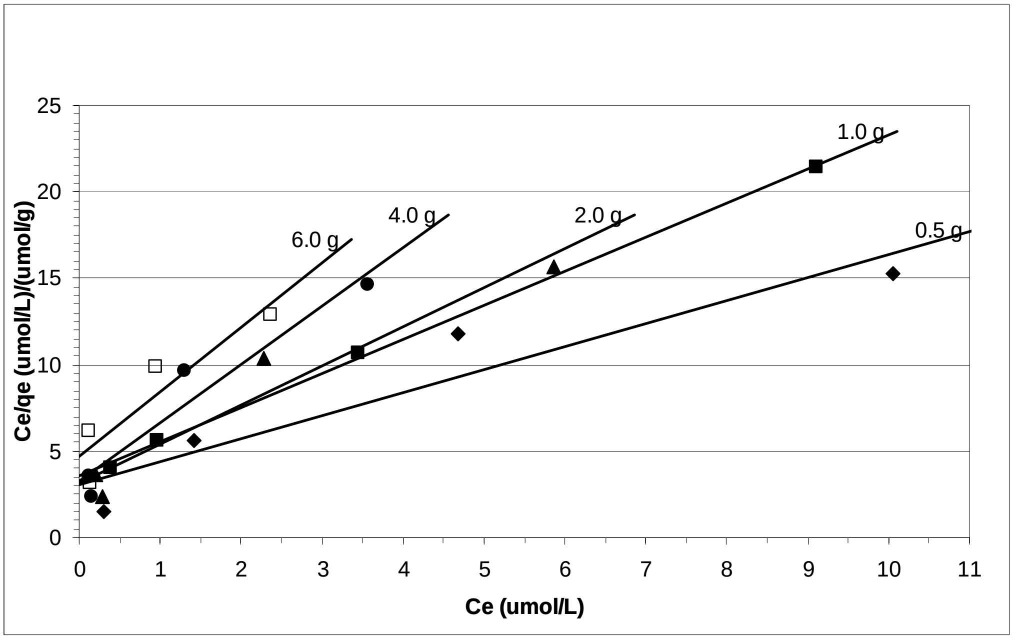

Figure 8. Langmuir adsorption plots for arsenic adsorption on Minnekahta Limestone powder (sieved to less than 74 microns). Batch experiment conditions: 0.5 to 6.0 grams of adsorbent in 100 mL of arsenic solution ranging from 100 to 1000 ppb, initial solution pH 8 ± 0.2 pH units, room temperature, duration 48 hours.

Initial Adsorbent Amount (grams)	**Correlation Coefficient R^2**	**b (1/umol)**	**Q_0 (umol/g)**
0.5	0.8955	0.438	0.75
1.0	0.9989	0.549	0.51
2.0	0.9413	0.725	0.44
4.0	0.9318	1.05	0.29
6.0	0.8481	0.788	0.27

Table 2. Langmuir isotherm parameters for arsenic adsorption on limestone powder as shown in Figure 8.

Effect of pH on Arsenic Removal by Limestone Powder

Arsenic removal by limestone is a process that operates effectively over a wide range of pH values. Figure 9 shows that arsenic removal has limited dependence on initial solution pH over a range from pH 4 to 10. The pH range of natural ground water is from about pH 6 to 8. Batch experiments were completed over a range of pH values, using either nitric acid (HNO_3) or sodium hydroxide (NaOH) to adjust initial solution pH. At the extremely low pH value of 2, dissolution of limestone by the acidic solution occurred. The pH values of the effluent solutions at the end of the experiment were about 7, indicating that limestone dissolution continued throughout the duration of the batch experiment. Final pH values for the pH 4 experiments were an average of 9.3. The two unit drop from pH 4 to pH 2 had a significant impact on system dynamics, causing pH to be suppressed throughout the duration of the experiment. Above pH 10, it appears that the hydroxide ions added to the solutions to adjust pH created ion interference and suppressed arsenic adsorption by the limestone.

Batch experiments were also completed to compare limestone arsenic adsorption capacity at three arsenic concentrations (100, 200, and 500 ppb) and at three pH values (4, 8, and 12). Figure 10 shows the results of this study. Adsorption capacity of the limestone increased as arsenic solution concentration increased. Significant influences of pH on adsorption capacity were limited and were observed at pH 12, where ion interference was seen due to the addition of hydroxide ions for pH adjustment. Also, the drop in arsenic adsorption capacity from pH 4 to 8 for the 500 ppb arsenic solution was greater than at lower arsenic concentrations.

Effect of Initial Arsenic Concentration on Removal by Limestone Powder

The results of this study show that arsenic uptake by limestone powder increases for increasing arsenic concentrations and increasing limestone dosages. In Figure 11, initial arsenic concentration values (100, 200, 500, and 1000 ppb) are plotted versus adsorption capacity at five different adsorbent dosages (0.5, 1.0, 2.0, 4.0, and 6.0 grams). For example, for C_0 = 100 ppb, capacity is 0.21 umol/g by 0.5 grams limestone and 0.020 umol/g by 6.0 grams limestone, whereas at C_0 = 1000 ppb, adsorption capacity is 0.66 umol/g by 0.5 grams limestone and 0.18 umol/g by 6.0 grams limestone. The data presented in Figure 11 fits the trend lines well (all R^2 values > 0.9) and this data may be useful in predicting limestone arsenic capacities for batch experiments under similar conditions at other arsenic concentrations between 100 and 1000 ppb for the five adsorbent dosages presented.

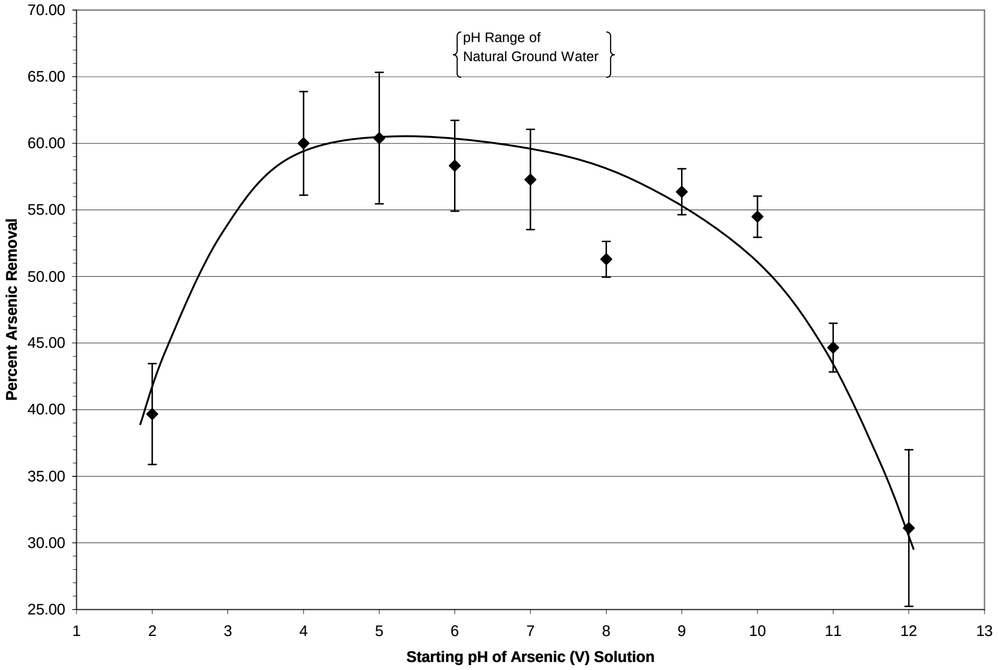

Figure 9. Influence of initial solution pH on arsenic removal. Initial batch experiment conditions: 0.5g ball-milled Minnekahta Limestone in 100 mL 100 ppb arsenic solution, room temperature, duration 48 hours.

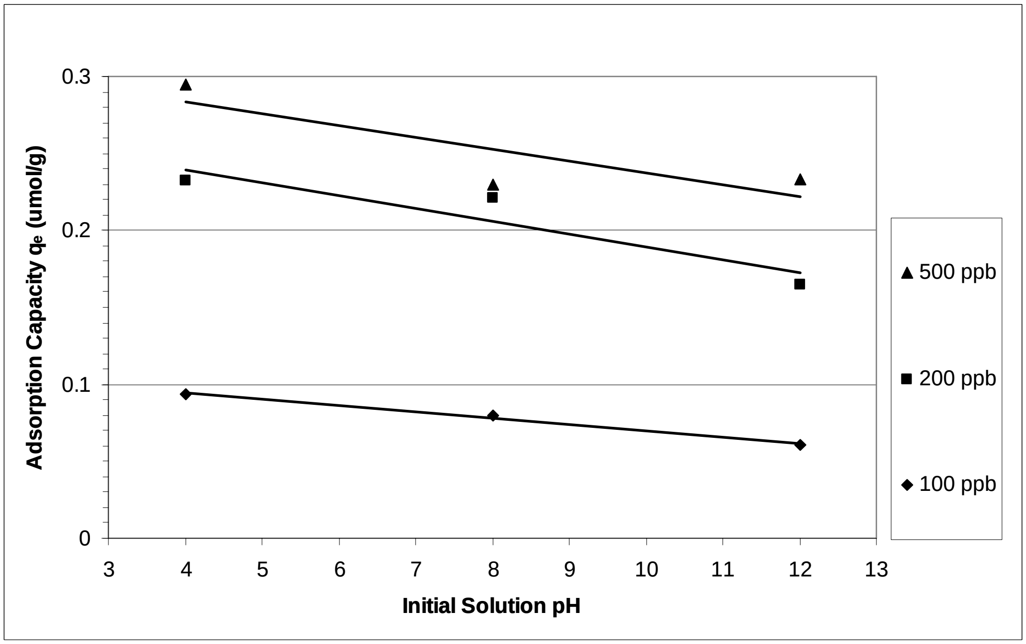

Figure 10. Adsorption capacity of limestone as initial solution pH and starting arsenic concentration are varied. Initial batch experiment conditions: 0.5 mg Minnekahta Limestone (sieved to less than 74 microns) in 100 ml arsenic solution, room temperature, duration 48 hours.

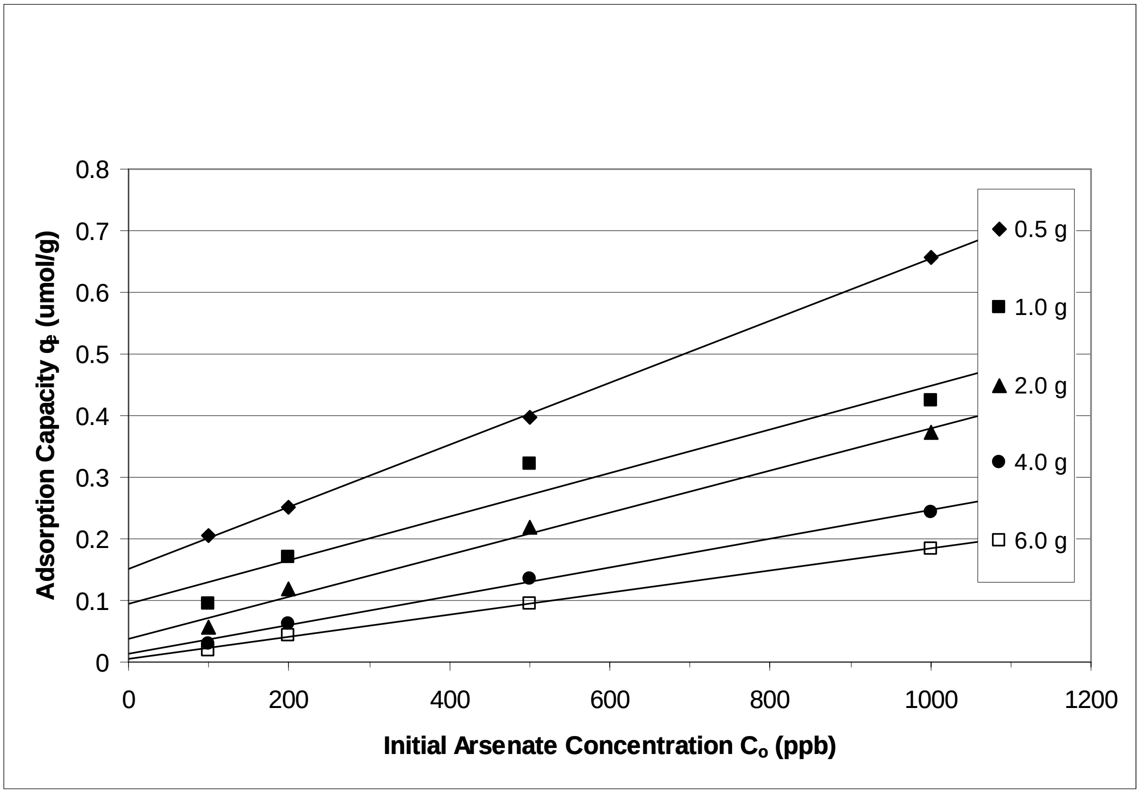

Figure 11. The effect of initial arsenic concentration on arsenic removal at different dosages of Minnekahta Limestone (sieved to less than 74 microns). Initial batch experiment conditions: Minnekahta Limestone (0.5, 1.0, 2.0, 4.0, 6.0 grams) in 100 mL of arsenic solution (100, 200, 500, and 1000 ppb), initial solution pH 8 ± 0.2 pH units, room temperature, duration 48 hours.

Arsenic Removal by Manufactured Granules

The adsorption capacity of 1-2 mm sized limestone-based granules (87 percent Minnekahta Limestone powder, 3 percent magnesium carbonate, and 10 percent Portland cement binder) at three arsenic concentrations (50, 100 and 50 ppb) was shown in Figure 7. Arsenic adsorption capacity of the 1-2 mm granules at 100 ppb starting solution is 5.4 ug arsenic/gram granules. In comparison, an equal mass of limestone powder, ungranulated, has an arsenic capacity of 5.9 ug arsenic/gram limestone, and crushed limestone sieved to 1-2 mm has an adsorption capacity of 4.2 ug arsenic/ gram limestone. Overall, in batch experiments, granulation improves arsenic capacity of the limestone media about 30 percent over the capacity of limestone chips of equal diameter. The arsenic capacity of limestone-based granules is about equal to the capacity of powdered limestone in batch experiments, with the added benefit that granules can be used as a filter media in a column-type filter device without impairing flow-through rates.

Cadmium Removal by Manufactured Granules

Initial batch experiments with cadmium solutions in the range of parts per billion removed all cadmium in solution. Batch experiments with 0.5 grams powdered limestone and 60 to 80 ppb cadmium at three pH values (5, 8, and 10) removed cadmium to below analysis detection limits (10 ppb). Solution concentrations were increased to part per million levels in order to reach effluent cadmium concentrations greater than 10 ppb.

Batch experiments were completed using 1.0 gram of limestone-based granules and 100 mL of solution with cadmium concentrations of 5, 20, and 50 ppm. At these concentrations, cadmium removal by the granules was greater than 99 percent for all three concentrations. Because cadmium removal was greater than 99 percent, an adsorption isotherm could not be developed.

Adsorption capacities of the granules at the three concentrations show that cadmium uptake increases dramatically for increasing cadmium concentrations. In Figure 12, initial cadmium concentration values (5, 20, and 50 ppm) are plotted versus adsorption capacity at an adsorbent dosage of 1.0 gram. At an initial concentration of 5 ppm, adsorption capacity is 4.4 umol/g while at an initial concentration of 50 ppm, adsorption capacity increases to 44.4 umol/g. The data presented in Figure 12 fits the trend line well (R^2 value > 0.9) and it follows that this figure may be useful in predicting limestone cadmium capacities for batch experiments under similar conditions at other cadmium concentrations in the range of about 0 to 60 ppm. From these results it is clear that the capacity for limestone-based granules to remove cadmium is much greater than the capacity for arsenic removal by granules.

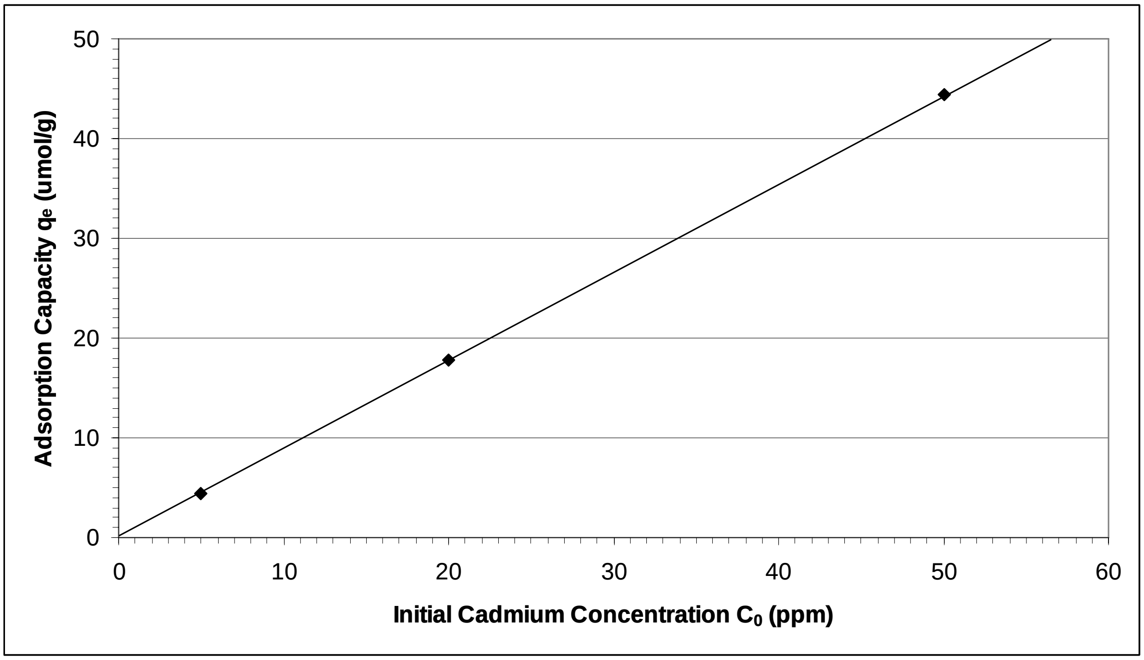

Figure 12. Cadmium adsorption capacity of limestone-based granules for initial cadmium concentrations of 5, 20, and 50 ppm. Initial batch experiment conditions: 1.0 g granules in 100 mL cadmium solution of three concentrations (5, 20, and 50 ppm), initial pH 8.0 ± 0.2 pH units, room temperature, duration 2 hours.

Lead Removal by Manufactured Granules

Initial batch experiments with lead solutions in the range of parts per billion removed all lead in solution. Batch experiments with 0.5 grams powdered limestone and 80 to 100 ppb lead removed lead to below analysis detection limits (10 ppb). Solution concentrations were increased to part per million levels to try to obtain effluent lead concentrations greater than 10 ppb. However, batch experiments using 1.0 gram of limestone-based granules and 100 mL of lead at concentrations of 0.5 ppm, 2 ppm, and 3 ppm, also resulted in lead concentrations below the analysis detection limits. From these results it is clear that the capacity for lead removal by limestone-based granules is much greater than the capacity for arsenic removal. Because adsorption at all lead concentrations was below analysis detection limits, an adsorption isotherm for lead could not be developed.

