Introduction

None

Research Program

During FY 2000, the South Dakota Water Resources Institute (SD WRI) used its 104 Grant Program funds to conduct research of local, state and national significance. A project dealing with remediation of arsenic in drinking water is of particular significance. The current MCL for arsenic in drinking water is 50 g/L, equivalent to 50 parts per billion (ppb). The EPA intends to lower the MCL for arsenic in the next few years to between 2 and 20 ppb. Arsenic is a known carcinogen.

A major concern associated with a reduction in the MCL for arsenic is treatment cost. Groundwater suppliers will bear the majority of the cost for this reduction, estimated to be between $187 million and $330 million per year to achieve a 20 ppb standard. These costs were outlined in the Bush Administration’s reasoning for delaying the reduction of the arsenic MCL. The focus of the project funded through the SD WRI is to determine the feasibility of developing a low cost remediation technology for removal of arsenic from drinking water. In specific, this study compared arsenic retention on limestone to other materials. Preliminary work on this project demonstrates arsenic adsorption of greater than 90% by limestone. Development of this technology could make it feasible to lower arsenic concentrations in drinking water to a level that would benefit human health without placing extreme hardships on small water treatment facilities.

The SD WRI is supporting research to study the effects of phosphorus in surface water due to manure application. A literature review was completed in November 2000 and has generated a great deal of interest in South Dakota, given the fact that agriculture is the state’s number one industry. Information is needed about phosphorus loss in runoff as affected by land applications of livestock manure so that South Dakota can develop reasonable regulations that protect the water quality of streams and lakes without placing undue hardships on livestock producers. There is a need to understand how high concentrations of P in soil can rise before causing environmental damage. The basis of regulations will be more sound if at least some of this research is conducted in South Dakota. The SD WRI, in cooperation with the South Dakota Agricultural Experiment Station and the South Dakota Cooperative Extension Service, will begin research on this issue in summer 2001. A conference dealing with this issue will be jointly hosted in August 2001.

A project to evaluate a non-point source pollution project on Pickerel Lake was funded for a second year to address the issue of how non-point source projects affect water quality, and to determine whether practices adopted during those projects are maintained after the management incentives end.

A second year of research was conducted to develop an on-the-go soil sensor to identify nutrient management zones to improve water quality. Research conducted during the first two years of the project evaluated whether precision nutrient management makes sense for South Dakota producers.
Another project was funded to provide laboratory support for a study on how poor water quality affects beef production. Many areas of South Dakota have poor surface water quality. This study will determine the relationship between water quality and livestock production, determine how livestock influence the water quality in the pastures where they graze, and evaluate the economic impacts of water quality on ranching enterprises.

**Basic Information**

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<td>James A. Rice</td>
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**Publication**

2. Williams, M. In Preparation. Selective sorption of DOC components to mineral surfaces. MS Thesis. Chemistry Department, South Dakota State University, Brookings, South Dakota.
4. 
**Problem and Research Objectives:**

The Big Sioux Basin is a hydrologic system which covers most of eastern South Dakota. Almost all studies have focused on the inorganic constituents of the basin’s surface- and groundwater. In 1989-1990 we conducted a geochemical baseline survey of the organic constituents of the basin’s groundwater that showed that dissolved organic carbon (DOC) levels are low, averaging 7.7 mg DOC/L. Aquifer recharge is primarily by downward percolation of surface water which makes the aquifers susceptible to contamination by anthropogenic and autochthonous organic substances present in the overlying materials. To begin to explore the relationship between the surface- and ground-water DOC concentrations, we recently established that DOC levels in wetlands, lakes and rivers in the basin that are hydrologically connected to the aquifers can be as much as 30 times higher. An investigation into the chemical nature of the DOC in the basin’s aquifers, its relationship to the organic matter in the predominate soil type in the region, and to several potential anthropogenic inputs of organic carbon into the groundwater is also near completion. However, the flux of organic carbon between hydrologic domains (e.g., between surface water and the groundwater, or between the soil and the groundwater), and the effect of sorption of components of the DOC to subsurface and aquifer materials on the chemical characteristics of the groundwater’s DOC as it moves from one hydrologic domain to the other are unknown.

This study will provide a broad-based understanding of the movement of DOC through hydrologic systems developed in alluvial and glacially-derived materials. It will provide a detailed description of the organic geochemistry of DOC in the Big Sioux Basin and an understanding of the mechanisms that control and affect the composition of DOC as it is transferred from surface-water to groundwater. The geochemical model of DOC transport from surface waters to the groundwater in the basin should capable of extension to other, similar systems in the North Central Region.

The hypothesis which drives this proposal is that selective sorption of surface-water DOC substantially alters the composition of the DOC which is actually introduced into the groundwater during aquifer recharge. The specific objectives of this proposal are to: (1) monitor the fluctuations in the dissolved organic carbon (DOC) concentration of the Big Sioux aquifer and connected wetland and surface water areas in the Big Sioux Basin; 2) use this data to create an estimate of the organic carbon flux into and through the aquifer; 3) perform sorption/desorption experiments using subsurface and aquifer material to quantify the binding of organic carbon to mineral surfaces; (4) assess the importance of sorption to mineral surfaces as a mechanism for controlling DOC composition and concentration in the aquifer, and; 5) identify the controls on organic carbon binding to mineral surfaces in subsurface and aquifer materials.

