South Dakota Water Research Institute
Annual Technical Report
FY 2010

Introduction

South Dakota's Water Resources Research Institutes (SDWRI) 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 Biosystems Engineering Department. The annual base grant from the United States Geological Survey (USGS) and a legislative appropriation of $98,651 form the core of the SDWRI budget. The core budget is supplemented by research grants from a variety of funding agencies as well as private organizations and industry interested in specific water issues.

The mission of the SDWRI is to address the current and future water needs of people, agriculture, and industry through research, education, and service. To accomplish this mission, SDWRI provides leadership in coordinating the research and training at South Dakota State University and other affiliated educational institutions and agencies across the state in the broad area of water resources. Graduate research training, technology transfer, and information transfer are the services that are provided through the Institute. This report is a summary of activities conducted during Fiscal Year 2010 to accomplish this important mission.

Research Program Introduction

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 2010, 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 and the upper Midwest region. These included two projects dealing with agriculture. One covered the use of cover crops to minimize loss of plant nutrients to water resources and the second one dealt with microbial and chemical indices of soils and water associated with vegetated treatments areas (VTAs) from two concentrated animal feeding operations (CAPOs) in South Dakota. A third project measured the human pharmaceutical compounds (HPC) in surface water. The final two projects involved the investigation of arsenic removal from water by microbiologically induced calcite precipitation and the final project involved protein-based mechanisms of uranium detoxification in subsurface bacteria.

During October 2010 the Advisory Committee reviewed six grant applications and recommended four projects for funding that addressed research priorities that had a good chance of success, and would increase our scientific knowledge. Emphasis was placed on the determination of microbial kinetics for the degradation of estrogens and triclosan in activated sludge systems, the investigation of the contribution of coliform contamination in runoff from scoured bed sediments, fate and transport of biogenic uraninite in the environment and the life cycle assessment analysis of engineered storm water control methods common to South Dakota. These projects were scheduled to begin March 1 2010, but because of delay in funding appropriation from the USGS funds were not released until May 25 2011.

As the quality of water continues to be a primary concern in the state, it becomes more important to design and build more efficient wastewater treatment plants. A study will be implemented to determine the biological kinetic parameters for the degradation of the hormones E2, EE2 and the antibacterial agent triclosan. Another study will involve storm water control methods in South Dakota. Both of these projects will study the surface water quality and its impact on the state and beyond.

Ground water in some areas of South Dakota is also contaminated with uraninite. A study to learn more about the transport of unraninite will be done to better learn how to use natural indigenous bacteria to end the transport of biogenic uraninite. 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 FY2009. 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.

Surface water is also affected by coliform bacteria. A study will be done to evaluate coliform contamination in runoff for both urban and nonurban areas.

Development of a Decision Support System for Water Resources Management of Shallow Glacial Alluvial Aquifers: A Laboratory Proof of Concept Study (Year 2)

Basic Information

Title:	Development of a Decision Support System for Water Resources Management of Shallow Glacial Alluvial Aquifers: A Laboratory Proof of Concept Study (Year 2)
Project Number:	2008SD131B
Start Date:	3/1/2009
End Date:	2/28/2011
Funding Source:	104B
Congressional District:	SD First
Research Category:	Climate and Hydrologic Processes
Focus Category:	Water Supply, Management and Planning, Groundwater
Descriptors:	
Principal Investigators:	Suzette R Burckhard, Patrick J. Emmons

Publications

1. Burckhard, S., 2008, Development of a GIS Based Hydrologic Model for Prediction of Runoff Using Remotely Sensed Data, presented at the 2008 Eastern SD Hydrology Conference, Oct 22-23, Brookings, SD.
2. Burckhard, S. And Emmons, P.J., 2008, Development of a Decision Support System for Water Resources Management of Shallow Glacial Alluvial Aquifers: A laboratory Proof of Concept Study, presented at the 2008 Eastern SD Hydrology Conference, Oct 22-23, Brookings, SD.
3. Claire K. Garry Peschong, Aaron M. Weinandt, Suzette R. Burckhard, and Patrick J. Emmons, 2008, A Laboratory Study of Streamflow and Groundwater Recharge, poster presented at the 2008 Eastern SD Hydrology Conference, Oct 22-23, Brookings, SD, and at SDSU Faculty Recognition Day, February 25, 2009, Brookings, SD.
4. Claire K. Garry Peschong, Aaron M. Weinandt, Suzette R. Burckhard, and Patrick J. Emmons, 2009, Laboratory Study of Streamflow and Groundwater Recharge, poster presented at the SDSU Undergraduate Research, Scholarship, and Creative Activities Day, April 23, 2009, Brookings, SD.
5. Burckhard, S., and P. Emmons, 2008, Development of a Decision Support System for Water Resources Management of Shallow Glacial Alluvial Aquifers: A Laboratory Study, presented at Annual Groundwater and Environmental Quality meeting, Pierre, SD.
6. Burckhard, S., and P. Emmons, 2009, Ever wonder how much stream flow makes it to groundwater: Results of a laboratory experiment, presented at the 21st Annual Environmental and Groundwater Quality conference, Fort Pierre, SD.
7. Amatya, S., S.R. Burckhard, and P.J. Emmons, 2010, Development Of Climate Scenarios Using Evaporation And Precipitation Data For Brookings, South Dakota, 2010 International Student Prairie Conference on Environmental Issues, University of Manitoba, Canada, June 7-8, 2010.
8. Basnet, N., S.R. Burckhard, , and P.J. Emmons, 2010, Development Of Climate Scenarios For Precipitation For Aberdeen, South Dakota, 2010 International Student Prairie Conference on

Environmental Issues, University of Manitoba, Canada, June 7-8, 2010.