An interesting phenomenon occurred when mixing the lead solutions. The solutions were initially mixed to concentrations of 5, 20, and 50 ppm. The solutions were pH-adjusted to about 8 using small quantities of concentrated sodium hydroxide. After pH-adjustment, it was noted that a fine white precipitate formed in the solutions. It is thought that this was a precipitate of lead hydroxide ($Pb(OH)_2$) that formed, reducing the dissolved lead concentrations of the mixed solutions. Lead hydroxide has a very low solubility, with a solubility product (K_{SP}) equal to 2.5×10^{-16}.

Arsenic Removal: Limestone Chips Versus Manufactured Granules - Column Experiments

Two column studies were completed to compare the efficiency of manufactured limestone-based granules to crushed limestone chips. One column was run with 1-2 mm sieve size untreated limestone and the other column was run with 1-2 mm size manufactured limestone-based granules (containing 87 percent Minnekahta Limestone, 10 percent Portland cement binder, and three percent reagent-grade magnesium carbonate) as a comparison. Both columns used a starting solution containing 100 ppb arsenic. Column size was 12 inches long by 1 inch in diameter.

The column of 1-2 mm washed Minnekahta Limestone chips was packed with 249.6 grams of material. Figure 13 is a plot of the measured effluent arsenic concentration during the total run time of 720 minutes (12 hours). Based on this graph, the time of breakthrough at 10 ppb occurred prior to the first sampling at 60 minutes. Flow through the column was 1.2 liters per hour (eight bed volumes per hour). About 14.5 liters of water passed through the column before complete exhaustion of the column material. This corresponds to about 97 bed volumes.

The column of 1-2 mm diameter manufactured limestone-based granules was packed with 159.248 grams of material. Figure 14 is a plot of the measured effluent arsenic concentration during the total run time of 1,740 minutes (29 hours). Based on this graph, the time of breakthrough at 10 ppb was about 600 minutes (10 hours). Flow through the column was 1.2 liters per hour (eight bed volumes per hour). About 12 liters of water passed through the column before breakthrough occurred. This corresponds to about 80 bed volumes. About 35 liters of water passed through the column before complete exhaustion of the column material. This corresponds to about 233 bed volumes.

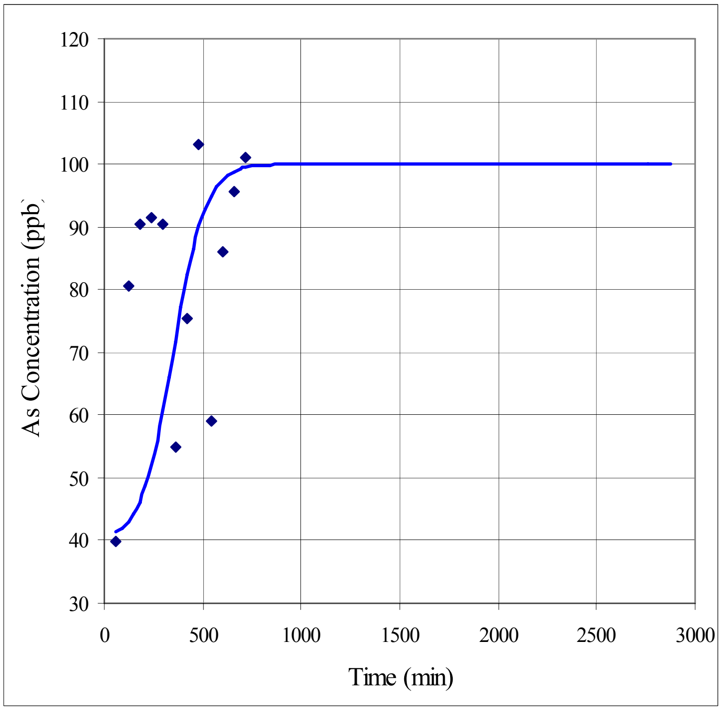

Figure 13. Results of column study using 12 inch by 1 inch diameter column, with Minnekahta Limestone, sieve size 1-2 mm, as the adsorbent, influent arsenic concentration of 100 ppb, and a flow rate of eight bed volumes per hour (1.2 L/hr) .

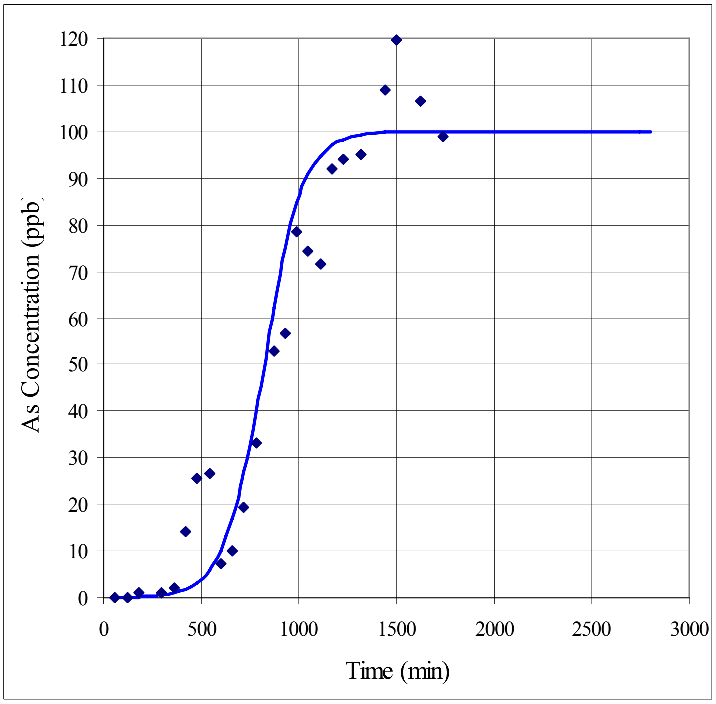

Figure 14. Results of column study using 12 inch by 1 inch diameter column, with limestone-based manufactured granules as the adsorbent, influent arsenic concentration of 100 ppb, and a flow rate of eight bed volumes per hour (1.2 L/hr).

This preliminary comparison column study shows that limestone-based granules with magnesium carbonate added as an additive performed about four times as well as the limestone chips of equal diameter. In these two column studies, the 1-2 mm limestone chips removed a total of about 5.8 ug arsenic/gram limestone while the 1-2 mm limestone-based granules removed about 22 ug arsenic/gram limestone.

Two column studies were completed to compare the capacity of arsenic removal by crushed limestone chips and manufactured limestone-based granules from water from a city well in Keystone, South Dakota. One column experiment was run with 0.2-0.5 mm sieve size untreated Minnekahta Limestone using a 12 inch long by 1.5 inch diameter column and the other experiment was run with manufactured limestone-based granules (containing 87 percent Minnekahta Limestone, 10 percent Portland cement binder, and three percent reagent-grade $MgCO_3$) in a 12 inch long by 1 inch diameter column. Both columns were run using water sample KEY-2 (water analysis shown in Table 3), which contained 50 ppb dissolved arsenic. Arsenic in the Keystone well is naturally occurring.

For the first column experiment, a column was packed with 587.208 grams of 0.2-0.5 mm sieve size washed Minnekahta Limestone. Figure 15 is a plot of the measured effluent arsenic concentration during the total run time of 1,620 minutes (27 hours). Breakthrough at 10 ppb occurred prior to the first sampling at 60 minutes. Flow through the column was 2.8 liters per hour (eight bed volumes per hour). About 75.5 liters of water passed through the column by the end of the experiment (at which point the column material was exhausted). This corresponds to about 217 bed volumes. Based on 75.5 liters of well water being treated by about 587 grams of limestone, it is estimated that a total of about 0.004 grams of arsenic was treated and that about 6.4 ug arsenic were treated by each gram of limestone.

For the second experiment, the column was packed with 168.681 grams of 1-2 mm diameter manufactured limestone-based granules. Figure 16 is a plot of the measured effluent arsenic concentration during the total run time of 1,620 minutes (27 hours). Breakthrough at 10 ppb occurred prior to sampling at 60 minutes. Flow through the column was 1.23 liters per hour (eight bed volumes per hour). About 33 liters of water passed through the column before the experiment was ended (column material was close to exhaustion). This corresponds to about 217 bed volumes. Based on 33 liters of well water being treated by about 168.7 grams of limestone, it is estimated that a total of about 0.0017 grams of arsenic was treated and that about 9.8 micrograms of arsenic were treated by each gram of limestone-based granules. This sorption capacity estimate indicates that the limestone under these conditions had a low capacity, although it is an improvement of about 1.5 times over the sorption capacity of the column experiment that was run with 0.2-0.5 mm crushed limestone.

Since breakthrough at 10 ppb was not observed in either column, it is suggested that the column flow through rates were too high and the columns should be run again with either larger columns or slower flow through rates. A preliminary examination of the water quality analysis completed for the Keystone City well (Table 3) does not provide a clear explanation as to why arsenic removal capacity of limestone decreases when using natural well water as compared to arsenic-spiked deionized water solutions.

Parameter	KEY-2, Sampled 11/12/04
Physical Properties	
Electrical Conductivity	461 umhos/cm
Hardness	116 mg/L
Total Dissolved Solids	252 mg/L
Total Suspended Solids	<5.00 mg/L
Turbidity	1.5 NTU
pH	8.06
Non-Metallics	
Acidity	<10.0 mg/L
Alkalinity	217 mg/L
Bicarbonate	264 mg/L
Carbonate	0.00 mg/L
Chloride	4.50 mg/L
Sulfate	23.8 mg/L
Metals – Total	
Aluminum	0.043 mg/L
Arsenic	0.053 mg/L
Cadmium	<0.001 mg/L
Chromium	0.001 mg/L
Copper	<0.005 mg/L
Iron	0.043 mg/L
Lead	<0.001 mg/L
Lithium	0.058 mg/L
Manganese	0.047 mg/L
Nickel	0.008 mg/L
Selenium	<0.005 mg/L
Silicon	5.33 mg/L
Strontium	2.69 mg/L
Vanadium	<0.001 mg/L
Zinc	<0.050 mg/L
Metals – Dissolved	
Aluminum	<0.010 mg/L
Arsenic	0.050 mg/L
Cadmium	<0.001 mg/L
Calcium	23.6 mg/L
Chromium	<0.001 mg/L
Copper	<0.005 mg/L
Iron	<0.050 mg/L
Lead	<0.001 mg/L
Lithium	0.058 mg/L
Magnesium	13.8 mg/L
Manganese	0.047 mg/L
Nickel	0.008 mg/L
Selenium	<0.005 mg/L
Silicon	5.21 mg/L
Sodium	62.5 mg/L
Strontium	1.33 mg/L
Vanadium	<0.001 mg/L
Zinc	<0.050 mg/L

Table 3. Water analysis from Keystone City Well No. 4, Keystone, South Dakota.

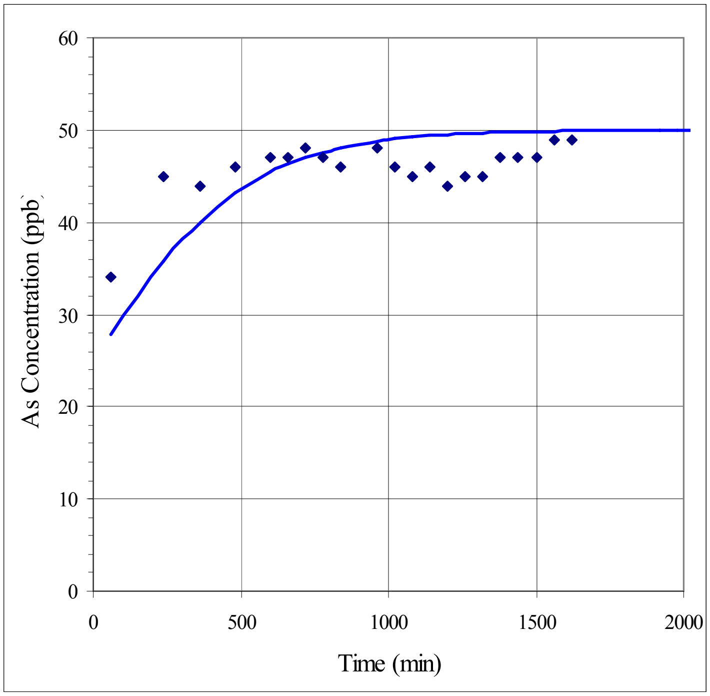

Figure 15. Results of column study using 12 inch by 1.5 inch diameter column, Minnekahta Limestone, sieve size 0.2-0.5 mm, influent arsenic concentration 50 ppb in KEY-2 water sample (source: Keystone No. 4 City Well), and a flow rate of 8 bed volumes/hour (2.8 L/hr).

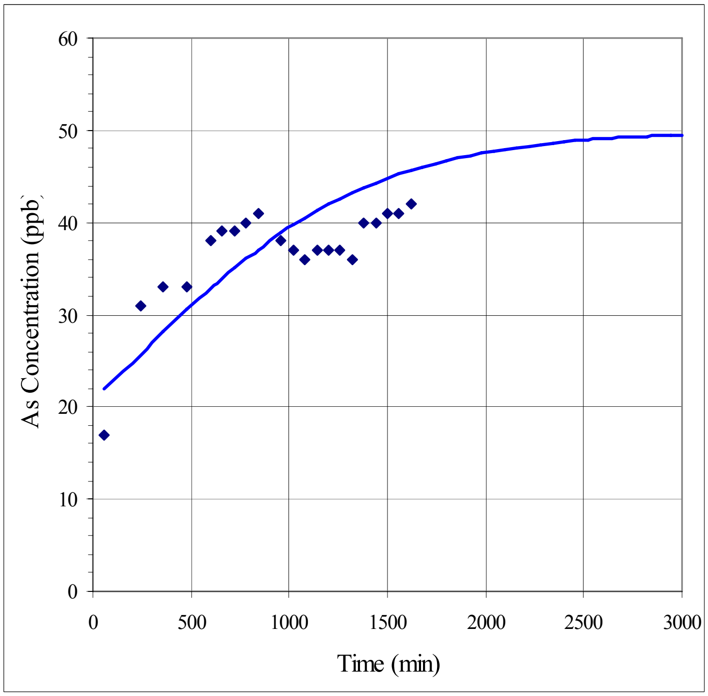

Figure 16. Results of 12 inch by 1 inch diameter column with manufactured 1-2 mm size limestone-based granules as the adsorbent, and influent arsenic concentration 50 ppb in the KEY-2 water sample (source: Keystone No. 4 City Well, Keystone, South Dakota), and a flow rate of 8 bed volumes/hour (1.23 L/hr).

CONCLUSIONS AND RECOMMENDATIONS

The purpose of this research was to develop an agglomeration process to increase the efficiency of limestone-based material to remove metals from drinking water. The end goal was to develop a granular adsorbent product that removes dissolved metals and that can be manufactured and sold for use at the drinking water source, at point-of-use, or point-of-entry. During earlier phases of this on-going project, laboratory research has shown improvements in metals removal with finer grain sizes of limestone. Agglomeration, the process of taking fine materials and forming them into larger spherical granules, provided a means to utilize the increase in surface area acquired through agglomeration while not compromising water flow through rates of the adsorbent material.

This research had three specific objectives, each of which was met during this research. Objective 1 was the development and testing of an agglomeration process for granulating limestone-based material as a filter media for metals adsorption. A bench scale agglomeration process was developed for granulating limestone powder using a coffee can, bottle roller, and water spray bottle. No specialized equipment was required to complete the process.

Objective 2 was the development of a granule formula. To develop the formula, several mixtures of limestone powder, binder, and additives were tested. It was found that cement works as an insoluble binder and can be added in powdered form to the limestone. Two additives were tested: magnesium carbonate and calcium carbonate. Magnesium carbonate was found to be the better additive for increasing arsenic removal. The granule formula chosen contained 87 percent powdered limestone (sieved to less than 74 microns), 10 percent Portland cement binder, and three percent reagent-grade magnesium carbonate powder. Preliminary testing found that limestone-based granules with three percent magnesium carbonate remove about the same quantity of arsenic as an equal mass of limestone powder.

Objective three was the investigation of the efficiency of the manufactured granules to remove arsenic, cadmium, and lead, using batch and column experiments. By performing an isotherm study, it was found that the adsorption of arsenic by limestone follows the Langmuir isotherm model. Arsenic removal by limestone does not show a pH dependence in the pH range from 4 to 10. Arsenic adsorption capacity of 1-2 mm sized manufactured granules at a starting concentration of 100 ppb arsenic was 5.4 ug arsenic per gram granules. In comparison, an equal mass of limestone powder has an arsenic capacity of 5.9 ug/gram and 1-2 mm crushed limestone chips have a capacity of 4.2 ug/gram. Agglomeration provides a means of maintaining the arsenic adsorption capacity of powdered limestone while providing a means for water flow-through in a column-type water treatment unit. This was demonstrated by column experiments which showed that 1-2 mm limestone-based granules had an adsorption capacity about four times greater than crushed limestone chips of the same diameter. Arsenic adsorption capacity by the granules dropped from 22 ug/gram to 9.8 ug/gram when naturally occurring groundwater with arsenic at 50 ppb was tested as the influent solution.

Limestone-based granules showed a very high adsorption capacity for both cadmium and lead. At concentrations from 5 to 50 ppm, greater than 99 percent of the cadmium was removed by the granules in batch experiments. Lead was removed to below detection limits for all concentrations measured (up to 3 ppm).

There are a number of directions in which this research may be expanded:

1. Test additional granule formulas. Materials such as granulated activated carbon, activated alumina, silica gel, or iron hydroxides (such as granulated ferric hydroxide) are known to remove arsenic, cadmium, and lead from drinking water. These materials could be added to the limestone granules to enhance metals removal. Also, a technique for loading iron onto the limestone surface (both crushed limestone chips and limestone powder) could be developed.
2. Test additional cation metals such as nickel, cobalt, zinc, manganese, and iron. These metals all have +2 oxidation states similar to cadmium and lead and would be expected to be removed by a limestone-based adsorbent.
3. Perform further batch experiments using naturally-occurring groundwater spiked with metals to develop isotherm models for removal by limestone powder and limestone-based granules. Naturally occurring water samples typically do not remove as much dissolved metals from solution as a starting solution of deionized water spiked with metals because of high total dissolved solids and multiple ion interferences. Further testing would quantify removal capacity of the limestone-based materials from natural waters, information that is important when designing full-scale treatment systems.
4. Perform additional column studies using naturally occurring groundwater for engineering scale-up purposes. Column experiments with multiple columns could be performed (increasing the material bed length) and the results used to scale-up a treatment unit for installation at an onsite pilot study. Column studies could be done using both crushed limestone chips and limestone-based granules as a comparison. Different metals could be tested by spiking the influent groundwater solution with the metals.
5. Test adsorption capacity with more than one metal in solution using batch and/or column studies to see if adsorption interference is observed between the metals.