**Methodology:**

This project involves a combination of field and laboratory studies to assess the flux of DOC between surface and groundwaters within the study site. An detailed hydrologic description of the study site is being prepared. DOC levels are regularly monitored to determine the flux of organic carbon through the site. Periodic bulk water samples are fractionated into hydrophobic and hydrophilic organic acids, bases, and neutral compounds to evaluate seasonal changes in the nature of the DOC. This same fractionation scheme will be used to assess the compositional affect of selective sorption of DOC components to mineral surfaces as surface water DOC percolates down into the groundwater. Finally, a model will be constructed to describe the flux of DOC through the system.
**Principal Findings and Significance:**

**Hydrology**

Weekly water levels were measured in 18 observation wells adjacent to a prairie pothole wetlands. Ground-water levels were observed to rise during the spring and early summer but declined from summer to mid-winter. Hydrographs of the observation wells in the project area show that the water level in the deepest well had an average weekly difference in water level of about 0.05 feet, with a maximum difference of 0.21 feet. In the shallowest well the average weekly difference was about 0.04 feet with a maximum of 0.14 feet and. The observation wells located southeast to the pond had the greatest difference in weekly water levels. Water levels do show a response to significant precipitation events. The May, 2000 water level is an average of 0.28 feet below the May 1999 water levels. Similar water level trends, such as seasonal fluctuation and response to precipitation, where observed in the pothole surface water.

Comparison of pothole water stage and ground-water levels indicate a consistent downward gradient since the spring 2000 thaw. Thus, the surface water is recharging the ground water. The seepage rate through the pond bottom to the underlying weathered till was calculated to be 0.005 feet/day.

As an aid in better understanding the ground water and surface water interaction at the prairie pothole, a digital ground-water flow model of the weathered till is being developed. The model will be used to test various combinations hydraulic properties, recharge to, and discharge from the weathered till.

**DOC Flux**

A large of enough database of DOC measurements were collected to describe trends in groundwater and surface water DOC levels. Data collected show that groundwater DOC levels peak in the fall and show little effect of spring snowmelt infiltration.

**Sorption to Mineral Surfaces**

Using DOC isolated from the surface waters at the intensive study site, and mineral materials (silica, alumina, kaolinite and montmorillonite), study of the sorption of the DOC components to the mineral surfaces has revealed that hydrophobic and hydrophilic acids (as defined by XAD-8/XAD-4 sorption fractionation) selectively sorb to the mineral surfaces. Removal of these components, compared to the original DOC isolate is not quantitative, but in all case more than 75% of these fractions are removed. There is very little, if any, sorption of either hydrophobic or hydrophilic neutral or base fractions to these surfaces. Fluorescent spectra of the original surface water isolate reveal two distinct fluorescent signals, one of these is essentially completely absent after sorption experiments and in the ground water. Chemical characterization, including solution-state $^{13}$C NMR, to further characterize the components being sorbed to mineral surfaces to better understand their role in controlling DOC composition as surface water percolates through the unsaturated zone to recharge the aquifer. Data reveal that it is primarily the aromatic acids present in the hydrophobic and hydrophilic acid fractions that are responsible for this change in the fluorescence spectra. Consequently, it appears that these components of the water’s DOC represent the primary constituents of the organic carbon sorbing to the mineral surfaces.
Basic Information

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<td><strong>Principal Investigators:</strong></td>
<td>David E. Clay, Kevin Dalsted, Douglas Malo, C. Gregg Carlson</td>
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Publication

Problem and Research Objectives:

1. Determine the influence of pedogenic processes on soil electrical conductivity.
2. Determine the impact nutrient management zones, as defined by 3 decision support systems (DSS), on water quality and crop production.

Methodology:

This project was designed as a three year study. Funds for the third year were not provided and therefore, the project was not completed. During the first two years of the three-year study representative landscapes in South Dakota were selected for characterization. At each site, a detailed topographic survey was conducted. At representative locations in the different landscape positions, soil samples from each horizon were collected. Soil samples were analyzed for soil salinity, cation exchange capacity (CEC), plant available nutrients (N, P, K), pH, and soil texture (clay, sand, and silt) by standard techniques. In addition, detailed soil characterization was conducted by USDA-NRCS. Long term climatic information for each site was obtained from the appropriate USDA-NRCS soil survey report and local weather station data. Findings from this study were used to:

- Construct a conceptual model relating topography to elevation;
- Determine the impact of soil temperature and water on apparent electrical conductivity;
- Develop an approach for identifying nutrient management plans;
- Determine the impact of adopting the management zone approach on over and under fertilizing fields.

During the third year of the study, what was learned during the first two years of the study was to be field tested in farmers fields and simulation analysis was planned to evaluate the impact of utilizing knowledge gained during the first two years of the study on water quality and land productivity.

Principal Findings and Significance:

Research conducted during the first two years of the project evaluated if precision nutrient management makes sense for South Dakota producers. In this project, 10 fields were grid sampled. In all fields: (i) there were areas with very high or very low P concentrations; (ii) the median was less than the mean; and (iii) the skewness values were positive (Table 1). The Moody field, which was sampled in 1995 and 1997, had an old feedlot/homestead on a summit areas located in the west central side of the field. The feedlot was abandoned during the 1930's, and manure had not been applied to the field for the past 15 years. Associated with the feedlot were very high P and K concentrations and elevated pH values.

The Brookings field, sampled in 1996, had two feedlot/homestead locations. These feedlot/homestead sites were located at summit landscape positions.
located on the south central part of the field while the other was located on the north eastern part of the field. The old homestead in the south-central area was removed in 1997 and the old feed lot located in the north eastern corner has been farmed for at least 15 years. Elevated P was found in both these areas. The high P concentration of these areas, had a profound impact on the P probability distributions and are responsible for the high variance.