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Fate of Disinfectants and Disinfection By-Products in Water Distribution Systems

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PART I.

Title: Fate of Disinfectants and Disinfection By-Products in Water Distribution Systems

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Focus Categories: WS, WQ, TRT

Descriptors: disinfection by-products, water distribution, Stage 2 D/DBP Rule,

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Problem Statement and Objectives:

Chemical disinfectants are dosed to water supplies to kill pathogenic organisms and provide a protective residual in the distribution system. The chlorine, chloramine and/or chlorine dioxide residuals decay in the distribution system through volatile escape, autodecomposition, or reaction with reducing agents such as metal pipe or organic matter. The residual disinfectants may react with organic matter to produce trihalomethanes (THMs) and haloacetic acids (HAAs). THMs and HAAs are potential carcinogens, and thus are regulated at the state and federal level under the Disinfectant/Disinfectant by-Product (D/DBP) Rule. Under the current rule, all water systems using a disinfectant sample for D/DBPs at locations representing the average and maximum residence times in the distribution system. These locations are chosen by the systems based upon known water use patterns and (primarily) distance from the water treatment plant. Annual average DBP concentrations are compared against the maximum contaminant level (MCL) to determine compliance with the Rule.

The next phase of D/DBP rule (Stage 2 D/DPB) will require systems to systematically determine the locations of the highest THM and HAA concentrations in the distribution system and sample at those locations to determine compliance with the MCL. As a result of this new approach, some South Dakota systems currently in compliance with the D/DBP Rule will likely exceed the MCL. Additionally, there are virtually no published reports relating distribution system characteristics, disinfectant types, and disinfectant residual concentrations to THM and HAA concentrations in South Dakota systems. Lacking these resources, South Dakota systems have little site-specific guidance for choosing sample locations for compliance with the Stage 2 D/DBP rule.

This project provides information that helps identify relationships between disinfection practices (distribution system characteristics, disinfectant types, and disinfectant residual concentrations) and THM and HAA concentrations in South Dakota systems. This knowledge will enable the systems to choose appropriate sample locations for the Stage 2 D/DBP rule and premeditate compliance issues, thus avoiding real costs and customer backlash associated with non-compliance with drinking water regulations.

The results will also be very helpful to primacy agencies as they work with systems to implement the Stage 2 D/DBP rule. The magnitude of system compliance efforts are a function of water source and population served by the system. Smaller systems are often required to sample less frequently and at fewer locations, requiring even greater wisdom in choosing appropriate sample locations.

South Dakota water systems use chloramine, free chlorine and chlorine dioxide as chemical disinfectants. They distribute water into systems of PVC and ductile iron pipes arranged in looped (municipal) and extensively branched (rural water) networks, containing storage tanks and booster disinfection systems. These system characteristics, along with water age and temperature, are primary factors affecting disinfectant residual decay and disinfection by-product (DBP) formation in these systems. While trihalomethanes (THMs) have been shown to increase with water age, haloacetic acids (HAAs) have been found to increase to a point in the distribution system, but then decrease, especially in areas of low disinfectant residual. Since water quality tends to have characteristics related to the hydrogeology of the water source, DBP formation in distribution systems tends to be region-specific.

The objectives of this project are to more fully understand the behavior of chlorine and disinfection by-products in distribution systems in the upper great plains region, and develop correlations between the characteristics of distribution systems and chlorine decay and DBP production. Results of the project can be used by water systems to assess the locations where water samples should be collected that will provide the maximum DBP concentration as required by the proposed Stage 2 Disinfectant/Disinfection By-Product Rule.

The project was accomplished by obtaining characteristic data from 4 water distribution systems in South Dakota that represent a range of disinfectant types, system size, and pipe materials. Correlations developed from the characteristic data were used select locations where additional samples should be collected to provide missing data regarding DBP formation. Samples collected at these locations were analyzed for DBP concentrations, the results of which were then correlated with system characteristics to develop relationships that can extend to other distribution systems.

Related Research:

The principal investigator has recently completed several studies in this region related to water treatment and distribution, the results of which provide background for this project. One such study (Cami 2003) used a hydraulic model to model chlorine/chloramine decay and DBP formation in a large rural water system in western South Dakota. However, lack of field data from the system prevented rigorous calibration of the model and prevented further applications of the knowledge gained from the study. Additionally, the impacts of disinfectants and oxidants on treated water quality have been studied at water plants treating the Missouri River (DeBoer 2003) and the Big Sioux River (Baumberger and DeBoer 2003). The three studies mentioned above all lacked full-scale distribution system data to enable correlation between water quality and system characteristics. This proposed project would provide data needed to close the gap between knowledge of system characteristics and knowledge of water quality in this region.

The principal investigator is not aware of other similar studies in this region that have been reported in the literature. However, several studies of distribution system water quality modeling (Gallard and von Gunten 2000, Vandermeyden and Hartman 2001), distribution system hydraulic modeling (DiGiano and Carter 2001), full-scale distribution system water quality (Hatcher et al. 2004), and pilot-scale distribution system water quality (Baribeau et al. 2000, Taylor et al. 2003) have been reported. The results of these studies provide correlations between system characteristics and water quality that form a basis for comparison with the results of this project. However, the results of the this study are specific to distribution systems in the upper great plains, and provide region-specific information that is generally lacking in the literature.

Methods and Procedures:

South Dakota water distribution systems were solicited to participate in this research study. The systems were selected to represent systems most significantly affected by the Stage 2 D/DBP Rule. The four South Dakota distribution systems that volunteered to be a part in the study included Sioux Falls, Watertown, Randall Community Water District (RCWD), and Mid Dakota Rural Water System (Mid Dakota). Sioux Falls and Watertown represent municipal systems that utilize a blend of ground water and surface water. Mid-Dakota and RCWD represent rural systems that utilize surface water sources. Sioux Falls and Mid-Dakota presently use chloramine as a secondary disinfectant; however, Sioux Falls used free chlorine prior to 2001. Watertown and RCWD utilize free chlorine as a secondary disinfectant. Thus, the systems provided the range of information that would characterize systems most impacted by the Stage 2 Rule.

Historical data that was requested and obtained from these systems included: disinfectant use (type, concentration), source water characteristics, chlorine residual concentrations, TTHM/HAA5 concentrations, temperature, flow, and any additional information deemed helpful to the study. Hydraulic models of the systems were reviewed when available. Some of the systems provided more information than others due to greater sampling obligations for the Stage 1 D/DBP Rule. Information was also obtained from the South Dakota Department of Environment and Natural Resources (SDDENR) as well as from volunteering consecutive systems.

ESRI ArcGIS 9.0® and Microsoft Excel® were used to analyze the factors affecting DBP formation in South Dakota systems. The main factors analyzed include: disinfectant residual type and concentration, temperature, and relative water age. ESRI ArcGIS 9.0® was utilized to provide a statistically based, visual representation of the spatially and temporally varied disinfectant residuals in each system. Data were also analyzed using Microsoft Excel® and correlations were made relating the aforementioned factors to DBP formation. Once trends had been established, maximum TTHM/HAA5 locations were predicted and two rounds of TTHM/HAA5 sampling were scheduled for the months of highest and lowest temperature. This is a similar procedure as would be followed for systems developing an Initial Distribution System Evaluation (IDSE) required by the Stage 2 D/DBP Rule. Field sampling was scheduled and completed in three of the four distribution systems. The samples were collected in August, 2005 and March, 2006.

Results and Discussion:

Factors that typically influence DBP formation include disinfectant type, disinfectant dose, source water quality and bromide content, temperature, water age, pH, pipe type and wall environment, and distribution system layout (Adams 2005, Carlson and Hardy 1998, Clark and Sivaganesan 1998, EPA 2003, Liang and Singer 2003). Based on historical data from water systems examined in this study, the main factors influencing DBP formation in South Dakota appear to be residual disinfectant type, temperature, and water age. It will be important for water distribution systems to analyze these three factors in order to accurately develop their IDSE. Additional factors certainly have a potential to effect DBP formation in these systems but were not extensively researched in this study. This is either because the factors were held relatively constant and thus would not contribute to DBP concentration and disinfectant residual variations, or they were not factors that water distribution systems could easily use to predict peak THM and HAA5 locations for their IDSE. They were and should, however, be considered and will thus be mentioned in the results and discussion.

Residual Disinfectant Literature has shown that chemical disinfectants can react with the natural organic matter (NOM) present in water to form DBPs (Adams et al. 2005, Carlson and Hardy 1998, Speight and Singer 2005). Studies have also shown that there are correlations that can be made relating disinfectant residual characteristics and behavior with DBP formation in water distribution systems (Clark and Sivaganesan 1998, Speight and Singer 2005). The DBP concentrations in the four South Dakota systems were shown to be notably affected by residual disinfectant type, concentration, and behavior. Residual disinfectant and DBPs were correlated in these systems.

Residual Behavior Watertown and RCWD use chlorine (free chlorine) as a secondary disinfectant. Mid-Dakota uses chloramine as a secondary disinfectant. Sioux Falls switched from free chlorine to chloramine as the secondary disinfectant in 2001 and thus contributed chlorine data prior to June of 2001 and chloramine data thereafter. The disinfectant changeover in Sioux Fallswas very beneficial for the purpose of comparing the behavior of the two residual types, and, consequently, Sioux Falls data were frequently used as the basis for comparison to the other systems. Based on the data provided by these systems, chloraminated systems yielded more stable and persistent disinfectant residuals throughout the distribution systems. Results from the systems using free chlorine were found to be less stable and less persistent. Figure 1 illustrates the relative variations of disinfectant residuals throughout the distribution systems using chloramine and free chlorine as secondary disinfectants.

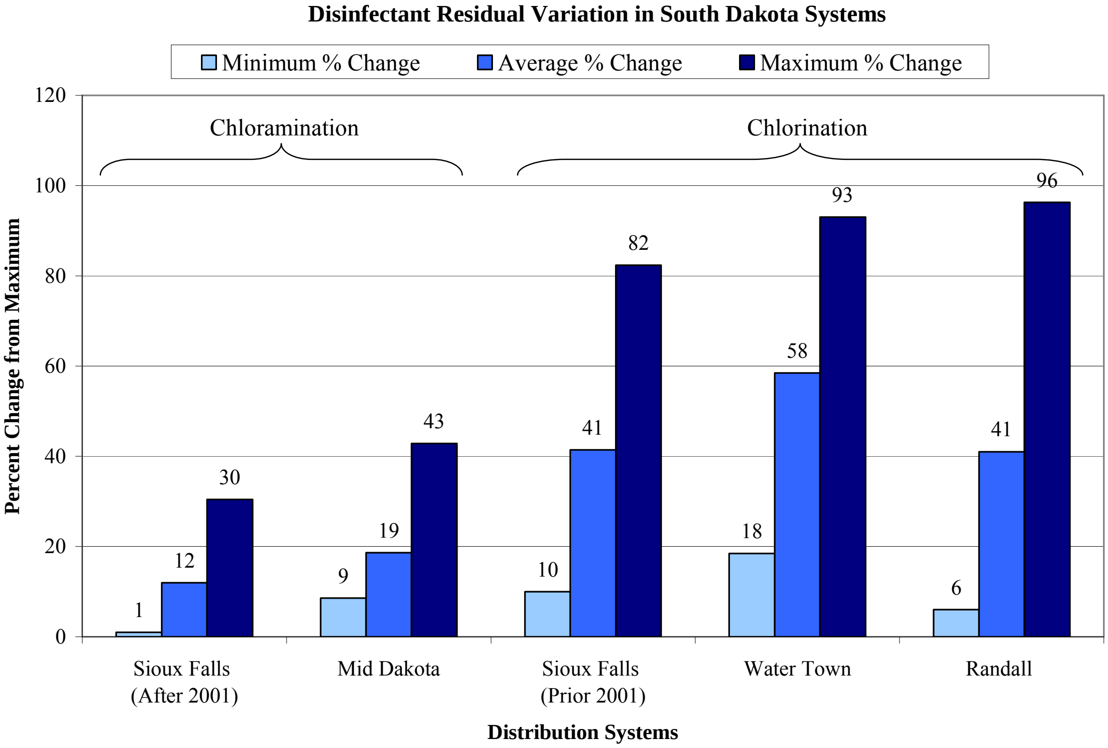

Figure 1. A comparison of disinfectant residual persistence and stability for four water systems

Figure 1 shows that the systems utilizing chlorine exhibited percent differences across their systems ranging from 6 to 96 percent while the systems utilizing chloramine had percent differences across the system ranging from 1 to 43 percent. The lower percent difference across the systems indicates that chloramine exhibits a higher stability and more persistent residual than does free chlorine. These results agree with studies reported in literature that found chloramine residuals were consistently more stable across a distribution system (Norton and LeChevallier 1997, Sung et al. 2005).

The spatial analysis features of ESRI ArcGIS 9.0® were used to envision residual dose and behavior across the distribution systems. Kriging was used to estimate chlorine residual concentrations where field sample data were not available, enabling development of maps showing chlorine residual contours across the distribution system. These maps were developed on quarterly intervals using historical data, with selected months also being representative of temperature variation and water usage. Figure 2 illustrates the variation of chlorine residual across the Sioux Falls water distribution system in February 2001, ranging between 1 and 2.5 mg/L. The brown (darker) color represents higher chlorine residual concentrations, and the lighter (yellowish) color represents lower chlorine residual concentrations. In comparison, Figure 3 shows the variation of a chloramine residual for the city of Sioux Falls, South Dakota in February of 2002. The consistent brown color in Figure 3 exemplifies the conclusion that chloramine is a more persistent residual than is chlorine and indicates the residuals are at a higher concentration than when free chlorine is used as the secondary disinfectant. Relative to implementing the Stage 2 D/DBP Rule, these results infer systems utilizing free chlorine will likely have good potential to create correlations between chlorine residual and DBP formation, since greater residual decay occurs across the system. On the other hand, systems utilizing chloramine as a secondary

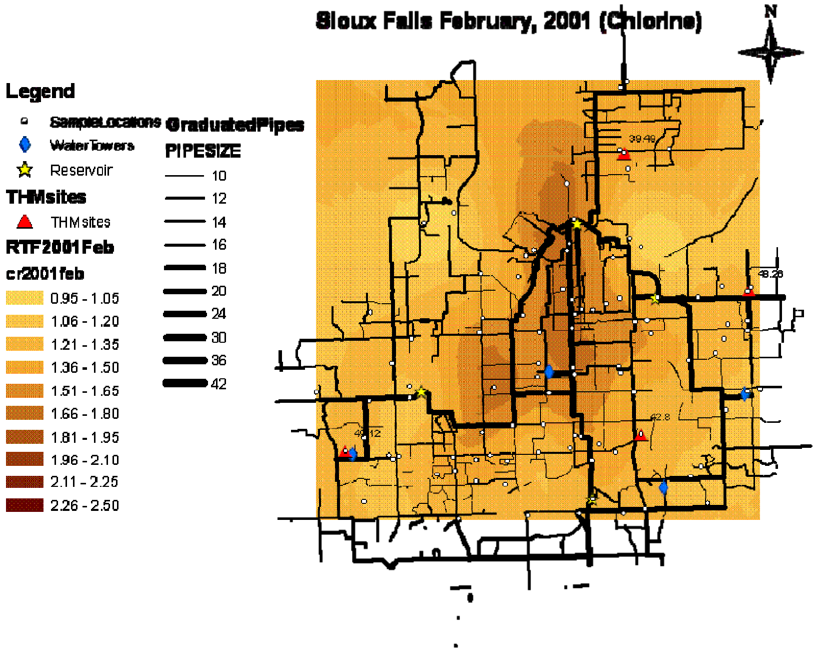

Figure 2. Chlorine residuals present in the Sioux Falls water distribution system (February 2001).

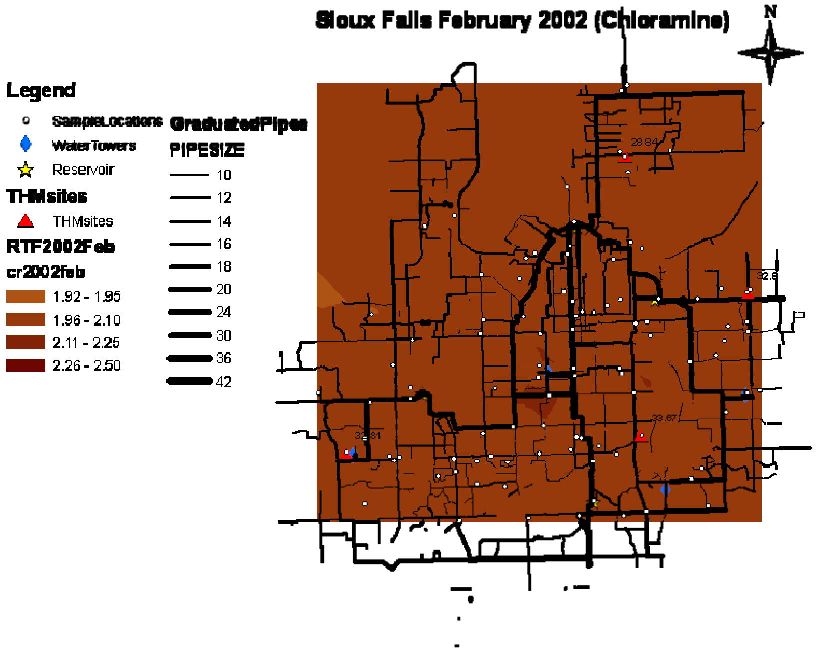

Figure 3. Chloramine Residuals present in the Sioux Falls water distribution system (February 2002).

disinfectant will experience greater difficulty creating reliable correlations, since the residual disinfectant residual concentrations exhibit little variation across the distribution system.

Residual Type-Impact on DBPs Free chlorine reacts with NOM in the water to form DBPs at a faster rate then does chloramine. The DBP data collected and analyzed for the South Dakota systems exhibited this quality. Generally, the systems utilizing chlorine had higher THM/HAA values then the systems using chloramine. The data in Table 1 indicate higher THM/HAA5 concentrations in systems utilizing free chlorine as a disinfectant residual rather than chloramine.

Table 1. Ranges of THM/HAA5 concentrations for four South Dakota water distribution systems

	CHLORINATION		**CHLORAMINATION**	
	THM	**HAA**	**THM**	**HAA**
Water System	**mg/l**	**mg/l**	**mg/l**	**mg/l**
Sioux Falls	29 -140	9.4-52	20-59	6.8-27
Watertown	25.8-142	4.5-128		
Mid Dakota			17.8-57	8.6-46.4
RCWD	30.2-100	4.5-91		

Sioux Falls provides an excellent example of the impact of disinfectant residual type on DBP formation. Figure 4 illustrates the behavior THM and disinfectant residual levels over time in Sioux Falls.

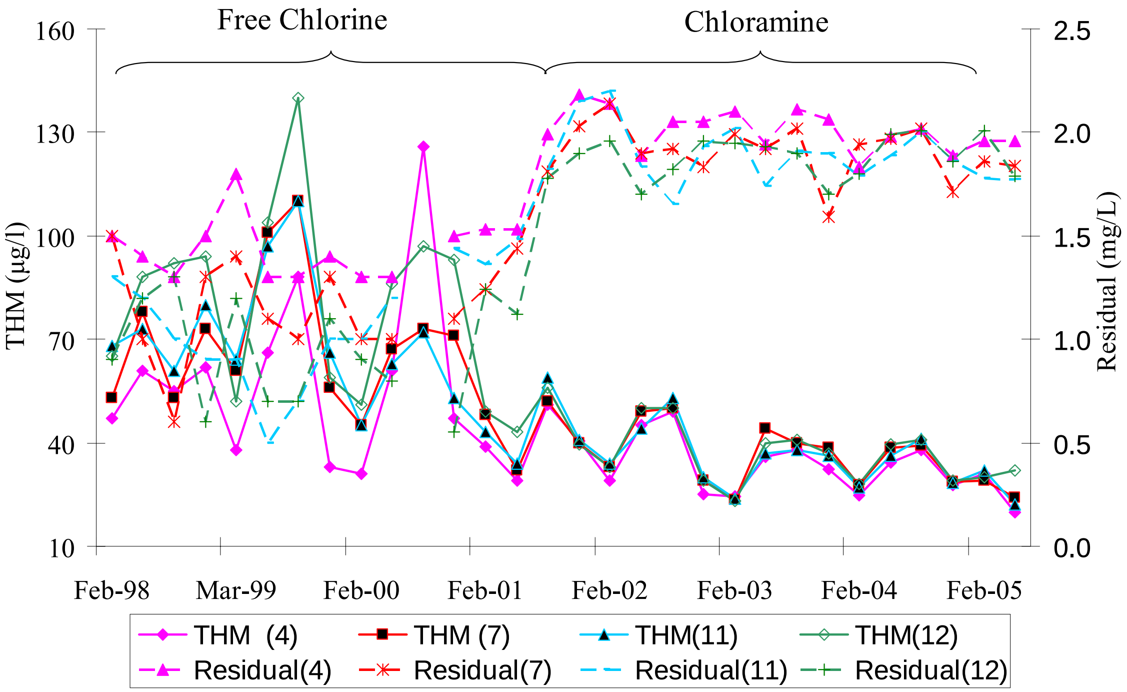

Figure 4. Sioux Falls historical THM concentrations and disinfectant residual concentrations. (Numeric values 4, 7, 11, and 12 represent different sample locations.)

Sioux Falls initiated secondary disinfection with chloramine residual in 2001. From Figure 4, one can see how the chlorine residuals and THM concentrations varied widely when free chlorine disinfection was utilized. THM concentrations are elevated and at times exceeded regulatory MCLs, although the system was always in compliance with the pertinent MCLs when the annual average concentrations were calculated for compliance. After switching to chloramine as a secondary disinfectant, THM concentrations decreased markedly and were more uniform across the distribution system. Chlorine residual concentrations increased and were more consistent. Data from other water distribution systems in South Dakota yielded similar relationships between disinfectant type and DBP production. Acknowledging the other possible affecting factors that could skew observable correlations, it is also evident that the other systems utilizing free chlorine resulted in higher overall THM/HAA5 values than did systems utilizing chloramine (see Table 1).

Residual Concentration-Impact on DBPs Studies have shown that the relative concentrations of DBPs increase with decreasing disinfectant residual creating an inverse relationship between residual disinfectant concentration and DBP formation (Clark et al. 1998, Gang et al. 2002). This is apparent in South Dakota systems utilizing either free chlorine or chloramine although the chloramine concentration exhibited lower impact on DBP formation than free chlorine. Figure 5 illustrates the inverse correlation between TTHM and chlorine residual for RCWD.

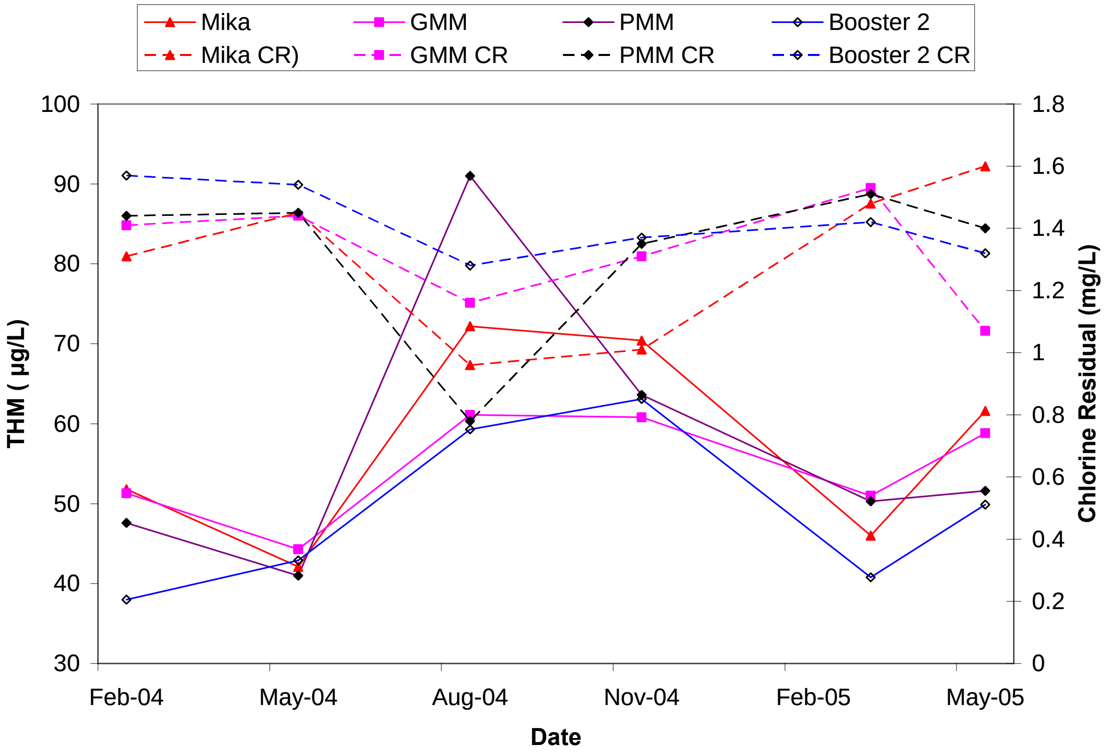

Figure 5. Free Chlorine residual and the TTHM concentration with respect to the date. Mica, GMM, PMM, and Booster 2 represents different sample locations.

In Figure 5, one can see that the peaks in TTHMs typically occur at periods of lower chlorine residuals. Similar analysis of the four South Dakota systems produced comparable results. Figure 5 also shows the peak TTHM concentration occurred in the month of August which will support a subsequent conclusion that temperature is also an important factor affecting the formation of DBPs.

While TTHMs have been found to form directly from the consumption of chlorine (Clark and Sivaganesan 1998, Pereira et al. 2004), HAAs have been found to increase to a point in a distribution system and then decrease due mainly to biological activity and chemical degradation of one of the forms of HAA (trichloroacetic acid) to TTHM. HAAs have been found to degrade when the disinfectant residual decays to a concentration of approximately 0.5 mg/l or less (Chen and Weisel 1998). This effect was observed in the Watertown Lake Plant HAA data on a few occasions.

In regard to the impact on IDSE implementation, based on the South Dakota systems reviewed in this study, systems would typically find highest THMs in areas of lowest free chlorine or chloramine residual. In areas where the free chlorine residual drops below 0.5 mg/L, HAA5s may decrease through degradation, and thus the highest HAA5s would be found in the distribution system adjacent to the low chlorine residual location. Systems in South Dakota using chloramine as a secondary disinfectant would typically experience very low variation in DBP concentrations (both TTHM and HAA5) and low variation in chlorine residuals as well. In chloraminating systems, the maximum TTHM and HAA5 concentrations both would likely exist at the maximum residence time in the system.

Temperature Research has shown that DBP concentration and rate of formation tends to increase with increases in temperature (Clark and Sivaganesan 1998). A study by Chen and Weisel (1998) found that TTHM concentrations in summer were almost double the concentrations in winter but found that HAA5s did not exhibit a statistically significant increase in concentration in summer versus winter. They also found that the reaction rate of DBPs increases with increase in temperature - the higher temperature in the warm season accelerates the rate of DBPs production in the distribution system as compared to the cold season. Temperature variations occur more predominantly in surface waters rather than ground waters. Lastly, temperature effects are more typically pronounced in systems utilizing free chlorine rather than chloramine.

Temperature appeared to have a direct affect on the formation of DBPs in South Dakota systems. In the four systems examined in this study, DBP concentrations were higher in the summer than in the winter. Figure 6 shows the effect of temperature on the formation of DBPs in RCWD, a system using free chlorine. Generally speaking, each of the four locations in Figure 6 exhibits higher DBP values with increasing temperature. Specifically, TTHMs are shown in this figure. The average rate of change of

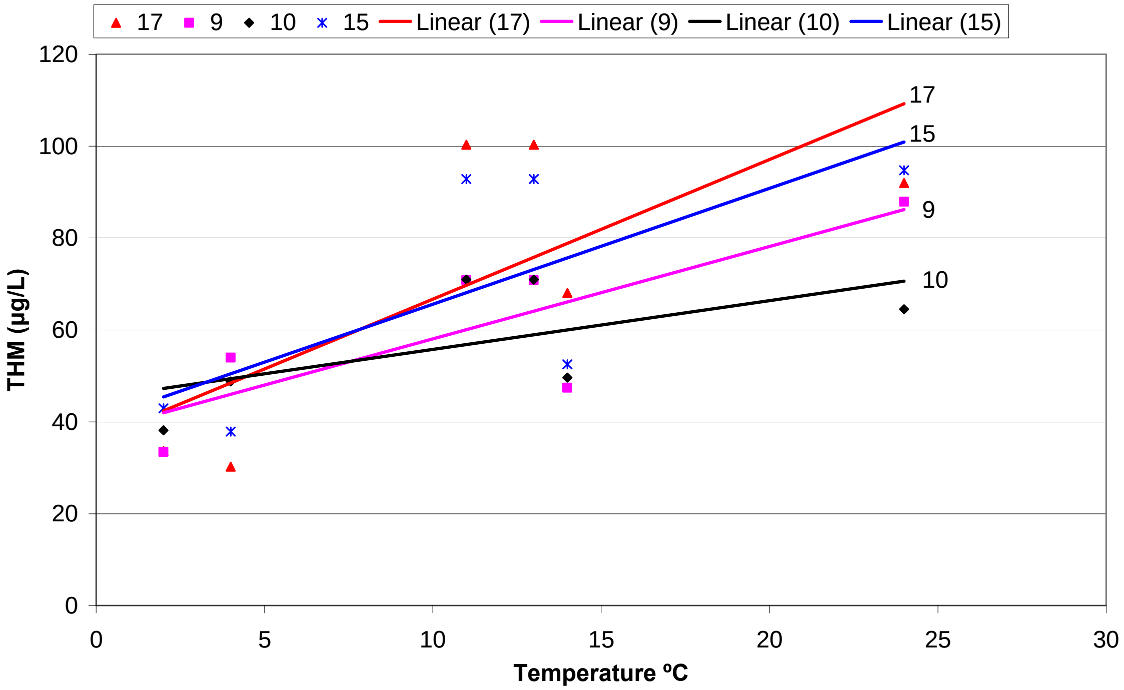

Figure 6. THMs versus Temperature in Randall Community Water District, a system using free chlorine. Numeric values 17, 9, 10, and 15 represent different sample locations.

TTHM with respect to temperature (change in TTHM per degree change in temperature) is 0.9 µg/L. HAAs, not shown, exhibited a less pronounced effect but did exhibit higher values in summer than in winter. These patterns were comparable in the other systems using free chlorine as a disinfectant as well.

The temperature effect in the systems utilizing chloramine was less than in the systems using free chlorine. Figure 7 shows the impact of temperature on DBPs for Mid Dakota, a system that uses chloramine as a residual disinfectant.

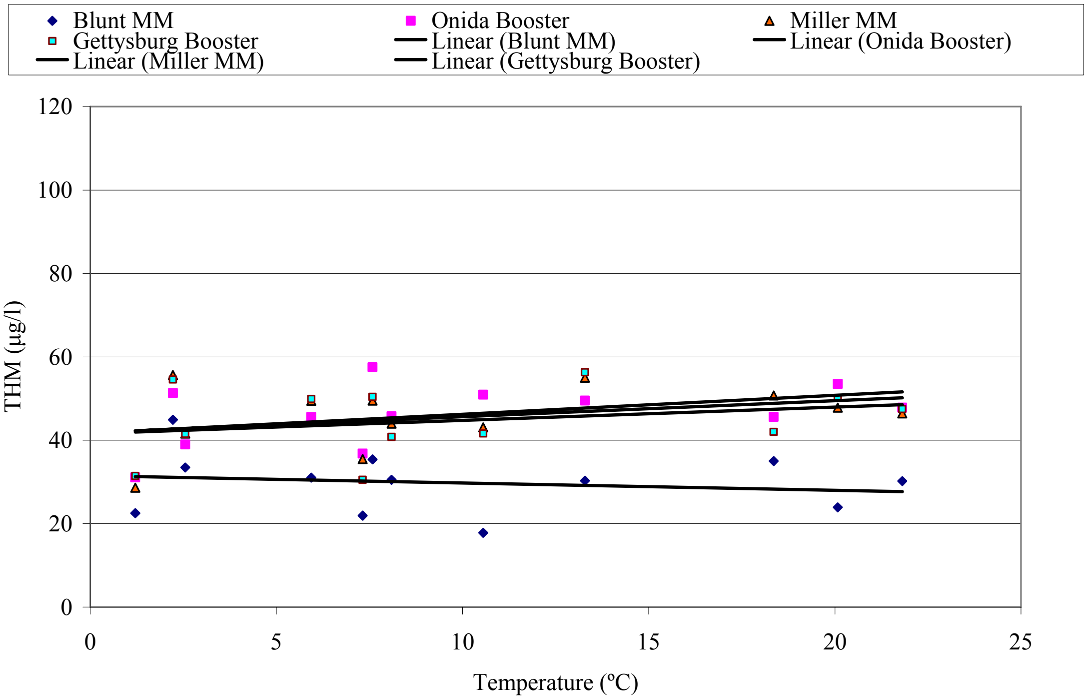

Figure 7. Relationship between the DBP and temperature in chloraminating system (MDRWC). Blunt MM, Onida Booster, Miller MM and Gettysburg Booster are sample locations.

Although the effect of temperature appears not as strong as in the systems using free chlorine, the overall trends in the systems using chloramine nonetheless exhibit increasing DBP concentrations with increasing temperature. The average rate of change of TTHM with respect to temperature (change in TTHM per degree change in temperature) was found to be 0.2 µg/L.

Figure 8 illustrates TTHM behavior in the city of Sioux Falls prior and after the switch to chloramination. From Figure 8, one can see that the concentration as well as rate of change of TTHM is higher in warmer months (May through Aug.) compared to colder months (Nov. through Feb.) supporting earlier stated conclusions. The temperature effect is generally present whether free chlorine or chloramine is used.

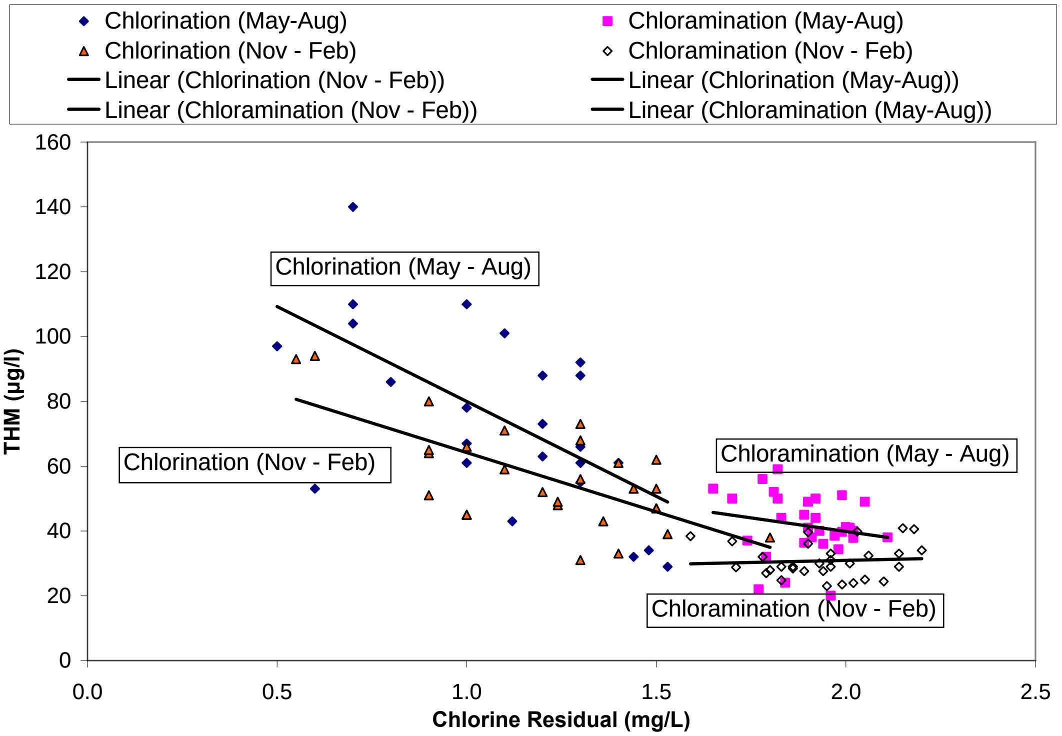

Figure 8. Temperature effect on THM in Sioux Falls distribution system. (May–Aug. represents the warmer months and the Nov.– Feb. represents the colder months.)

It is important to consider the comparative impact that this factor had on DBP formation observed in this research. In all the systems that used surface water or blended surface/ground water sources, peak DBP concentrations occurred in the warmest months. As stated previously, surface waters generally experience greater temperature fluctuation and degrees of water quality variation than do ground waters. This, in turn, effects DBP formation. Generally, higher DBP values are expected during the summer months. This can also be seen in Figure 4 shown previously.

The trend of increased DBP formation with increased temperature may not be true in ground water systems (that exhibit minimal temperature change throughout the year). This is illustrated in Figure 9, showing the variation in DBPs, specifically THM concentration measured at two sites in Brookings, SD from January 2004 to December 2005. Brookings water distribution utilizes groundwater as its water source.