The Beresford field had an area where a high manure rate was applied to the south central part of the field between 5 and 10 years ago. Soil samples collected in 1997 and 1998 showed that this area still has very high P concentrations. Between 1997 and 1998, the P average concentration remained relatively constant. However, the variance was reduced from over 1600 to less than 550. Similar reduction in the skewness, kurtosis, nugget, and sill values were observed. These reductions may be the result of the incorporation of precision treatments in this field, i.e., P was not applied where it was not needed.

The Flandreau field had an area where high a high rate of manure had been applied several years ago. In this area, very high P concentrations were measured in 1997 and again in 1998. From 1997 to 1998 the average and median P concentration increased while the variance decreased. Similar hot spots were observed in the other fields.

Table 1. The means, medians, variances, skewness, and kurtosis values for 10 fields located in Eastern South Dakota.

<table>
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<tr>
<th>Field identification</th>
<th>Mean</th>
<th>Med.</th>
<th>Variance</th>
<th>Skewness</th>
<th>Kurtosis</th>
<th>Nugget</th>
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<td>11</td>
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<td>1.7</td>
<td>6.4</td>
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<td>15</td>
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<td>HeldtW</td>
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In summary fields containing nutrient hot spots was the norm and an economic, GIS, and simulation analysis of these sites showed that in order for the management zone concept to provide useful information, the management induced hot spots must be identified and sampled separately.
The Moody, Brookings, and Flandreau fields were used for a preliminary study to determine if electromagnetic sensors can be used as a directed soil sampling tool, in fields with varied histories. In these fields, soil samples were collected from at least a 60 by 60 m grid. Elevation was measured by a survey grade single frequency DGPS, and apparent electrical conductivity ($EC_a$) was measured between 2 to 4 times in each field between 1995 and 1999 by an EM 38. The $EC_a$ at the different sampling dates was positively correlated to each other. High correlations between sampling dates were attributed to toeslope soils generally having similar or higher water contents and salt concentrations than summit soils. In other words, the high $EC_a$ in footslope areas resulted from the combined effect of high salt and high moisture. This information was used to develop a conceptual model (Figure 1).

There were areas that did not fit the conceptual model. In areas where the apparent soil electrical conductivity was higher than expected, soil nutrient concentrations tended to be high. We attributed high nutrient and electrical conductivity values to old homestead, animal confinement areas, or high manure application rates. Research showed that these areas should be sampled separately from the rest of the field.

![Figure 1. A conceptual model relating topography, $EC_a$. In model B, manure was applied to a summit area.](image-url)
Basic Information

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Publication

Problem and Research Objectives:

The U.S. EPA’s maximum contaminant level (MCL) for arsenic is currently 50 µg/L, equivalent to 50 parts per billion (ppb). Canada’s MCL is 25 µg/L, and Australia’s is 7 µg/L (Smith et al., 1999). The EPA intends to lower the U.S. MCL. The new MCL is likely to be between 2 and 20 µg/L. It is believed that this will reduce arsenic-attributable skin cancer risk to 1 in 10,000 (Frey and Edwards, 1997). Below 10 µg/L of arsenic in water, food becomes the major inorganic arsenic source (Smith et al., 1999). A new MCL should be announced in the next one to two years.

The ability of water suppliers to comply with the new standard understandably varies, based on the raw water’s arsenic concentration. Forty percent of water supplies in the U.S. have arsenic concentrations > 1 µg/L, and 5% are > 20 ppb (Welch et al., 1999). Another source indicates that 25% of water supplies exceed 2 ppb, 6 to 17% exceed 5 ppb, and 1 to 3% exceed 20 ppb. Also, 20.7% of suppliers would not meet a 2 ppb standard, 9.3% would not meet a 5 ppb standard, 3.6% would not meet a 10 ppb standard, and 1.7% would not meet a 20 ppb standard (Frey and Edwards, 1997). Ground water averages an even higher arsenic content: 36% > 1 ppb, 25% > 2 ppb, 14% > 5 ppb, 8% > 10 ppb, 3% > 20 ppb, and 1% > 50 ppb (Focazio et al., 2000).

Obviously lowering the MCL will increase costs for many water suppliers and consequently their customers. That industry predicts a cost of $600 million/year and $5 billion in capital costs to meet a 10 ppb arsenic standard. The U.S. EPA believes the same standard can be met at a cost of $187 million/year (WaterWorld, 2000). Another study predicts costs of $330 million/year to achieve a 20 ppb standard. Most industry estimates are 10 to 20 times the EPA’s cost predictions. Regardless of actual cost, ground-water suppliers will bear the majority, 62 to 82%, of the cost (Frey et al., 1998).

This research investigated the feasibility of developing a low-cost remediation technology for removal of arsenic from surface water and ground water. Arsenic retention and transport were characterized. Because of the ready availability of limestone, its use for arsenic remediation would be relatively inexpensive. If successful, it is anticipated that the technology could be readily adapted to small rural water supply systems as well as private, domestic, and stock wells. For example, elevated levels of arsenic in water from wells in the Arikaree aquifer have been observed on the Rosebud Indian Reservation. However, observations of arsenic contamination from mining and native mineral sources in the northern Black Hills indicate that arsenic appears to be retained by the karstic Madison Limestone aquifer. Benefits of this research will include a low-cost treatment technology that reduces arsenic below maximum contaminant levels, helping operators of small or rural water supply systems to meet anticipated new rules.

The specific objectives of this work were to: (1) establish the capacity of limestone to retain arsenic, (2) determine the effect of pH and surface area on the adsorption efficiency, and (3) compare arsenic retention on limestone with other materials such as Arikaree sandstone and pure CaCO₃. Preliminary work that has
recently been completed by the principal investigators demonstrates arsenic adsorption of greater than 90% by limestone.