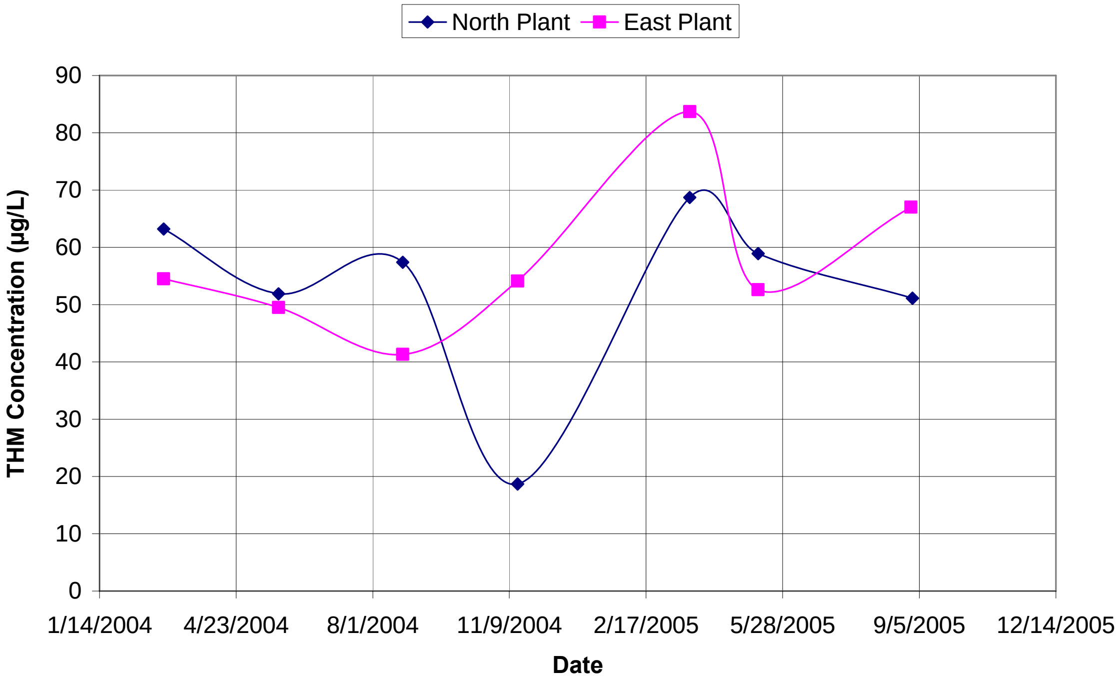

Figure 9. THM concentration in the Brookings distribution system from 2004 to 2005.

As shown in Figure 9, maximum THM concentrations occurred during the cold season. The likely reason for this behavior is the fairly constant temperature of ground water. Since much less water is used in the winter than summer, the water age in the system is much longer in the winter, yielding longer reaction times to form THMs. Because of this, water age predominates over temperature as a major factor effecting DBP formation, and DBP concentrations increase in the winter.

Water Age As water age increases, the reaction time between DBPs and NOM naturally present in water increases. If water age models have not been developed from existing hydraulic models, water age in a distribution system can be approximated from factors such as distance and flow. Typically, water ages increase with decreasing flow (demand) and with distance from the treatment plant. Other factors that can increase water age include storage tank operations and pipe network configuration. These factors were not studied for this project but can have a marked effect on water age and thus DBP formation. Figure 10 and Figure 11 illustrate two of the factors that can be attributed to water age and thus DBP formation.

Figure 10 compares flow versus DBPs, specifically TTHMs for the city of Sioux Falls during chloramination from 2001 to 2005. As flow increases, DBP concentrations increase, indicating another factor affecting DBP formation. The relationship between flow and DBP concentrations illustrated in Figure 10 are opposite what might be expected. This apparent contradiction is most likely due to temperature variations. Temperature was observed to play a greater role in DBP formation than water age for the four surface water systems examined in this study.

Distance from the treatment plant also affects water age. This is a factor that could have an effect on wholesaler and consecutive systems that must transport water over great distances for water use. Figure 11 consists of one of the wholesale South Dakota systems studied and a variety of consecutive systems. This system utilizes free chlorine as a secondary disinfectant.

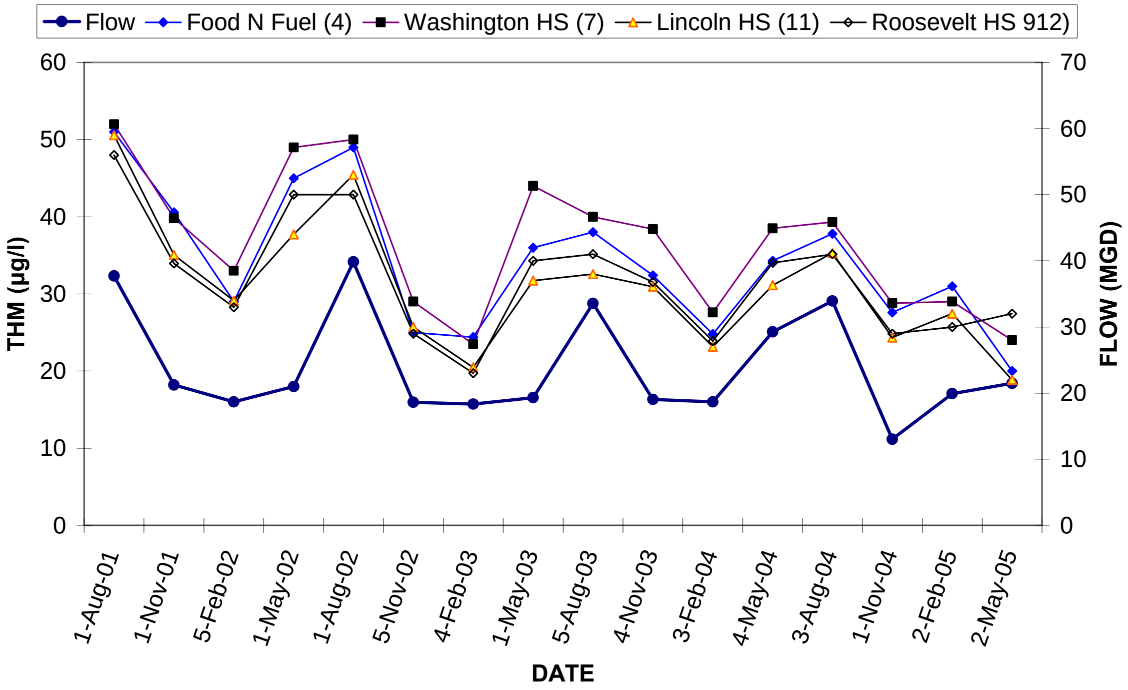

Figure 10. Variation of flow and THM from Feb. 1998 to May 2001 for Sioux Falls, SD. (during chloramination)

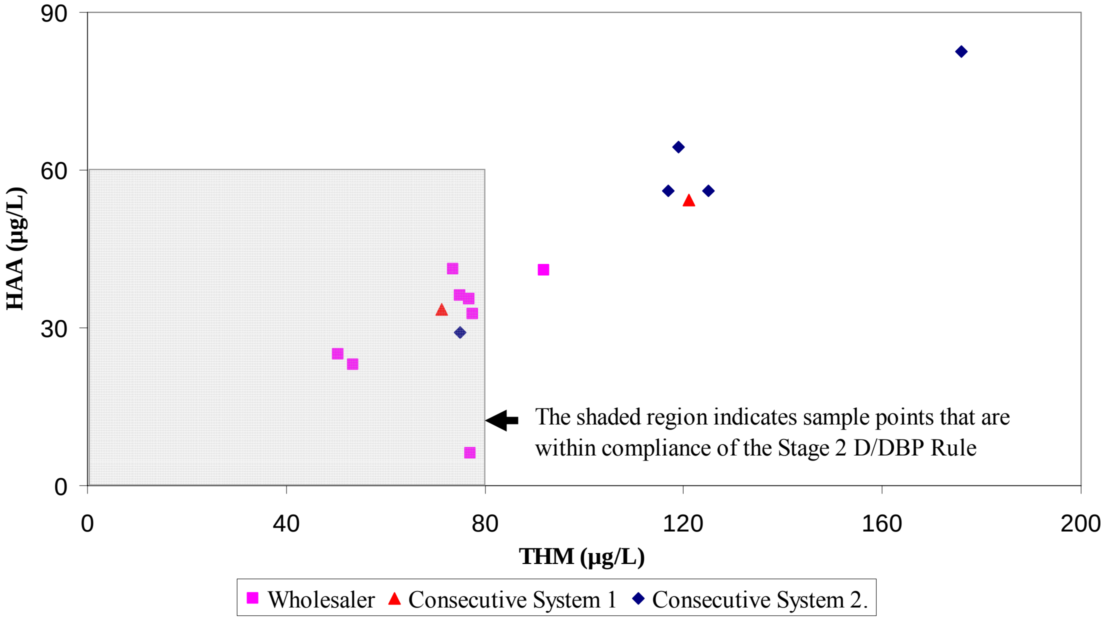

Figure 11. DBP's in Consecutive Systems in which the Wholesaler Boosts Free Chlorine Residual

As observed in the right-hand side of Figure 11, DBP formation has continued to increase throughout as the water moved from the wholesaler to the consecutive system. In this case, unless measures are taken, the two consecutive systems may be out of compliance for the Stage 2 D/DBP Rule. In this system, the chlorine residual was boosted at the location where the water passed from the wholesaler to the consecutive system. The chlorine levels maintained in this system supported both THM and HAA production.

<u>TTHM and HAA5 Behavior</u> Other than the Watertown Lake Plant distribution system mentioned above, THM and HAA5 concentrations both increased with water age in the distribution systems examined in this study. One potential reason for this is that the disinfectant residual maintained in the distribution systems are typically greater than 1.5 mg/L for systems using free chlorine and greater than 2.0 mg/L for systems using chloramine. Figure 12 shows the THM and HAA5 relationship in Sioux Falls, SD when free chlorine was utilized.

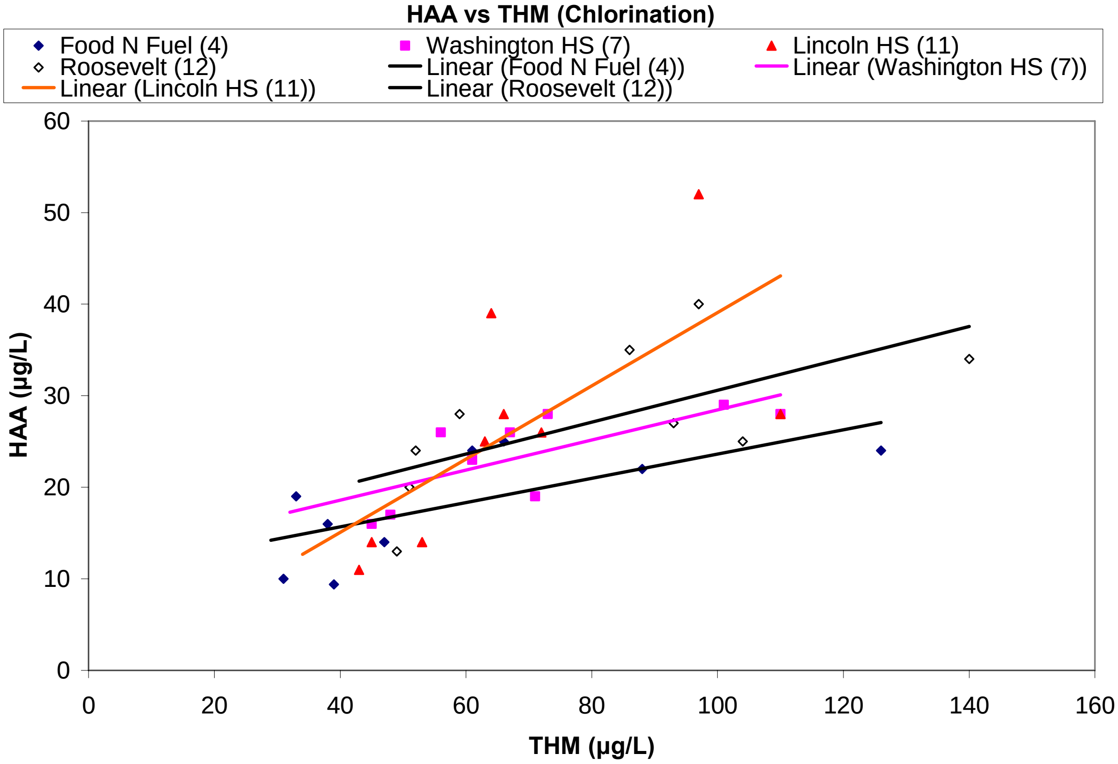

Figure 12. Relationship between HAA5 and THMs in Sioux Falls, SD, during the use of free chlorine as a secondary disinfectant. Numbers 4,7,11 and 12 are sample locations.

The approximate correlations shown in Figure 12 reveal that for every 1 µg/L THM formed, 0.13 to 0.4 units of HAA5 were formed. Similarly, for RCWD (not shown), for every 1 µg/l of TTHM formed, an average of 0.2 µg/l of HAA5 were formed. This would suggest that the rate of TTHM formation was higher in than HAA5 formation in the distribution system. Also, the difference in slopes shows the irregularity and the sensitivity of THM and HAA5 formation to the other factors such as water age and temperature. Figure 13 illustrates TTHM versus HAA5 formation for Sioux Falls, SD after the switch to

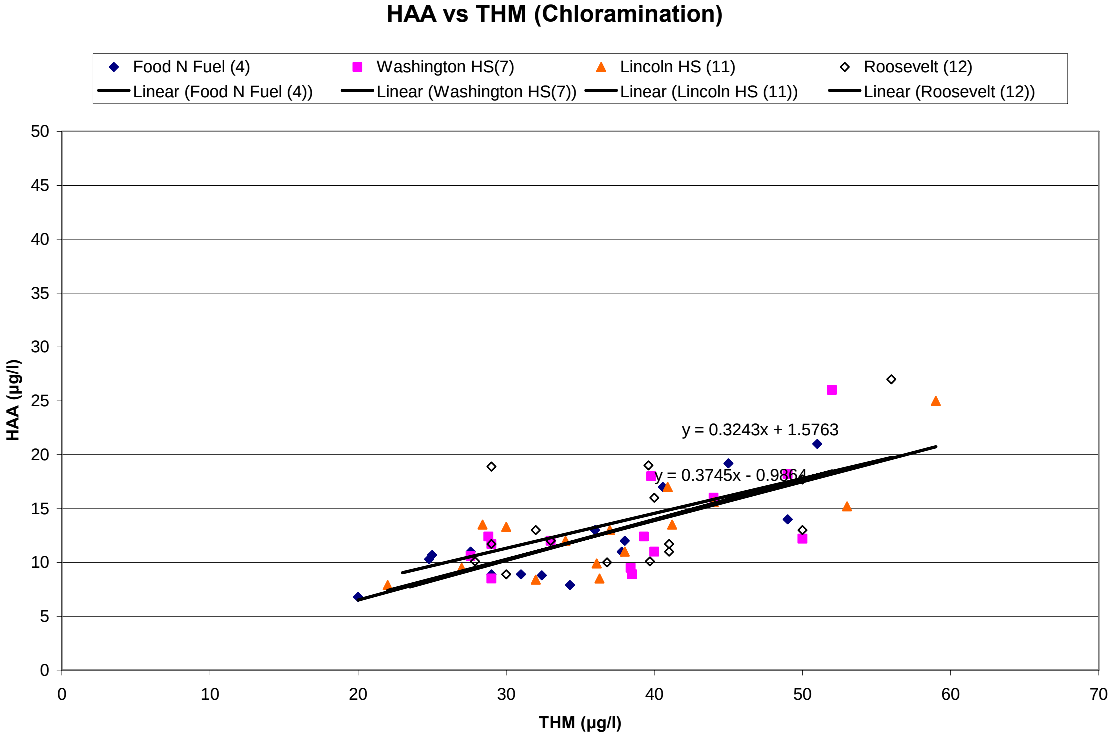

Figure 13. Relationship between HAA5 and THMs in Sioux Falls, SD, after the start of chloramination. Numbers 4,7,11 and 12 are sample locations.

chloramination. These data are more closely bunched together, indicating less variation between THM and HAA5 across the distribution system.

Other Factors Studies have shown that the main factors that typically influence DBP formation include disinfectant type, disinfectant dose, source water quality and bromide content, temperature, water age, pH, pipe type and wall environment, and distribution system layout (Adams et al. 2005, Carlson and Hardy 1998, Clark and Sivaganesan 1998, EPA 2003, Liang and Singer 2003). Factors not extensively studied in this research project either because the factors were held relatively constant and thus would not contribute to DBP concentration and disinfectant residual variations, or they were not factors that South Dakota water distribution systems could easily use to predict peak THM and HAA5 locations for their IDSE include:

- **Source water quality:** The most significant source water quality parameter affecting DBP formation is the NOM content and type. NOM can be divided into a hydrophobic or hydrophilic carbon type. Hydrophobic carbon contributes to DBP formation more than the hydrophilic portion; however, the hydrophobic is also the portion that is most readily removed by enhanced coagulation with alum or ferric chloride (Liang and Singer 2003).
- **pH:** pH affects the rate of DBP formation. THMs formation rates have been found to increase as pH increases above 8 while HAA5 formation rates have been found to increase at a lower pH of 6 (Diehl et al. 2000, Liang and Singer 2003).
- **Pipe type**: Pipe type and the corresponding wall environment can affect DBP formation by affecting the disinfectant residual through reactions at the pipe wall (Hallam et al. 2002). The

rural water systems studied in this project were comprised almost entirely of PVC pipe which is a considered a relatively non-reactive pipe that would not impact chlorine residual. The municipal systems both contain older distribution system sections that have sections that are not PVC and are most likely lined iron pipe. However, some unlined iron pipe might also be present. These areas could have influence DBP formation by exerting a chlorine demand at the pipe wall.

- **Pipe environment**: Biofilm can have a pronounced effect on DBP formation, specifically HAA5 formation. Chen and Weisel found that as THMs continued to increase in distribution systems, HAA5s were found to increase and than decrease. Speight and Singer noticed the same phenomena. This occurs where biofilms are present, and biofilms typically grow at low disinfectant residuals. There were no strong trends that exemplified these phenomena in any of the distribution systems that were analyzed most likely due to high enough residuals that prevent biofilm growth in the distribution systems.
- **System Layout**: The distribution systems analyzed consisted of two municipal or looped systems and two rural or branched systems. All had storage tanks. These characteristics directly relate to water age. Looped systems are designed to minimize distribution system dead ends that could increase water age substantially. Branched systems in comparison are used primarily for transport of water over long distances. Storage facilities store and thus age water especially if the storage system has the possibility of stagnation due to lack of movement. All of these characteristics can affect DBP formation because of the effect they have on water age. Thus, the system layout affects DBP production directly through water age.

Principal Findings and Significance

The following relationships were observed from data collected at the 4 water distribution systems that were in studied South Dakota.

- Chlorine residuals can be used as an indicator of THM formation – the lower the chlorine residual, the greater the THM concentration.
- Systems using free chlorine as a secondary disinfectant exhibited higher DBP formation than systems utilizing chloramine.
- Systems using free chlorine will likely find chlorine residuals a useful tool for identifying areas of high DBP concentrations for the maximum DBP sample site required by the Stage 2 DBP rule. However, systems using chloramine residuals will likely have less success identifying high DBP concentrations using disinfectant residual concentration because of the quenching effect of chloramine on DBP formation. For these systems, water age will likely be the best indicator of DBP formation.
- When the chlorine residual in the distribution system is held above 0.5 mg/L, chlorine residuals can also be used as an indicator of HAA5 formation – the lower the chlorine residual, the greater the HAA concentration. When the chlorine concentration falls below 0.5 mg/L, HAA5 concentrations may drop, likely due to microbial degredation.
- When surface water is used as the water source, DBP concentrations increase with increased treated water temperature. However, due to lack of temperature variation, ground water systems exhibiting significant DBP formation may experience highest DBP formation in the winter, when water age is the longest.
- When the chlorine residual in the distribution system is held above 0.5 mg/L, TTHM and HAA5 concentrations increase with water age in the distribution system. The rate if increase is greater when using free chlorine as the final disinfectant as compared to using chloramine as the final disinfectant.
- In the presence of substantial free chlorine residual, TTHM and HAA5 concentrations continued to increase in consecutive distribution systems, potentially to concentrations exceeding the MCLs.

These findings will enhance the ability of regulators and systems to meet the requirements of the

Stage 2 D/DBP rule. Consecutive systems who have not yet gathered D/DBP data are encouraged to obtain early samples to be able coordinate compliance efforts with the wholesale system.

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PART II:

Information Transfer Program:

The results of this study were to be communicated to engineers, operators and managers of water supply systems through presentations at conferences. Thus far, the results have been communicated through presentations at 4 conferences and with poster presentations at 2 events.

Student Support:

Two graduate students studying in the Civil and Environmental Engineering Department, Morgan Gagliano and Akshaya Niraula, were supported by this research project. They have used the data in preparation of their MS in Engineering thesis. They expect to graduate in the Summer/Fall 2006 term.

Publications/Presentations:

Presentations:

Delvin E. DeBoer. "SDSU Water Research: DBPs, Membrane Concentrate, Mixing." Presented at the 71th Annual Conference of the South Dakota Water and Wastewater Association, Brookings, SD, September 15, 2005.

Delvin E. DeBoer. "Fate of DBPs in the Distribution System: Preparing for the IDSE." Minnesota Section of AWWA 89th Annual Conference – Duluth, MN, October 6 2005.

Akshaya Niraula and Delvin E. DeBoer. "Fate of DBPs in the Distribution System: Preparing for the IDSE." South Dakota Water and Wastewater Association Water Operators Seminar, Sioux Falls, SD, February 8, 2006.

Delvin E. DeBoer. "Fate of Disinfectants and DBPs in Water Distribution Systems." 18th Annual Environmental and Ground Water Quality Conference, Pierre, SD, March 16, 2006.

Poster Presentations:

Morgan Gagliano. "Fate of Disinfectants and Disinfectant Byproducts in Water Distribution Systems." South Dakota Board of Regents Research Day at the Capital, Pierre, SD, February 8, 2006.

Morgan Gagliano and Akshaya Niraula. "Fate of Disinfectants and Disinfectant Byproducts in Water Distribution Systems." Surface Water Treatment Workshop, ND/MN/SD Sections of AWWA, Fargo, ND, April 26, 2006.

Invertebrate and Aquatic Plant Studies of Two Mesotrophic Lakes in South Dakota

Basic Information

Title:	Invertebrate and Aquatic Plant Studies of Two Mesotrophic Lakes in South Dakota
Project Number:	2004SD20B
Start Date:	3/1/2004
End Date:	2/28/2006
Funding Source:	104B
Congressional District:	First
Research Category:	Not Applicable
Focus Category:	Ecology, Acid Deposition, Water Quality
Descriptors:	
Principal Investigators:	David R. German

Publication

Annual Progress Report

State Water Resources Institute Program (SWRIP)
March 2005 to February 2006

Title: *Invertebrate and Aquatic Plant Studies of Two Mesotrophic Lakes in South Dakota*

Principal Investigator: Mr. David R. German, South Dakota Water Resources Institute

Introduction

The purpose of this study was to describe the macro-invertebrate fauna, the aquatic macrophyte community, and current trophic state of two relatively rare lake habitats in South Dakota. The potential for exotic species such as zebra mussels, eurasian water milfoil and the rusty crayfish to negatively impact the native fauna in these lakes was a concern.

Introduced exotic species could have a severe impact on native flora and fauna in these lakes. In 1986, a ship released ballast water into Lake St. Clair, Michigan and introduced the zebra mussel. This organism can kill native clams and competes with larval fish and other aquatic organisms for food. The zebra mussel has spread throughout the Great Lakes and has been found in the Mississippi and Minnesota Rivers. If this exotic species is introduced into Enemy Swim and Pickerel Lakes it is expected to have a large impact on the ecological balance.

A second exotic species, Eurasian water milfoil, has already been introduced to Lake Sharp in South Dakota. Milfoil is a fast growing aquatic weed that crowds out native plants and forms dense mats in shallow water. This plant can reproduce from a single fragment and is easily carried from lake to lake on boats and trailers. Fishermen traveling from Minnesota to fish in South Dakota waters may eventually introduce zebra mussels and/or milfoil to these habitats. South Dakota fishermen traveling to the Missouri River or out-of-state lakes are also potential carriers of exotics back to South Dakota.

If invasion by exotic species does occur, data from this study would allow future managers set goals for reestablishing a more natural ecosystem and mitigate the impacts of the exotic species. Data presented in this summary report includes invertebrates and plants collected since 2002 and results of water sampling conducted in 2005.

Objectives

The objectives of this research were to:

1). To prepare a list of aquatic macro-invertebrates and their relative abundance for all major habitats in Enemy Swim and Pickerel Lakes.

2). To prepare a list of aquatic plants and their general distribution in both lakes.

3). To assess the current trophic state of the lakes by monitoring selected water quality parameters.

Lake Description

Enemy Swim is natural glacial lake located in northeast Day County about eight miles north of the town of Waubay, South Dakota. The lake covers approximately 2,146 acres and has a 22,310-acre watershed located mostly in Roberts County. The lake is not deep enough to form a thermally stratified system in most years (German, 1997). Most natural lakes in South Dakota are simple basins, but Enemy Swim has been described by Game, Fish and Parks Fisheries personnel as a "complex lake basin with highly variable substrate including rock, boulders, gravel, cobble, sand, etc." The varied habitat accounts for a diverse population of fish; twenty-one species have been reported in Enemy Swim Lake.

Pickerel Lake is also a natural glacial lake located in northeastern Day County about ten miles north of the town of Waubay, South Dakota. The lake covers approximately 955 acres to an average depth of 22 feet, and a maximum depth of 43 feet. The lake bottom is predominately rubble with scattered areas of sand and gravel. Silt and organic clay are found in the bays and deeper areas of the lake. Haworth (1972) reported that the north bay of the lake contains 24 feet of sediment, which has accumulated over the 12,000 years since the lake was formed. The lake is deep enough to thermally stratify during the summer months (Day Conservation District, 1991, German, 1996).

Pickerel Lake is the deepest natural lake in South Dakota and also has a highly variable substrate with many of the same characteristics as Enemy Swim. The main difference between the lakes is Enemy Swim has an extensive system of shallow bays whereas Pickerel Lake has fewer bays and much more deep water habitat.

Enemy Swim and Pickerel Lakes are mesotrophic to lower eutrophic which represents a relatively rare habitat in South Dakota. Most natural lakes are eutrophic to hypereutrophic and many have been identified as impaired because they are not meeting their designated beneficial uses. The State of South Dakota has assigned the following beneficial uses to both Enemy Swim and Pickerel Lakes:

- Warm water permanent fish life propagation
- Limited contact recreation

- Immersion recreation; and
- Wildlife propagation and stock watering

Methodology

Objective 1: Aquatic macro-invertebrates

Shoreline habitats sampled for macro-invertebrates included rocky/rubble, sand/gravel, and muddy vegetation and were sampled at several locations. Mid-lake samples were collected in several locations to describe deeper water habitats. Samples were collected by a variety of methods including the use of Eckman dredges and a Wildco Biological Dredge. Manual collection of organisms by D-frame dip net and picking organisms from rocks, plants, and submerged wood was also conducted. Snorkeling and scuba gear were used to collect clams in deeper waters. A photographic history of many organisms collected was also kept during 2002 and 2003 and was expanded in 2005.

Objective 2: Aquatic macrophytes

Plants were collected by wading in shallow water and by snorkeling. All sampling locations were recorded using a portable GPS unit. Aquatic plant identifications were verified by Dr. Gary Larson at South Dakota State University (SDSU). Several specimens were pressed and added to the SDSU Herbarium collection under the direction of Dr. Gary Larson.

Objective 3: Trophic State

Trophic state was assessed by using the same water quality monitoring methods used during the Lake Protection study in 1991-1995 (German, 1997). In-lake water quality samples were collected with a Van Dorn-type water sampler from three mid lake stations using a boat. A composite surface sample for the lake was formed by mixing equal amounts of water from each site. A composite near bottom sample was formed by mixing water collected near the bottom from each of the three sites in each lake. Parameters analyzed on lake samples included:

1. Total phosphorus
2. Total dissolved phosphorus
3. Organic nitrogen
4. Ammonia
5. Nitrate + nitrite
6. Suspended solids
7. pH
8. Air and water temperature
9. Dissolved oxygen
10. Secchi depth
11. Chlorophyll a (surface samples only)

12. Fecal coliform bacteria (surface samples only)

Water sampling was conducted at Enemy Swim Lake in mid June, July and August in 2005. Sampling was conducted at Pickerel Lake in mid May, June, July, August and September in 2005. Dennis Skadsen from the Day Conservation District, the Pickerel Lake Sanitary District, and the Enemy Swim Lake Sanitary District contributed to this effort.

Results

Objective 1: Aquatic macro-invertebrates

The invertebrate fauna in both lakes are more diverse than expected based on published studies of the invertebrate fauna in other South Dakota lakes. (Benson and Hudson 1975, Boehmer et. al. 1975, Donaldson 1979, Gengerke and Nickum 1972, German 1978, Hartung 1968, Hudson 1970, Schmulbach and Sandholm 1962, Smith 1971, Wolf and Goeden 1973). The presence of fishflies and stoneflies was particularly surprising because they had not been reported from this area of South Dakota prior to this study. Johnson (1997) first reported the presence of fishflies in South Dakota based on larvae collected in Lacreek refuge. The first adults reported in the state were collected during this project at both Enemy Swim and Pickerel Lakes in 2002. These specimens have been deposited in the Insect Research Collection at SDSU. Insects comprised the largest portion of the invertebrate fauna. The list of macro-invertebrates collected and identified so far at Enemy Swim and Pickerel Lakes is presented in Table 1.

Insects

Order	Family	Genus/Species	Common Name
Ephemeroptera			
	Ephemeridae	*Hexagenia* sp.	
	Heptageniidae	*Stenonema* sp.	
	Caenidae	*Caenis* sp.	
Odonata			
	Aeshnidae		
		Anax junius	Common green darner
		Aeshna constricta	Lance-tipped darner
		Aeshna interrupta	Variable darner
	Corduliidae		
		Epitheca cynosura	Common basketail
	Limbellulidae		
		Libellula luctuosa	Widow skimmer
		Libellula Lydia	Common whitetail
		Libellula pulchella	Twelve-spotted skimmer
		Libellula quadrimaculata	Four-spotted skimmer
		Sympetrum costiferum	Saffron-winged meadowhawk
		Sympetrum internum	Cherry-faced meadowhawk
		Sympetrum rubincundulum	Ruby meadowhawk
		Sympetrum obtrusum	White-faced meadowhawk

Order	Family	Genus/Species	Common Name
Odonata (cont.)			
	Limbellulidae (cont.)	*Sympetrum corruptum*	Variegated meadowhawk
		Perithemis tenera	Eastern amberwing
		Pachydiplax longipennis	Blue dasher
		Erythemis simplicicollis	Eastern pondhawk
		Tramea lacerata	Black saddlebags
		Tramea onusta	Red saddlebags
		Leucorrhinia intacta	Dot-tailed whiteface
		Celithemis eponina	Halloween pennant
		Celithemis elisa	Calico pennant
	Coenagrionidae	Numerous species	Pond Damsels
		Enallagma antennatum	Rainbow Bluet
		Enallogma hageni	Hagen’s Bluet
Trichoptera			
	Helicopsychidae	*Helico borealis*	Snail shell caddisfly
	Hydropsychidae		
	Hydroptilidae		Micro caddisfly
	Limnephilidae	2 species	Portable case makers
	Polycentropodidae	2 species	Trumpet net Caddisfly
	Leptoceridae	5 species	Longhorned casemakers
	Phryganeidae		Giant casemakers
Megaloptera			
	Corydalidae	*Chauliodes rastricornis*	Fishfly

Hemiptera			
	Belostomatidae	*Belostoma* sp.	Small giant water bug
	Corixidae		Water boatman
	Nepidae	*Nepa apiculata*	Water scorpion
	Notonectidae		Back swimmers
	Gerridae		Water strider
Coleoptera			
	Gyrinidae		Whirligig beetles
Diptera			
	Ceratopogonidae		Noseeums
	Chironomidae	Numerous species	Midges
	Sub Family	Tanypodinae:	
		Procladius sp	
		Tanypus sp	
	Sub Family	Chironomidae:	
		Chironomus plumosus	
		Chironomus attenuatus	
		Chironomus sp. (several)	
		Cryptochironomus sp.	
	Culicidae		Mosquitoes
	Chaoboridae	*Chaoborus* sp.	Phantom midge

Crustacea

Order	Family	Genus	Common Name
Amphipoda			
	Gammaridae	Gammarus	Scuds
Decapoda			
	Cambaridae	*Orconectes virilis*	Northern crayfish

		Orconectes immunis	Calico crayfish
		Unidentified Species	

Snails

Order	Family	Genus	Common Name
Lymnophila			
	Physidae		Tadpole snails
	Lymnaeidae		Pond snails

Clams

Order	Family	Genus	Common Name
Pelecypoda			
	Unionidae	*Lampsilis*	Fat mucket
		Anodonta grandis	Giant floater

Hirudinea (leeches)

Order	Family	Genus	Common Name

Objective 2: Aquatic macrophytes

The list of macrophytes collected and identified so far at Enemy Swim and Pickerel Lakes is presented in Table 2. No new records of aquatic macrophytes for the state or for the area were recorded. There was no evidence of Eurasian water milfoil in either lake.

Table 2. Macrophytes collected at Enemy Swim and Pickerel Lakes

Common Name	Scientific Name
Water plantain	Alisma gramineum
Coontail	Ceratophyllum demersum
Needle spikesedge	Eleocharis acicularis
Spikerush	Eleocharis erythropoda
Mare's-tail	Hippuris vulgaris
Water milfoil	Myriophyllum sibiricum
Naid	Najas flexilis
pondweed	Potamogeton friesii
Variable pondweed	Potamogeton gramineus
Illinois pondweed	Potamogeton illinoensis
Floatingleaf pondweed	Potamogeton natans
Sago pondweed	Potamogeton pectinatus
Whitestem pondweed	Potamogeton praelongus
Claspingleaf pondweed	Potamogeton richardsonii
Flatstem pondweed	Potamogeton zosteriformis
Widgeon-grass	Ruppia cirrhosa
Arrowhead	Sagittaria latifolia
Hardstem bulrush	Schoenoplectus acutus
River bulrush	Schoenoplectus fluviatilis
Common bladderwort	Utricularia vulgaris
Water stargrass	Zosterella dubia

Objective 3: Trophic State

Water quality data collected for Enemy Swim Lake in 2005 is presented in Table 3. Water quality data collected for Pickerel Lake in 2005 is presented in Table 4.

Trophic state is a way of describing how productive or enriched a lake is compared to other lakes. Lakes range from nutrient poor (oligotrophic), to moderately rich (mesotrophic), to highly enriched (eutrophic), to excessively enriched (hypereutrophic). Pickerel Lake and Enemy Swim Lake exhibited characteristics of lakes that are described as mesotrophic to early eutrophic in 2005 (Tables 3 and 4).

Table 3. Water quality values from Enemy Swim in 2005.

Enemy Swim Lake, 2005 Parameters	Unit	**May** 5/20/2005		**June** 6/17/2005		**July** 7/15/2005		**August** 8/15/2005		**September** 9/15/2005	
Air Temperature	°C	NA		NA		NA		NA		NA	
Transparency	ft	10.3		10.1		7.4		5.5		5.6	
		Surface	Bottom	Surface	Bottom	Surface	Bottom	Surface	Bottom	Surface	Bottom
Water Temperature	°C	NA	NA	19.7	19.2	26.0	24.7	22.7	22.0	19.7	19.2
Dissolved Oxygen	mg/L	NA	NA	8.1	7.6	7.8	7.0	6.0	5.6	8.1	7.6
pH	--	8.49	8.57	8.60	8.61	8.51	8.43	8.61	8.55	8.60	8.61
Suspended Solids	mg/L	2.75	43.70	3.25	4.84	3.50	4.00	5.16	11.30	4.67	7.00
Total Kjeldahl N	mg/L	0.59	0.70	0.74	1.01	0.70	0.83	0.78	0.79	0.91	0.82
Nitrate (NO_3)	mg/L	0.04	0.03	0.03	0.03	0.06	0.07	0.03	0.04	0.06	0.05
Organic N	mg/L	0.57	0.67	0.66	0.92	0.64	0.75	0.73	0.71	0.83	0.77
Ammonia (NH_3)	mg/L	0.02	0.03	0.08	0.09	0.06	0.08	0.05	0.08	0.07	0.05
Total Phosphorus	mg/L	0.01	0.02	0.02	0.02	0.02	0.02	0.04	0.03	0.03	0.03
Total Dissolved P	mg/L	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01

Table 4. Water quality values from Pickerel Lake in 2005.