**Methods:**

Numerous experiments were performed using Minnekahta Limestone to remove arsenic from water. This approach was supported by previous research regarding the removal of arsenic by the formation of calcium arsenate (Bothe and Brown, 1999). Mobilization of arsenic from sediment is most likely when the sediment is low in iron and calcium carbonate (Brannon and Patrick, 1987). A reasonable conclusion is that arsenic is immobilized in iron and/or calcium compounds. Work on arsenic-rich mine drainage and the subsequent decrease of arsenic content down gradient from where discharges crossed limestone outcrops indicated that limestone is a possible arsenic removal medium (Davis et al., 1999).

Both batch and column experiments were done in this research. Batch experiments tested various combinations of rock material and arsenic-rich waters. Shake time, mass of rock material, and pH also were varied in batch experiments. The column experiments tested the effectiveness of Minnekahta Limestone of different grain sizes in removing arsenic. Subsequently, one arsenic-saturated column was slowly rinsed in an attempt to determine the mobility of arsenic after removal by limestone. The limestone used in all experiments had been crushed and sieved, thus separating the various grain sizes.

Batch experiments involved the use of flasks containing a rock material, usually Minnekahta Limestone, and a solution. The solution normally consisted of deionized water and arsenic. These flasks were placed in a shaker to facilitate mixing. Samples of the resulting solution were tested for conductivity, pH, temperature, and arsenic content. Eighteen batch experiments were performed to define the parameters that had the most effect on arsenic removal.

Column experiments consisted of running arsenic-rich water through a polyvinyl chloride (PVC) pipe filled with Minnekahta Limestone. This was accomplished by adding arsenic-rich water to the top of the column while draining an equivalent amount of water from the bottom of the column. The resulting sample was tested for pH, conductivity, temperature, and arsenic content. This process occurred twice a day for the duration of the column experiment. Five column experiments were run to test the effectiveness of various grain sizes of limestone in removing arsenic from both standard solutions and natural water. One column experiment tested the ability of limestone to retain arsenic when rinsed with deionized water.
Principal Findings and Significance:

Batch Experiments

Samples of rock material weighing approximately 1, 5, 10, 40, and 100 grams were each combined with 100 mL of arsenic solution at pH = 8 +/- 0.2. A 10-gram duplicate and a 10-gram blank, using deionized water rather than an arsenic solution, also were prepared. Rock material and arsenic solution were combined in a 250-mL round-bottomed flask and shaken for two days, then allowed to settle for about one hour. An aqueous sample was collected and tested for pH and conductivity. A filtered portion (0.45 µm filter) of the sample was taken to Mid-Continent Laboratories in Rapid City, South Dakota, for determination of arsenic concentration. The detection limit for arsenic at Mid-Continent Laboratories is 5 ppb. Samples testing below detection limit (BDL) are plotted within the shaded area on the graphs.

Five batch experiments, using 100-ppb arsenic solution and limestone, tested the effect of grain size on arsenic removal. The first experiment was a test run, so results only from experiments 2 through 5 are presented here. Minnekahta Limestone samples of various grain sizes, having been previously crushed and sieved, were used. Batches with smaller grain size limestone were more effective in removing arsenic. All four experiments showed effective removal of arsenic, resulting in observed concentrations at or below 5 ppb when using 40 grams of limestone of any grain size. The graphs indicate that much less than 40 grams would likely have been sufficient.

Batch experiment 2

Batch experiment 2 mixed various quantities of 4.7-6.7 mm limestone and 100 mL of 109 ppb arsenic solution. The initial pH of the solution was 7.9. The seven bottles were shaken for two days. Forty grams of limestone were sufficient to reduce the arsenic content of the solution to 5 ppb. Data from batch experiment 2 are shown on Figure 1.

Batch experiment 3

Batch experiment 3 mixed various quantities of 2-4.7 mm limestone and 100 mL of 108 ppb arsenic solution. The initial pH of the solution was 8.0. The seven bottles were shaken for two days. Forty grams of limestone were sufficient to reduce the arsenic content of the solution below 5 ppb. Data from batch experiment 3 are shown on Figure 2.

Batch experiment 4

Batch experiment 4 mixed various quantities of 1-2 mm limestone and 100 mL of 106 ppb arsenic solution. The initial pH of the solution was 8.0. The seven bottles were shaken for two days. Forty grams of limestone were sufficient to reduce the arsenic content of the solution below 5 ppb. Data from batch experiment 4 are shown on Figure 3.
Batch experiment 5

Batch experiment 5 mixed various quantities of 0.5-1 mm limestone and 100 mL of 91 ppb arsenic solution. The initial pH of the solution was 8 +/- 0.2. The seven bottles were shaken for two days. Forty grams of limestone were sufficient to reduce the arsenic content of the solution below 5 ppb. Data from batch experiment 5 are shown on Figure 4.

Other Materials

Batch experiments were run to test the ability of some other materials to remove arsenic. The materials included very fine calcium carbonate, sea sand, Arikaree aquifer material, and agricultural limestone. The results of the pure calcium carbonate batch experiment were inconsistent and thus inconclusive. The sea sand nominally removed some arsenic; however the chemical makeup of the sand was unknown. The Arikaree material added arsenic to solution. This was expected based on conditions in the Grass Mountain area. After being exposed to the Arikaree material, the deionized water used in the blank contained more than 30 ppb arsenic. The agricultural limestone consistently reduced arsenic to some extent. An apparent clay fraction of the material led to clumping of the 40 and 100 gram agricultural limestone samples.

Variations of pH

A batch experiment was run with arsenic solutions that were adjusted to different pH values. The varying pH, within the range normally seen in ground water, had no effect on the amount of arsenic removed.