Pickerel Lake, 2005 Parameters	Unit	**May** 5/20/2005		**June** 6/17/2005		**July** 7/15/2005		**August** 8/15/2005		**September** 9/15/2005	
Air Temperature	°C										
Transparency	ft	8.3		15.3		13.8		6.6		5.4	
		Surface	Bottom	Surface	Bottom	Surface	Bottom	Surface	Bottom	Surface	Bottom
Water Temperature	°C	15.2	12.3	19.5	18.7	25.8	23.3	22.8	22.3	19.7	19.6
Dissolved Oxygen	mg/L	10.7	8.9	12.2	9.0	10.5	1.8	8.7	6.8	12.5	7.5
pH	--	8.63	8.42	8.35	8.18	8.3	7.81	8.22	8.12	8.48	8.5
Suspended Solids	mg/L	3	8	1.75	2.25	1.25	5	4	12	13.8	15.7
Total Kjeldahl N	mg/L	0.66	1.01	0.73	0.76	0.77	1.11	0.76	0.97	0.81	0.89
Nitrate (NO_3)	mg/L	0.03	0.04	0.03	0.03	0.06	0.06	0.04	0.04	0.06	0.05
Organic N	mg/L	0.64	0.99	0.65	0.60	0.69	0.75	0.73	0.83	0.74	0.85
Ammonia (NH_3)	mg/L	0.027	0.016	0.086	0.165	0.081	0.356	0.03	0.146	0.075	0.042
Total Phosphorus	mg/L	0.024	0.043	0.029	0.038	0.026	0.046	0.018	0.053	0.035	0.059
Total Dissolved P	mg/L	0.016	0.012	0.016	0.022	0.014	0.019	0.012	0.015	0.01	0.012

Transparency

The transparency of lake water is important to the aesthetic value of a lake. In most lakes, water transparency is determined by variations in suspended sediment or algal populations. It is used as an indirect indicator of algal populations in lakes without significant suspended sediment. In reservoir systems, transparency may be a function of sediment load or turbidity. Most of the time water transparencies in Pickerel and Enemy Swim Lakes are a function of algal populations. Transparency in Enemy Swim Lake ranged from 10.3 feet in May 2005 to 5.5 feet in August 2005 (Table 3). Transparency in Pickerel Lake ranged from 15.3 feet in June 2005 (Table 4) to 5.4 feet in September 2005 (Table 4). Transparencies in this range are common in mesotrophic to eutrophic lakes.

Suspended Solids

Low suspended solids concentrations are desirable in lakes for aesthetic reasons and maintenance of a healthy fishery. Fish populations can be affected by high suspended solids in several ways. Fish can be killed directly or their growth, resistance to disease and reproduction success may be reduced. Migrations can also be affected (EPA, 1976). High suspended solids concentrations result in reduced aesthetic value of a lake which can limit recreational use. The state standard for maintaining a warm water permanent fishery is 90 mg/l. This standard was not exceeded on any of the sampling dates reported for either lake in 2005 (Tables 3 and 4).

Phosphorus

Phosphorus is required for the growth of all forms of algae, but relatively small quantities are needed. If other nutrients are available, one pound of phosphorus can produce 500 pounds of algae (Wetzel, 1983). It is often the nutrient that limits the growth of algal populations. It is therefore also the nutrient that must be controlled in order to maintain good water quality. Total phosphorus concentrations for Enemy Swim Lake surface samples ranged from 0.013 mg/l on 5/20/05 to 0.040 mg/l on 8/15/05 (Table 3). Total phosphorus concentrations for Pickerel Lake surface samples ranged from 0.018 mg/l on 8/15/05 to 0.035 mg/l on 9/15/05 (Table 4). Using phosphorus as a trophic state index, a concentration of .03 mg/l value represents the border between mesotrophic and eutrophic lakes. A concentration of 0.03 to 0.1 mg/l would be classified as eutrophic (Wetzel, 1983). Enemy Swim would be classified as mesotrophic and Pickerel Lake would be mesotrophic to eutrophic based on phosphorus concentrations.

Dissolved phosphorus is the most available form for use by algae and other plants. It is rapidly consumed by algae and seldom reaches high concentrations in surface waters unless other factors are limiting algal growth. Dissolved phosphorus enters lakes from runoff but it is also released from sediments into the water under anoxic conditions (oxygen levels near zero). In 2005 higher concentrations of dissolved phosphorus were observed in bottom waters compared to surface waters in Pickerel Lake in June, July, August, and September. Pickerel Lake was weakly stratified and oxygen concentrations were lower in deeper waters compared to surface waters in May, June, and July 2005 (Table 4). This probably contributed to the release of phosphorus from the sediments in Pickerel Lake. In Enemy Swim Lake concentrations of oxygen in surface samples was essentially the same as bottom waters in 2005 (Table 3). Concentrations of dissolved phosphorus were observed in bottom water samples at Enemy Swim were similar when compared to surface water samples in 2005.

Nitrogen

Nitrogen is present in lakes in several forms, both inorganic and organic. The inorganic forms (ammonia, nitrite and nitrate) are important nutrients available for plant growth. Organic nitrogen represents nitrogen incorporated into living (or once living) material and can be used to define trophic state. Wetzel, (1983) reports that mesotrophic lakes worldwide generally range from 0.4 to 0.7 mg/l and eutrophic lakes have up to 1.2 mg/l of organic N. Organic N concentrations in Pickerel Lake surface water ranged from 0.80 mg/l on 8/13/04 to 0.99 mg/l on 9/14/04 (Table 4) indicating eutrophic conditions. The median concentration of organic nitrogen in Pickerel Lake from 1991 to 1995 was .62 mg/l which represents mesotrophic conditions (German, 1997). This indicates a possible increase in productivity in the lake and a move toward more eutrophic conditions based on organic nitrogen. Organic N concentrations in Enemy Swim surface samples ranged from 0.67 mg/l on 6/18/04 to 0.86 mg/l on 8/13/04 (Table 3). The median concentration of organic nitrogen in Enemy Swim surface samples from 1991 to 1995 was 0.68 mg/l which represents mesotrophic conditions (German, 1997).

Ammonia is generated as an end product of bacterial decomposition of dead plants and animals and is also a major excretory product of aquatic animals. Ammonia is directly available for plant growth and is the most easily used form of nitrogen. It can support the rapid development of algal blooms if other nutrients are present. Ammonia concentrations in Pickerel Lake surface samples ranged from 0.03 mg/l on 5/20/05 (Table 4) to 0.086 mg/l on 6/17/05 (Table 4). Ammonia concentrations in Pickerel lake surface samples ranged from below the detection limit to 0.15 mg/l with a median value of 0.01 mg/l in the period from 1991 to 1995 (German, 1997). Ammonia concentrations in the bottom of Pickerel Lake samples ranged from 0.016 mg/l on 5/20/05 to 0.356 mg/l on 7/15/06. This is much higher than the ammonia in surface samples and probably represents the release of ammonia from sediments. Ammonia concentrations in Enemy Swim surface samples ranged from 0.02 mg/l on 5/20/05 to 0.08 mg/l on 6/17/05 (Table 3). Bottom samples exhibited slightly higher ammonia concentration when compared to surface samples.

Dissolved Oxygen

Adequate dissolved oxygen is necessary to maintain a healthy lake. Lakes with good oxygen concentrations throughout the year are more likely to have a diverse population of aquatic organisms rather than one that is dominated by a few hardy species. Low oxygen concentrations are detrimental to populations of many organisms and usually reduces diversity and stability in a lake ecosystem. .

Oxygen concentrations can also affect other chemical parameters in lakes. For example, when anoxic conditions form at the bottom of a lake, dissolved phosphorus, ammonia, and hydrogen sulfide and other undesirable substances are released from the lake sediments into the water column. These nutrients can contribute to algal growth when lakes turn over. Ammonia and hydrogen sulfide may also be toxic to aquatic organisms if they are present in sufficient concentrations.

Oxygen concentrations in Pickerel Lake and Enemy Swim Lake surface samples were consistently above the state standard of 5.0 mg/l in 2005. This was also true of the 1991-1995 period as well (German, 1997). Weak thermal stratification and depressed oxygen concentrations near the bottom were observed in Pickerel Lake in July 2005. From 1991 to 1995 oxygen concentrations less than 5 mg/l were observed near the lake bottom on 10 of 15 sampling dates (German, 1997).

Overall the health of Pickerel Lake and Enemy Swim is good although they may be drifting to a more eutrophic condition. Collecting additional data in the next few years will help determine if this is normal year to year variation or a true trend. A large amount of construction has occurred around the shoreline in recent years especially on Pickerel Lake and land in CRP has been put back into production, which can cause more nutrients to enter the lake. Installation of the sewer system on Pickerel Lake has probably helped reduce nutrients from septic tanks but other measures to control nutrients from construction, farming and lawn care should be considered.

Youth Education

The scope of the project includes the participation of several local agencies. Dennis Skadsen of the Day Conservation District initiated an educational program called “Lakes Are Cool” to educate youth in the watershed about the importance of keeping lakes clean. The project involves teachers and students from local schools that participated in the “Lakes Are Cool” program that was held in 2002, 2003, 2004, and 2005 as part of the Enemy Swim Lake Watershed Improvement Project. This EPA funded watershed project sponsored by the Day Conservation District allowed local students to participate in the collection and identification of aquatic macro-invertebrates.

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Evaluating Glomalin and Its Role in the Sorption of Organic Contaminants

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Final Report

State Water Resources Institute Program (SWRIP)
March 2005 to February 2006

PART I.

Title: Evaluating Glomalin and Its Role in the Sorption of Organic Contaminants

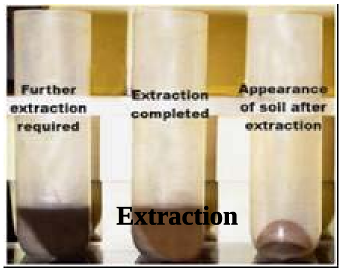
Investigators: Dr. Frank V. Schindler, Dept. of Chemistry and Biochemistry
Dr. James A. Rice, Dept. of Chemistry and Biochemistry

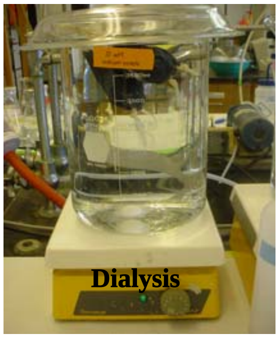
The following is a final report discussing the results of the research project titled ”Evaluating Glomalin and Its Role in the Sorption of Organic Contaminants.” This project was designed and proposed as a three year project, but received only one year of funding. The information gathered from this project has provided valuable information regarding glomalin’s chemical and structural character, which may have profound implications regarding glomalin’s role in contaminant sorption and soil nutrient availability. The objective of this study was to conduct preliminary elemental and structural characterization of glomalin extracted from whole soils through a series of chemical assays and solid-state NMR and infrared spectroscopic techniques.

Methodology:

Soils. The mineral soil samples used in this study were collected in eastern South Dakota, USA and are described by Malo (1994). They are referred to as the Poinsett silt loam (fine-silty, mixed, superactive, frigid Calcic Hapludolls), and the Hetland (fine, smectitic, frigid, Pachic Vertic Argiudolls). The Pahokee peat, an International Humic Substances Society (IHSS) reference material (Cat. No. BS103P), was used in this study and contained 45% C, 15% ash, 4.7% H, and 3.1% N (IHSS, 2006). All mineral soils were collected as random grabs from the top 0-15 cm of soil after the initial plant litter had been removed (Kohl, 1999). Mineral soil samples were air dried, crushed, and sieved to pass a 2mm mesh.

Glomalin extraction and purification. Glomalin was extracted using the total protein extraction procedure described by Wright et al. (1996). Eight mL of a 50mM sodium citrate solution was placed into a centrifuge tube containing one gram of whole soil. Samples were autoclaved for 60 minutes at 121°C followed by centrifugation at 3000 to 5000 xg for fifteen minutes to pellet the soil particles. The supernatant was decanted and stored at 4°C until purified. Repeated extractions were performed to effect complete glomalin extraction as evidenced by a transparent supernatant (Wright et al., 1996).





To assess the effect of purification method on the chemical and structural characteristics of glomalin, extracted glomalin samples were subjected to either the trichloroacetic acid (TCA) (i.e., Het-TCA, Poin-TCA or Peat-TCA) or hydrochloric acid (i.e., Het-HCl, Poin-HCl or Peat-HCl) precipitation procedures (Wright, 2004). The HCl method is recommended if the carbon (C) and nitrogen (N) concentrations are measured, since TCA may adhere to glomalin during the precipitation process and produce inaccurate C results (Wright et al., 1996). Glomalin extracts were added to centrifuge tubes in a 1:1 ratio with ice cold 20% TCA and incubated for 1 hr. Samples were centrifuged, the supernatant decanted, and the solid material reconstituted with 1 mL of 100 mM sodium borate solution. This was transferred to hydrated dialysis tubing (3500 Daltons). The tubing was placed in 10 mM borate solution (pH =8) and dialyzed at 8 hr intervals under constant stirring. The dialysis solution was changed at least 3 times to ensure proper purification. The purified dialyzate was centrifuged at 10,000 rpm for 15 min to remove any extraneous particles. The supernatant was transferred to freeze drying flasks, immediately frozen in liquid N_2, and lyophilized. Extracted glomalin samples were also purified and reconstituted similarly except 1N HCl and 0.1 M NaOH were used for precipitation and reconstitution, respectively (Wright, 2004). All reagents used in extraction and purification were purchased from Aldrich Chemical Co. Inc. at 99+% purity.

Protein Assay. The protein content of glomalin extracted from whole mineral and organic soils was quantified using the standard Bradford assay (Bradford, 1976). One hundred mg Coomassie Brilliant Blue G-250 (Sigma-Adrich Co.) was dissolved in 50 mL 95% ethanol and 100 mL of 85% phosphoric acid was added. The resulting solution was diluted to a final volume of 1 L, filtered thorough a Whatman #1 paper, and used as the color reagent for protein quantitation. Standard solutions of reagent grade Bovine Serum Albumin (Equitech-Bio, Inc., Kerriville, TX) were prepared containing 20 to 200 µg protein. Color reagent was added to both standard and sample unknowns in a 50:1 (v:v) reagent to sample ratio, vortexed, and allowed to incubate for 10 min before absorbance measure at 595 nm. The protein in unknown samples was determined by fitting a least squares regression curve of the quantity of standard protein vs. absorbance. All standard and sample unknowns possessed the same solution matrix.

Solid-state ^{13}C NMR. Glomalin was characterized by quantitative solid-state ^{13}C NMR using the technique described by Mao et al. (2000). Glomalin samples were placed in a 4 mm o.d. zirconia rotor equipped with Kel-F endcaps and characterized on a Bruker AVANCE 300 (7.4T) widebore spectrometer. All spectra were acquired at 75 MHz using direct-polarization magic angel spinning (DPMAS) combined with a spin-lattice relaxation correction (T_1^C) and total sideband suppression (CP-TOSS) (Mao et al., 2000). T_1^C values used for DPMAS ranged from 3 to 6 sec. High-power pulse lengths and power levels were optimized with respect to an external reference consisting of a mixture of L-leucine-1-^{13}C, glycine-2-^{13}C, and L-alanine-3-^{13}C in a 1:1:1 ratio. During spectrum acquisition, rotor spin rate and the number of scans were held constant at 13 kHz and 20 000, respectively. The ^{13}C NMR spectra were integrated according to the following chemical shift regions: 0-50 ppm = aliphatic carbon, 50-108 ppm = carbohydrate carbon, 108-160 ppm = aromatic carbon, and 160- 200 ppm = carboxyl carbon, and 200-220 ppm = carbonyl carbon (Mao et al., 2000; Wilson, 1987).

Chemical Analyses. Glomalin and BSA samples were sent to Huffman Laboratories, Inc. in Golden, Co. for C, H, N, O, Fe, Na, P, and ash content determinations. Iron, P, and Na were performed after mixed acid decomposition of the samples ending with complete oxidation of organic material by refluxing with perchloric acid. The diluted digestion solutions were analyzed by inductively coupled atomic emission spectroscopy (ICP-AES) following EPA method 200.7 protocol and using a Perkin-Elmer Optima 3000 analyzer. Carbon and H were determined using a custom built analyzer which uses coulometric detection. Ash content was determined by high temperature combustion of the sample until a constant weight was obtained. Moisture content of samples was determined by Karl Fisher titration. All elemental analyses presented in Table 1 are reported on a water-free basis. All non-ash elements reported on a water and ash-free basis.

Statistical Analyses. The values listed in Table 1 were compared via analysis of variance and Duncan's multiple-range posteriori test using SAS software for Windows version 8.0 (SAS Institute, 1999). All statistical comparisons were made among soil type and between purification methods and were based on duplicate values. All statistical comparisons were evaluated at the 95% probability level. Statistical evaluations listed in Table 2 are based on the mean C-distribution percentage of precipitation methods and are evaluated between soil types only. Statistical comparison of BSA and glomalin C-type distribution were not warranted since C-type distributions of BSA were based on the integration of a single NMR sample spectrum.

Principal Findings and Significance:

Selected characteristics of whole soil, glomalin extracted material, and bovine serum albumin (BSA) protein standard are presented in Table 1. The Bradford assay ranged from 54 to 114 mg protein g^{-1} of extracted material (Table 1), which corresponds to 3 to 56 mg of Bradford sensitive protein g^{-1} of soil. This range is within that reported for mineral and organic soils (Lovelock et al., 2004; Wright, 2002). On average, glomalin accounted for 25% and 52% of the total C in the mineral soils (Hetland and Poinsett) and organic soil, respectively. This is consistent with the literature for a typical mineral soil (Wright, 2002). The protein content of the glomalin extract from the peat soil was significantly higher than that of the mineral soils. No statistically significant difference ($P > 0.05$) in protein content existed between the glomalin precipitation methods (i.e., HCl vs. TCA) for the peat soil however, higher protein contents were observed in the mineral soils when HCl was used as the precipitating reagent.

It has been reported that glomalin is comprised of N-linked oligosaccharides (Wright and Upadhyaya, 1998; Wright et al., 1998). The presence of N-linked oligosaccharides on arbuscular mycorrhizal (AM) fungus hyphal protein was used to support a proposal that glomalin is a glycoprotein (Wright et al. 1998). If glomalin is a glycoprotein, it would contain significant amounts of mannose units linked to N-acetylglucosamine groups (Kyte, 1995). The NMR spectra of glomalin show very little carbohydrate carbon (Fig. 1). Even the spectrum of BSA (Fig. 1g), which contains little carbohydrate relative to a typical glycoprotein, e.g., α1-acid glycoprotein, displayed a more pronounced carbohydrate signature than the glomalin extracts (Table 2). Given glycoproteins high mannose composition, one would have expected that glomalin's ^{13}C NMR spectra show a significant carbohydrate fingerprint (Fig. 1). Literature suggests that glomalin contains approximately 60% carbohydrate (Wright and Upadhyaya, 1998) which is contrary to our findings (Table 2 and Fig. 1).

Another interesting observation is how similar glomalin is to humic substances. The solid-state ^{13}C NMR spectrum of the IHSS Pahokee Peat humic acid (PHA) fraction (IHSS, 2006) bears a carbon type distribution similar to that of the glomalin samples evaluated in this study. The PHA contains high aromatic (47%) and carboxyl (20%) carbon types and relatively low aliphatic and carbohydrate carbon (IHSS, 2006). Furthermore, the molar H:C and C:N ratios of the PHA are 0.81 and 17.8, respectively, which are similar to the glomalin ratios reported here (Table 1). Mao et al. (2000) also showed how certain humic acids contain very little aliphatic (12%) and carbohydrate (14%), but large amounts of aromatic and carboxyl carbon (i.e., 48% and 26%, respectively). Mao et al. (2000) discussed how this functional group arrangement could be expected with older humic acids given the long exposure to microorganism attack and the more rapid degradation of the easily decomposing compounds such as proteins, carbohydrates, and phenolic groups. Additional ^{13}C NMR experiments need to be performed on the humic acid fractions of the Poinsett and Hetland soils to lend additional support to the humic acid and glomalin structural similarities.

The NMR results indicate that the glomalin extracts display spectra and carbon-type distributions that are very similar to humic acid. The C/N ratios suggest that the glomalin extracts are not pure proteins, but have nitrogen contents between a protein and humic acid. Thus it appears that what is currently being operationally referred to as glomalin may actually be a mixture of humic acid and proteinaceous material. This should not be unexpected however. Both glomalin and humic acid are substances that are operationally-defined and are extracted using essentially the same set of conditions. The high pH of the glomalin extraction solution (i.e., pH = 8.0) is very likely to extract at least some humic acid because humic acid is only soluble under alkaline conditions (Stevenson, 1985). The final acid precipitation step in the isolation of glomalin is also the final step in the isolation of humic acid. Nichols and Wright (2005) have recently reached a similar conclusion. They concluded that extraction of humic acid likely co-extracted glomalin nor was it possible to isolate protein-free humic acid by first extracting the glomalin.

Preliminary matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI TOF MS) analyses of the extracted glomalin were performed on a Bruker Biflex MALDI-TOF instrument using a nitrogen laser operating at 337 nm. Resolving the spectra was difficult do to glomalin's heterogeneity. Equipment was purchased from Genomic Solutions that allow us to perform one and two dimensional separations to isolate the glycoprotein. The separation would give us a pure substance to subject to mass spectrometry for adequate protein identification. This study was a springboard for a second phase of glomalin's characterization. A student as part of the National Science Foundation's Research Experiences for Undergraduates (REU) program at SDSU will perform separations and isolations the glycoprotein, and then subject the pure substance to mass spectrometry for protein identification.

Table 1. Chemical characteristics of extracted glomalin samples and bovine serum albumin (BSA). †

Soil Type	Mass of Extract§	Protein Content¶	% C	% H	% N	% O	% P	H/C	C/N
	—— (mg g^{-1})	———	————	————	(weight %)	————	————		
Poinsett-HCl††	18	64.3a#	45.3e	5.9bc	4.0bc	44.8bc	0.100a	1.5a	13.3b
Poinsett-TCA‡	20	53.8b	41.4f	6.3ab	3.4c	48.9a	0.089ab	1.8a	14.4ab
Hetland-HCl	18	63.1a	48.9d	4.9cd	3.7bc	42.5c	0.073b	1.2b	15.6ab
Hetland-TCA	15	45.1c	44.3e	5.7bc	3.6bc	46.4ab	0.050c	1.5a	14.4ab
Pahokee Peat-HCl	414	111.8d	58.6a	4.1d	4.1b	33.2d	0.033cd	0.8c	16.6a
Pahokee Peat-TCA	402	113.7d	56.5b	4.3d	4.0bc	35.2d	0.042c	0.9c	16.3a
BSA	nd	nd	53.9c	7.1a	15.5a	23.5e	0.015d	1.6a	4.1c

† Elemental analyses are weight percents that are average of duplicate analyses. C, H, N, P, and O are reported on a moisture-free, ash-free basis.

†† 1.0 M HCl precipitation; 0.1 M NaOH reconstitution.

‡ 20% TCA precipitation; 100 mM sodium borate reconstitution.

§ milligrams of extracted material per gram of soil (i.e., initial sample mass = 1.0 g). Values are reported on an ash-free basis.

¶ milligrams of Bradford sensitive protein per gram of extracted material (n=2).

\# Means within a column followed by the same letter are not significantly different at $\alpha = 0.05$.

nd not determined.

Table 2. Carbon type distributions determined by solid-state ^{13}C NMR of glomalin extracted whole samples and bovine serum albumin (BSA).

Glomalin Type	Aliphatic (0-50 ppm)	Carbohydrate (50-108 ppm)	Aromatic (108-160 ppm)	Carboxyl (160-200 ppm)	Carbonyl (200-220 ppm)
			(% of total C)		
Poinsett-HCl†	9.2	4.7	44.3	30.2	1.6
Poinsett-TCA‡	10.6	9.9	50.8	26.7	2.7
Mean	9.9a§	7.3a	47.6a	28.5a	2.2a
Hetland-HCl	5.3	16.0	49.2	27.7	1.8
Hetland-TCA	4.4	7.1	42.1	24.2	2.2
Mean	4.9b	11.6a	45.7a	26.0a	2.0a
Pahokee Peat-HCl	3.9	11.9	49.1	30.4	4.7
Pahokee Peat-TCA	6.1	3.8	41.0	26.6	2.4
Mean	5.0b	7.9a	45.1a	28.5a	3.6a
BSA	53.5	14.9	11.9	18.9	0.8

† 1.0 M HCl precipitation; 0.1 M NaOH reconstitution.

‡ 20% TCA precipitation; 100 mM sodium borate reconstitution.

§ Means within a column followed by the same letter are not significantly different at $\alpha = 0.05$. Values represent the average of the HCl and TCA samples.

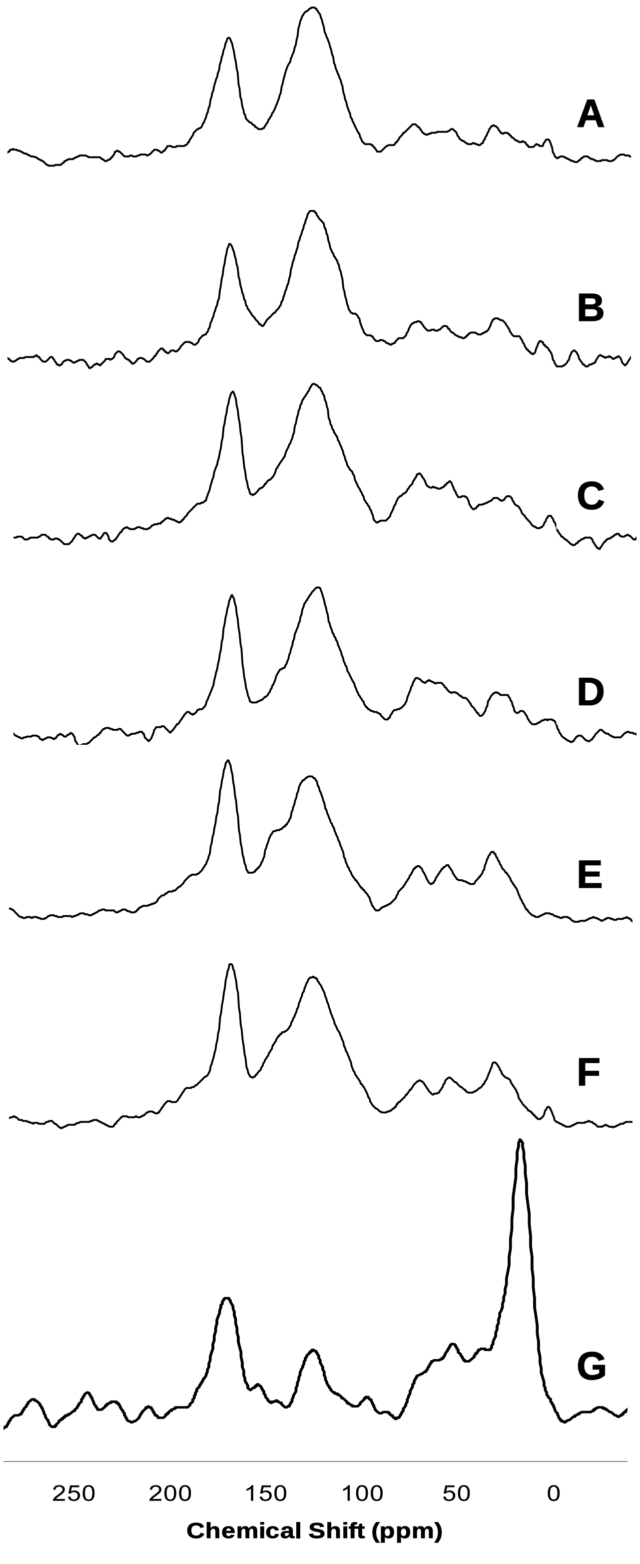


Figure 1. ^{13}C DPMAS NMR spectra of glomalin extracted from Hetland-HCl (A), Hetland-TCA (B), Poinsett-HCl (C), Poinsett-TCA (D), Pahokee peat-HCl (E), Pahokee peat-TCA (F), and bovine serum albumin (G). The HCl and TCA designations represent 1.0 M HCl precipitation/0.1 M NaOH reconstitution and 20% TCA precipitation/100 mM sodium borate reconstitution, respectively. Chemical shift regions: 0-50 ppm (aliphatic C), 50-108 ppm (carbohydrate C), 108-160 ppm (aromatic C), 160- 200 ppm (carboxyl C), and 200-220 ppm (carbonyl C).

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PART II:

Information Transfer Program: The results have been presented at a national and international meeting and a manuscript has been prepared and is currently in review with the *Soil Biology and Biochemistry* Journal. Furthermore, the results of this study, which significantly contribute to the current understanding of glomalin's structural character, have prompted interest and interdepartmental discussions among other researchers at SDSU.

Student Support: This project made it possible for an undergraduate student from St. Olaf College in Northfield, MN, Miss. Erin Mercer, to participate in the National Science Foundation's (NSF) Research Experiences for Undergraduates (REU) program at SDSU. Miss. Mercer was able to present her work at the Sigma Xi Annual Meeting and Student Research Conference in Montréal, Quebec and at the National Meetings of the American Chemical Society in San Diego, California. Furthermore, this project was instrumental in Miss Mercer's decision to enroll in graduates studies in the Department of Chemistry and Biochemistry at South Dakota State University for Fall 2006.

Based on the results of this project, a second REU student has been acquired for summer 2006 to perform one and two dimensional separations and isolate the glycoprotein. The student will isolate a pure substance to subject to mass spectrometry for protein identification.

Publications/presentations:

Schindler, F.V., E. J. Mercer, and J. A. Rice. 2006. Chemical Characteristics of Glomalin Extracted from Soils of Varying Organic Matter Content. Soil Biology and Biochemitry. In review.

Mercer, E.J., F.V. Schindler, and J. A. Rice. 2005. Solid-state ^{13}C NMR Evaluation of Glomalin Extracted From Soil, 226th National Mtg., Am. Chem. Soc., Geochem. Div., Mar. 2005, San Diego, CA, abstracts.

Mercer, E.J., F.V. Schindler, and J. A. Rice. 2004. Elemental and Structural Assessment of Glomalin. Sigma Xi Annual Meeting and Student Research Conference. Montréal, Quebec, Canada. Nov. 11-14, 2004.

Information Transfer Program

Information dissemination is an important part of the South Dakota Water Resources Institute (SD WRI) program. Other methods of information dissemination include a web site, fact sheets, water analysis interpretations, workshops, presentations, and water festivals. Emphasis is also placed on publication of scientific papers. Institute staff also participate in state, federal, and local committees and organizations. Feedback to these agencies is often given in the form of presentations at state meetings, local zoning boards, and informational meetings for non-point source and research projects.

SD WRI also encourages faculty, staff, and students to participate in science related activities. These activities range from giving talks, presentations and demonstrations to K-12 students as well as area producers and judging at science fairs. SD WRI staff also routinely responded to questions from the general public, other state agencies, livestock producers, and County Extension Agents. These inquiries include water quality and quantity, stream monitoring, surface water/ground water interactions, livestock poisoning by algae, lake protection and management, fish kills, soil-water compatibility, and irrigation drainage.

Information Transfer

Basic Information

Title:	Information Transfer
Project Number:	2005SD52B
Start Date:	3/1/2005
End Date:	2/28/2006
Funding Source:	104B
Congressional District:	First
Research Category:	Not Applicable
Focus Category:	None, None, None
Descriptors:	
Principal Investigators:	Van C Kelley, David R. German, Jennifer L. Pickard

Publication

FY2005 Information Transfer Program

South Dakota Water Resources Institute

PUBLIC OUTREACH

Public outreach is an important part of the South Dakota Water Resources Institute's Information Transfer Program. Information Transfer takes many forms. One of the most recent at SD WRI is a newsletter. The South Dakota Water Resources Institute *Water News* newsletter is in its second year of publication. This is an effective format to disseminate information about activities in which the Institute participates, funds, and promotes. The newsletter is published quarterly via e-mail, as well as a link on the SD WRI homepage (http://wri.sdstate.edu) in PDF format to view past and present issues. Water-related research including updates on present projects, notification of requests for proposals, state-wide water conditions, as well as information on youth activities are highlights in each issue. SD WRI's web site has been redesigned to improve user access to the updated links which include publications to help diagnose and treat many water quality problems. The site allows the public to keep in touch with the activities of the Institute, gather information on specific water quality problems, learn about recent research results and links with other water resource related information available on the Web. The "Research Projects" section of the SD WRI Web is updated with past and present research projects, highlighting the Institute's commitment to improving water quality.

SD WRI made the region's drought situation a priority in its outreach/information transfer efforts by posting information for farmers and ranchers on this subject on the Institute's web page (http://wri.sdstate.edu/drought.htm). The SDSU Agricultural Communications Department also developed a press release and special web page dealing specifically with the drought. This web page referred producers who had questions about their water quality to the SD WRI web page.

An extensive library of information has been developed and continues to be updated on-line. Information regarding analytical services available at the Oscar E. Olson Biochemistry Labs Water Quality Laboratory and information that may be used to address drinking water problems is available on-line.

Another important component of the Institute's Information Transfer Program is the Water Quality Laboratory (WQL). The lab was consolidated with the Oscar E. Olson Biochemistry Labs in 2004. The WQL continues to provide important testing services to water users across the state. Water Resources Institute staff continues to provide interpretation of analysis and recommendations for use of water samples submitted for analysis. Assistance to individual water users in identifying and solving water quality problems is a priority of the Institute's Information Transfer Program. Interpretation of analysis and recommendations for suitability of use is produced for water samples submitted for livestock suitability, irrigation, lawn and garden, household, farmstead, heat pump, rural runoff, and land application of waste. New topics for publication including fecal coliform and tastes, colors, and odors in water have been researched. These publications facilitate public awareness and promote education.

The drought in western South Dakota which continued to a lesser degree in 2005 has demonstrated the importance of the services offered by the Water Quality Laboratory. The inherent quality of surface waters in western South Dakota is commonly low, leading to chronic livestock production problems. However, drought has intensified this problem for livestock producers in these semi-arid rangelands. Many dugouts and ponds degraded to the point of causing cases of livestock illness and, in some instances, deaths. Lab services provided by the WQL and interpretation of results by WRI staff is important to livestock producers as they try to manage risks associated with water shortages and poor water quality. Although water quality problems in western South Dakota are common, some isolated cases of livestock illness and deaths due to poor surface water quality have occurred in eastern South Dakota as well.

SD WRI staff also routinely responded to water resource questions unrelated to laboratory analysis from the general public, other state agencies, livestock producers, and County Extension Agents. These inquiries include water quality and quantity, stream monitoring, surface water/ground water interactions, livestock poisoning by algae, lake protection and management, fish kills, soil-water compatibility, and irrigation drainage. WRI continues to provide soil and water compatibility recommendations for irrigation permits to the SD Division of Water Rights.

AGENCY INTERACTION

The SD WRI Information Transfer program includes interaction with local, state, and federal agencies/entities in the discussion of water-related problems in South Dakota and the development of the processes necessary to solve these problems. One of the most productive agency interactions is with the Non-Point Source (NPS) Task Force. The NPS Task Force coordinates, recommends, and funds research and information projects in this high priority area. Participation on the NPS Task Force allows SD WRI input on non-point source projects funded through the state and has provided support for research in several key areas such as phosphorus in soil and lake research. Many of the information transfer efforts of the Institute are cooperative efforts with the other state-wide and regional entities that serve on the Task Force.

Another example of this interaction to solve water quality problems is a program started by the Cooperative Extension Service (CES) to help livestock producers identify unsuitable water sources. The CES provides many of its Extension Educators with hand-held conductivity meters for use in the field. If samples are shown to be marginal by field testing, they are sent to the Water Quality Lab for further analysis. Often, high sulfates limit the use of waters that have elevated conductivity.

Another important interaction is with the South Dakota Department of Environmental and Natural Resources (DENR). Completion of Total Maximum Daily Load (TMDL) studies on South Dakota lakes has been a priority for DENR over the past several years. SD WRI is providing technical assistance to local sponsors working with DENR to complete the TMDL water quality assessments on several publicly owned lakes that do not have an established lakeside community.

Several other local and state agencies conduct cooperative research with SD WRI or contribute funding for research. Feedback to these agencies is often given in the form of presentations at state meetings, local zoning boards, and informational meetings for non-point source and research projects.

YOUTH EDUCATION

Non-point source pollution contributes to the loss of beneficial uses in many impaired water bodies in South Dakota. An important part of reducing non-point pollution is modifying the behavior of people living in watersheds through education. Programs designed to educate youth about how their activities affect water is important because attitudes regarding pollution and the human activities that cause it are formed early in life. For these reasons, Youth Education is an important component of SD WRI's Information Transfer Program.

Water Festivals provide an opportunity for fourth grade students to learn about water. Since they began in 1992 Water Festivals have been held in seven sites including Spearfish, Rapid City, Pierre, Huron, Vermillion, Brookings and Sioux Falls. Since their inception, Water Festivals in South Dakota have impacted approximately 87,000 Fourth Grade state wide. The Big Sioux Water Festival, held locally in Brookings, has recorded attendance of over 16,600 kids, 2,150 adults and 3,450 workers since 1993. SD WRI staff members continued to support and participate in Water Festivals throughout the state in FY2005. SD WRI also supported water quality education in local schools including classroom presentations and assisting local educators with field trips. Institute staff also conducted sessions on aquatic invertebrates and their use as water quality indicators for the "Lakes are Cool" field trip in conjunction with the Enemy Swim Lake 319 project in Day County and at the Sportfishing Day held in Aberdeen annually.

PUBLICATIONS

Distribution of research findings to the public, policy makers and sponsors of non-point source pollution control projects is another important component of the SD WRI Information Transfer program. This is needed so that the lessons learned through research and implementation projects are not lost as the next generation of projects develops. SD WRI is committed to making this material readily available to persons within South Dakota as well as in other states. A library is maintained at SD WRI to make these materials readily available. Abstracts of research projects funded by the institute have been placed on the WRI web site along with photos and summaries showing progress on these projects will be published on the site as they become available.

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	3	0	0	0	3
Ph.D.	2	0	0	0	2
Post-Doc.	0	0	0	0	0
Total	11	0	0	0	11

Notable Awards and Achievements

Publications from Prior Projects

None