Column Experiments

Column experiments used PVC pipe columns, approximately 4 inches in diameter and 3 feet long, filled with Minnekahta Limestone. Four columns containing different sizes (0.5-1 mm, 1-2 mm, 2-5 mm, and 5-7 mm), the same grain sizes as used in the batch experiments, of Minnekahta Limestone were saturated with distilled water. A slug of either standard solution or well water was added to the top of the column. A sample of the slug was collected and sent to the lab once a week throughout the experiment. Fluid level was maintained at the top of the column by simultaneously taking a sample from the bottom of the column. Subsequently, 500 mL of slug (or distilled water for the nitrate tracer experiments) was added to the column and resulting samples were taken twice a day. Sample volume, pH, conductivity, temperature, and time of day were recorded. A small part of the sample was filtered (0.45 um filter) and sent to Mid-Continent Laboratories for analysis of arsenic concentration. The experiment ended when sample concentration began to approach slug concentration, i.e. material was becoming chemically saturated.

Columns 1, 2, 3, and 4 underwent a nitrate tracer test to show the behavior of a non-reactive species as it was flushed through the column. A single 250 mL slug of 100...
parts per million (ppm) nitrate solution was added to the water-saturated column. Subsequently, 500 mL of water was added to the top of the column while an equal size sample was removed from the bottom of the column. Conductivity measurements were taken from each sample. A series of solutions of varying concentrations were made to relate nitrate concentration and conductivity. Using a calibration curve, estimates of nitrate concentration for each sample were determined. The resulting concentrations showed that nitrate moved through the columns with little or no adsorption, as expected, and provided a background for comparison of arsenic transport through the columns.

Column experiments using four different grain sizes were run with 100-ppb arsenic solutions to determine the limestone’s ability to remove arsenic without agitation. These tests simulated the proposed implementation of the limestone-based arsenic removal process as a water line cartridge. The smaller grain sizes reduced arsenic to below 5 ppb for a longer period of time; thus, removing arsenic from a much larger volume of water. The finest grain size clearly was the most effective for arsenic removal.

**Column experiment 1**

Column 1 contained 5725 grams of 0.5-1 mm limestone. A solution of ~100 ppb arsenic at a pH of 8 +/- 0.2 was run through the column at a rate of one liter per day. Arsenic breakthrough occurred after 66 days and approximately 34 pore volumes. The limestone adsorbed approximately 0.0065 grams of arsenic before breakthrough occurred. This is $1.1 \times 10^{-6}$ grams of arsenic per gram of limestone. Data from column experiment 1 are shown on Figure 5.

**Column experiment 2**

Column 2 contained 5590 grams of 1-2 mm limestone. A solution of ~100 ppb arsenic at a pH of 8 +/- 0.2 was run through the column at a rate of one liter per day. Arsenic breakthrough occurred after 25 days and approximately 13 pore volumes. The limestone adsorbed approximately 0.0024 grams of arsenic before breakthrough occurred. This is $4.3 \times 10^{-7}$ grams of arsenic per gram of limestone. Data from column experiment 2 are shown on Figure 6.

**Column experiment 3**

Column 3 contained 5989 grams of 2-4.7 mm limestone. A solution of ~100 ppb arsenic at a pH of 8 +/- 0.2 was run through the column at a rate of one liter per day. Arsenic breakthrough occurred after 13 days and approximately seven pore volumes. The limestone adsorbed approximately 0.0012 grams of arsenic before breakthrough occurred. This is $2 \times 10^{-7}$ grams of arsenic per gram of limestone. Data from column experiment 3 are shown on Figure 7.
Column experiment 4

Column 4 contained 6343 grams of 4.7-6.7 mm limestone. A solution of ~100 ppb arsenic at a pH of 8 +/- 0.2 was run through the column at a rate of one liter per day. Arsenic breakthrough occurred after 10 days and approximately six pore volumes. The limestone adsorbed approximately 0.0009 grams of arsenic prior to breakthrough. This is $1.4 \times 10^{-7}$ grams of arsenic per gram of limestone. Data from column experiment 4 are shown on Figure 8.

Discussion and Significance

The batch experiments successfully demonstrated the removal of arsenic by Minnekahta Limestone. Smaller grain size limestone removed more arsenic per unit weight of limestone. None of the other materials tested removed arsenic as efficiently as Minnekahta Limestone did. Most of the arsenic removal occurs quickly; additional removal continues at a slower rate. Fine particulate matter is beneficial in further reducing arsenic concentrations. Increased high ionic activity, indicated by high TDS values, reduces the ability of limestone to preferentially remove arsenic. The arsenic removal process is unaffected by the standard solution’s initial pH, within the natural range for ground water.

Column experiments are a more realistic representation of the type of device necessary for implementation of the process in a residential situation. Columns 1 through 4 all effectively reduced the arsenic concentration of the standard solution. These columns reiterated the importance of grain size: the smaller the grain size, the more efficient the arsenic removal. Eventually the limiting factor controlling grain size will be the required flow velocity through a column of limestone. At some lower limit of permeability the water will not flow through the column, or cartridge, at a sufficient rate. Residence times necessary to reduce arsenic to an acceptable level will be an important, related factor. The shorter the necessary residence time, all else being equal, the greater the rate of flow that can be treated. Maximizing flow rate will be of the utmost importance when developing a marketable product.

The results of the series of experiments are encouraging, although implementation of a limestone-based arsenic removal process for natural waters will take much additional work. Minnekahta Limestone consistently removes arsenic from water. Exposure to the limestone routinely reduced arsenic concentrations from ~100 ppb to less than 5 ppb.

Surface area is a key parameter controlling the efficiency of the process. Smaller grain sizes result in a greater surface area per unit weight, thus better arsenic removal. This was demonstrated in the batch experiments and became very apparent in the column experiments. The 0.5-1 mm grain size column reduced the arsenic concentration to below 5 ppb of 66 liters of ~100 ppb standard solution. The 4.7-6.7 mm grain size column reduced the arsenic concentration of only 10 liters of the same standard solution to less than 5 ppb.
An area of concern is the stability of the arsenic-saturated limestone waste product. The inability of the limestone to completely retain the arsenic when rinsed with water was discouraging. A method for disposal or reuse of the waste product is needed.

While arsenic is consistently removed by limestone, widespread use of the process will require its applicability to a sufficient range of natural water conditions. Fortunately, the pH of the arsenic-rich water did not affect the efficiency of the process. Arsenic was consistently reduced in solutions with pHs from 6 to 8.5. This bodes well for applying the process to a wide variety of natural waters. However, elevated TDS has the potential to greatly reduce the effectiveness of the process, most likely by ionic interference. Additional work is necessary to quantify the ionic effect and to identify the specific ions responsible for the interference. Overall, the limestone-based arsenic removal process shows promise but will require a significant amount of further work to implement at field sites.
Figure 1. Graph of data from batch experiment 2. Shaded area is BDL (below detection limit).

Figure 2. Graph of data from batch experiment 3. Shaded area is BDL.
Figure 3. Graph of data from batch experiment 4. Shaded area is BDL.

Figure 4. Graph of data from batch experiment 5. Shaded area is BDL.
Figure 5. Graph of data from column experiment 1. Shaded area is BDL.

Figure 6. Graph shows data from column experiment 2. Shaded area is BDL.
Figure 7. Graph of data from column experiment 3. Shaded area is BDL.

Figure 8. Graph of data from column experiment 4. Shaded area is BDL.
References Cited:


Basic Information

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Publication

Problem and Research Objectives

Pickerel Lake became the first lake protection project recommended for funding to the US EPA by the Non-Point Source Task Force. A lake protection project sponsored by the Day Conservation District started in 1992. The project was completed in 1996 (Skadsen and German, 1996). Several other lake protection projects have since been funded and are currently in various stages of completion. There have been no efforts made to determine the effectiveness of these projects. Have measurable water quality improvements occurred in the targeted lakes? Have farmers continued to use management practices designed to improve water quality after cost share incentives ended? Did the lake protection project have a lasting affect on land use in the watershed? This project was designed to provide quantitative answers to these questions using Pickerel Lake as a case study. This study will provide a means of comparing in-lake water quality before, during and after the Pickerel Lake Protection project to determine if measurable water quality changes have occurred. Evidence of water quality improvement or maintenance of current water quality could be used to support similar efforts underway, or planned for other lakes that have been designated for lake protection projects. A more thorough understanding of a lake’s response to watershed treatment will improve our ability to manage these lakes. This study will provide better insight into farmer’s attitudes and degree of acceptance of lake protection projects. It will also provide a measure of whether watershed treatment measures remain in place after financial incentives have ended. This information will be used by future non-point source projects to improve farmer acceptance and increase the permanence of watershed treatment measures.

Methodology

This project involves use of a Geographic Information System (GIS) in order to compare pre-project, post-project, and current watershed conditions. The GIS will be evaluated as a tool for watershed assessment and post-project evaluation. A graduate student in Geography will produce a thesis based on the use of GIS as a watershed evaluation or assessment tool. The graduate student will combine water monitoring and GIS to develop pollutant values for various areas of the watershed, and use a watershed model to predict future water quality and loadings if land use in the watershed changes. In-lake water quality samples were collected from three mid lake stations on Pickerel Lake. A composite surface sample for the lake and a composite near bottom sample was formed by mixing water collected near the bottom from each of the three sites in each lake. Composite samples were collected within six days of mid-month in June, July, August, September and October. 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)

In the second year of the project lack of snow and generally dry conditions in the summer of 2000 resulted in the lack of runoff from the small watersheds under study. Runoff samples and flow measurements planned for the project were not collected on any of the four land use categories (cropland, CRP, pasture, and hayland) in the watershed until snowmelt produced runoff in March 2001 at the end of the project. With insufficient data available, runoff coefficients from the literature were used for the GIS analysis of the watershed.

**Principal Findings and Significance**

During the first year of this study, the graduate student: 1) Evaluated Arc/Info versus ArcView software for best suitability to accomplish the project goals, 2) Completed course work in the modeling, and spatial applications of ArcView, and basic cartographic and land use land cover philosophies. (He also developed a thesis proposal and plan which is under review for application to the South Dakota State University Graduate School.), 3) Conducted a literature search on the use of GIS as a watershed management tool, and 4) Selected representative small watersheds and installed monitoring sites for each land use practice. Four monitoring stations were established in the watershed representing four major land uses. Dry conditions existed following establishment of the sites and no samples were collected.

In the second year of the project, GIS analysis of the watershed continued. The graduate student: 1) evaluated the literature findings and determined that ArcView was the software best suited for completion of the projects GIS goals, 2) identified readily available, inexpensive online data sources for the data layers necessary for completion of the GIS analysis, 3) collected all data layers available from online sources 4) digitized land use/land cover and roads data layers, 5) delineated watershed and sub watersheds using ArcView, 6) compared the computer delineated watershed boundaries to those determined by traditional delineation methods and found that the ArcView representation was accurate, 7) completed writing of literature review and methodology sections of thesis, 8) developing runoff coefficients from literature to complete land use analysis, 9) completed all coursework necessary for degree program, 10) developed survey guidelines for collecting information on management practices of local landowners, 11) submitted these to Graduate School Human Studies Review Board and were approved for use, 12) collected management practices information. Analysis of the layers to determine changes in land use and retention of management practices cost shared by the EPA 319 project earlier in the decade have not been completed at this time.

In-lake water quality monitoring in both years indicated no significant change in water quality has occurred at Pickerel Lake. Water quality data was made available to the South Dakota Department of Environment and Natural Resources and a summary of project
activities was published in a newsletter published by the Upper Waubay Watershed Improvement Project, sponsored by the Day and Roberts Counties Conservation Districts.
# Basic Information

| **Title:** | Laboratory Support for a Study of Water Quality and Beef Production and Sustainability of Water for Livestock Use |
| **Project Number:** | B-05 |
| **Start Date:** | 3/1/2000 |
| **End Date:** | 2/28/2001 |
| **Research Category:** | Water Quality |
| **Focus Category:** | Water Quality, Surface Water, None |
| **Descriptors:** | Salinity, water quality, livestock health effects |
| **Lead Institute:** | South Dakota Water Research Institute |
| **Principal Investigators:** | Patricia S. Johnson, David R. German |

# Publication
Problem and Research Objectives:

Water is a critical resource on semi-arid rangelands of western South Dakota. Livestock production on these rangelands is absolutely dependent on adequate quality water. We know that very poor quality water can kill livestock. It is not clear, however, the extent to which sub-lethal quality water affects production and health of grazing animals and the overall profitability of ranching enterprises. Recently, several range livestock operations in western South Dakota have experienced livestock losses due to poor weight gains, health problems, and, in some cases, livestock deaths which have been blamed, to a large degree, on poor water quality.

Water quality issues also have the potential to impact rangeland livestock operations through non-point source pollution regulations. The wording of recent regulations may allow scrutiny of livestock operations to expand beyond confinement operations to rangeland grazing. Information is needed to evaluate the effects of grazing livestock on the quality of water so that any decisions regarding regulations of grazing as it relates to pollution can be based on facts rather than assumptions and fears.

Methods:

This study is being conducted at the Cottonwood and Antelope Research Stations in western South Dakota. Both stations have a variety of water sources, including stock dams, streams, wells, and, at Cottonwood, rural water. The two stations maintain native grass pastures typical of ranches in the region. Meteorological recording stations are located at the Cottonwood Research Station and at Buffalo, South Dakota, 13 miles from the Antelope Station.

Waters from both sites were tested to determine water sources with water quality in the ranges needed for the study. Efforts are still underway to search for sources of even poorer water quality to use in the evaluation of economic loss due to poor performance of the animals. Initial water samples from each source were analyzed for alkalinity, electrical conductivity, total dissolved solids and all cations and anions. Subsequent analyses for each source focused on changes in important components identified in the initial sample. Water sources were ranked according to quality, and sources were selected from both stations representing the range from highest to lowest quality. This activity continues this year. Grazing on summer-grazed pastures will begin in Year 2 and continue in Year 3, as will all water, livestock, and vegetation measurements.

Principal findings:

In the first year of the study, steers were divided into two groups. One group was placed in pastures with water with electrical conductivity (EC) in the range of 6,000 to 7,000 microhmos/cm. The second group was placed in pastures with water that had EC in the range of 1,000 micromhos/cm. No difference in gain or overall health in the animals was observed in this portion of the experiment. There was a significant increase in the water consumption by the animals that were on the higher EC water. In the second year of the project, it is planned to use water with higher EC to determine the economic threshold using poor quality water. Cow/calf pairs may be used if cooperators can be located, since it is believed that lactating animals will be adversely affected at a lower threshold of EC than non-lactating animals.
Information Transfer Program

Water is one of the most important resources in South Dakota. Together with the state’s largest industry, agriculture, it has and will continue to 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. The South Dakota Water Resources Institute (SD WRI) base grant program, with support from state funds, was used to develop and maintain working relationships with local, state and federal agencies to enhance management of water resources in South Dakota.

The education and information transfer roles are an important part of the SD WRI programs. Information is routinely provided to the public, researchers, resource managers and agencies by SD WRI staff. This included responding to questions received from the general public, other state agencies, livestock producers and County Extension Agents concerning water quality issues related to stream monitoring, surface water ground water interactions, livestock poisoning by algae, lake protection and management, fish kills and other issues related to water quality. Due to dry conditions in South Dakota during 2000, dugouts used for watering livestock in the state especially in, but not limited to, western South Dakota became unsuitable for livestock use. Many reports of health problems and even animal deaths were reported. In many cases, these waters had high concentrations of sulfates, which is a common problem for livestock health and productivity in South Dakota. A statewide press release was used to alert producers to the problem so they could have their water tested and take action to protect their livestock. WRI staff worked individually with several producers, extension educators and others to find solutions. The SD WRI Water Quality Laboratory provided analysis services to livestock producers as well as other water users. Water Resources Institute staff also continued to provide interpretation of analysis and recommendations for use of water samples submitted for analysis for other uses, such as irrigation, lawn and garden, farmstead, and heat pump. SD WRI staff continue to update and improve information available to individuals with water quality problems. The advent of the Internet has dramatically increased the amount of information available for distribution. Educational materials concerning the effects of poor water quality and solutions available are given a high priority.

SD WRI staff have seen a continued concern from lab customers regarding agricultural practices and their effect on water quality. Information transfer to individuals concerned with these issues is becoming an important component of the Institute’s Information Transfer Program. SD WRI staff are in the process of updating the Institute and Water Quality Lab web pages to continue provide up-to-date information to the public about current issues in water quality.

EPA is moving toward national phosphorus regulations for land applications of waste. These regulations are in response to the fact that non-point source discharges of phosphorus, and in some instances nitrogen, are a primary cause of serious eutrophication problems in streams, lakes and wetlands, especially in some agricultural areas where large animal concentrations are present. South Dakota regulations for the application of animal waste are based upon the nitrogen needs of the crop. This results in excessive phosphorus applications (i.e. relative to the phosphorus needs of the crop), and it is likely that eutrophication problems will increase in South Dakota as a result. Information is needed about non-point losses of phosphorus in runoff as affected by land applications of livestock waste. This information will provide a basis for the state to develop reasonable regulations that protect the water quality of streams and lakes without placing undue hardships on livestock producers. SD WRI staff completed a literature review in an effort to identify what research has been conducted and further, to identify research needs applicable to this problem. The literature review was published and
distributed in November 2000 and three additional printings have been required to meet the demand for this information. This review will likely influence how animal wastes are managed in South Dakota in the future. In addition, the SD WRI, along with the South Dakota Agricultural Experiment Station and the South Dakota Cooperative Extension Service will be hosting a conference titled "Phosphorus, Manure and Water Quality" in Sioux Falls, SD in August 2001. The objectives of this conference are 1) to present recent scientific research on water quality concerns relative to land application of manure and phosphorus build up in the soil, 2) to present information on phosphorus policy in other states and countries and scientific basis of these policies, and 3) to present information on science-based solutions to the phosphorus problem. The targeted audience for the conference includes agricultural organizations, County Commissioners, County Zoning Officers, policy makers, commercial manure applicators, Extension Educators, and anyone interested in learning more about phosphorus and water quality. A research project will begin in summer 2001 using simulated rainfall to collect information on the effect that phosphorus accumulation in the soil has on runoff water quality.

South Dakota is currently developing Total Maximum Daily Loads (TMDL’s) for numerous water bodies. TMDL’s are an important tool for the management of water quality. The goal of a TMDL is to ensure that waters of the state attain water quality standards and provide designated beneficial uses. A TMDL is defined as "the sum of the individual waste load allocations for point sources and load allocations for both nonpoint source and natural background sources established at a level necessary to achieve compliance with applicable surface water quality standards". In other words, a TMDL limits the total pollution load of any given water body to the TMDL it can bear and still remain healthy. TMDL’s are required on waters that do not attain water quality standards or assigned beneficial uses. The SD WRI Water Quality Laboratory is providing laboratory support for three TMDL projects in eastern South Dakota, including The Central Big Sioux River Watershed Assessment Project, The Upper Big Sioux River Watershed Assessment Project, both being conducted by East Dakota Water Development District, and the Lake Thompsen project, being conducted by the SDSU Biology Department.

Water Festivals were included in the NPS Task Force’s Information and Education plan in 1992 with one Water Festival held in Spearfish, South Dakota. Water Festivals have since 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 41,000 fourth grade students state wide, 10,800 of which have attended our own local festival, the Big Sioux Water Festival (BSWF). SD WRI staff member David German has served as the Exhibit Hall Chair for the BSWF, held here at South Dakota State University since the festival was founded. The Exhibit Hall provides a hands-on learning experience for these students from all over eastern South Dakota. Exhibits ranged from groundwater contamination to live aquatic animals and plants. SD WRI staff members, David German, and Shirley Mittan also hosted exhibits and gave presentations titled "Under the Microscope", "Wonder What’s In Your Water?", and a computer quiz on water quality at the BSWF, as well as those in Huron and Sioux Falls, South Dakota. Another SD WRI staff member, Nancy Stuefen, has chaired the BSWF Guide Committee since 1994 and has assisted the Festival Coordinator in developing new presentations each year. The BSWF has also been chosen as a national model of water festivals as a result of our innovative approach to water education, and our festival coordinator has been chosen to serve on the National Water Festival advisory committee, "Tools for Tomorrow".

SD WRI continued other activities to support water quality education in local schools. WRI staff also presented information on water quality at a booth at Dakota Fest 2000 in Mitchell, South Dakota. A unit on stream insects was developed for a national Girl Scouts Jamboree held in Brookings. Over 200 Girl Scouts and their chaperones participated in the two-day stream side activities. Tours of the Water
Quality Lab were conducted for a plant science class (PS375, Water Quality in Agriculture), which discussed the role of the Water Quality Lab in assisting producers with irrigation, livestock waters, identification of pollution sources and other water quality problems.

Water education was also used as a training opportunity. Undergraduate students working in work study or summer positions at SD WRI participated as assistant instructors for the Big Sioux Water Festival and gave presentations at the James River Water festival in Huron. SD WRI staff continue to serve as a resource for SDSU students working on projects and papers related to environmental studies and water quality.
USGS Summer Intern Program
## Student Support

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### Notable Awards and Achievements

Research and related work on the Project titled "Arsenic Remediation of Drinking Water" (#B-04) were included in the list of major accomplishments of the U.S. Environmental Protection Agency’s Region VIII Pollution Program. Mr. Dennis Clarke of the South Dakota Department of Environment and Natural Resources was enthusiastic about the potential usefulness and applications of the research. Additional funds to continue this research have been awarded as follows:

- FY02 USGS 104 Grant Program - "Arsenic Remediation of Drinking Water: Phase II" - $9,469
- West Dakota Water Development District - "Development of a New Treatment Technology for Arsenic in Drinking Water" - $5,000
- South Dakota Department of Environment and Natural Resources-Prime funding source: U.S. Environmental Protection Agency, Region VIII - "Arsenic Removal from Drinking Water" - $42,500

### Publications from Prior Projects

None