9. Amatya, S., S.R. Burckhard, and P.J. Emmons, 2010, Development Of Climate Scenarios Using Pan Evaporation Data For Brookings, South Dakota, Poster presented at the 2010 Surface Water Treatment Workshop, April 27-29, 2010, Fargo, ND.
10. Basnet, N., S.R. Burckhard, and P.J. Emmons, 2010, Development Of Climate Scenarios For Precipitation For Aberdeen, South Dakota, Poster presented at the 2010 Surface Water Treatment Workshop, April 27-29, 2010, Fargo, ND.
11. Burckhard, S.R., and P.J. Emmons, 2009, Water Management Issues In These Changing Times, presented at the Eastern SD Water Conference, Nov 2-3, 2009, Brookings, SD.
12. Peschong, C., S.R. Burckhard, and P.J. Emmons, 2009, Comparison Of Climate Scenarios For Lake Levels Versus Stream Flow, Poster presented at the Eastern SD Water Conference, Brookings, SD, Nov 2-3, 2009.
13. Basnet, N, S.R. Burckhard, and P.J. Emmons, 2009, Development Of Climate Scenarios For Precipitation For Aberdeen, South Dakota, Poster presented at the Eastern SD Water Conference, Brookings, SD, Nov 2-3, 2009.
14. Amatya, S., S.R. Burckhard, and P.J. Emmons, 2010, Development Of Climate Scenarios Using Climate Data for Specific Stations in Eastern South Dakota, 2010 Eastern South dakota Water Conference, Brookings, SD, November 9-10. 2010.

Project report for: USGS 3F3496 "Development of a Decision Support System for Water Resources Management of Shallow Glacial Alluvial Aquifers: A Laboratory Proof of Concept Study"

Written by Suzette R. Burckhard, Civil and Environmental Engineering Department, South Dakota State University, Brookings, SD, 57007-0495

Introduction:

Starting in 2000, various regions across the United States, especially in the Western United States, saw a decrease in precipitation causing drought conditions. As these conditions have persisted, concerns have been raised regarding public and private water supplies. Many cities across the Western United States are developing plans for sustainable water supply alternatives to address concerns including climate changes and economic factors. Local water resources managers need tools they can employ in predicting water supply quantities and quality as a function of time especially when considering how to optimize the use of these resources in a sustainable manner. Previously, a GIS based model DSS was developed that predicted stream flow using remotely sensed data as part of a flood risk DSS. Improvements to the GIS based watershed scale model have been made that allow the model to predict event based groundwater recharge in stream channels. The quality of these improvements needs to be verified. A first step toward verification of the model is to acquire laboratory data by constructing a laboratory scale surface runoff/subsurface infiltration apparatus to verify groundwater recharge parameters that have been formulated as part of an existing GIS based runoff model. A previously funded USGS 104b project found that groundwater recharge parameters can be estimated from general properties. The goal of this proposed study is to incorporate the soil parameters into a GIS based flow model to estimate recharge to shallow glacial aquifers underlying intermittent streams. Sensitivity analyses will be performed on the GIS based model to assess the optimal quantity and quality of data necessary to achieve meaningful water resources management results.

Project information:

Information technology transfer program (8 presentations/posters)

- Papers and posters were presented at:
    - Amatya, S*, **Burckhard, S.R**., and Emmons, P.J., 2010, Development of Climate Scenarios Using Climate Data for Specific Stations in Eastern South Dakota, 2010 Eastern South Dakota Water Conference, Brookings, SD, November 9-10, 2010.
    - Amatya, S*, **Burckhard, S.R**., and Emmons, P.J., 2010, Development of Climate Scenarios Using Evaporation and Precipitation Data for Brookings, South Dakota, 2010 International Student Prairie Conference on Environmental Issues, University of Manitoba, Canada, June 7-8, 2010.

- Basnet, N*, **Burckhard, S.R**., and Emmons, P.J., 2010, Development of Climate Scenarios for Precipitation for Aberdeen, South Dakota, 2010 International Student Prairie Conference on Environmental Issues, University of Manitoba, Canada, June 7-8, 2010.
- Amatya, S*, **Burckhard, S.R**., and Emmons, P.J., 2010, Development of Climate Scenarios Using Pan Evaporation Data for Brookings, South Dakota, Poster presented at the 2010 Surface Water Treatment Workshop, April 27-29, Fargo, ND.
- Basnet, N*, **Burckhard, S.R**., and Emmons, P.J., 2010, Development of Climate Scenarios for Precipitation for Aberdeen, South Dakota, Poster presented at the 2010 Surface Water Treatment Workshop, April 27-29, Fargo, ND.
- **Burckhard, S.R.*,** and Emmons, P.J., 2009, Water Management Issues in These Changing Times, presented at the Eastern SD Water Conference, Nov 2-3, Brookings, SD.
- Peschong, C*, **Burckhard, S.R**., and Emmons, P.J., 2009, Comparison of Climate Scenarios for Lake Levels Versus Stream Flow, Poster presented at the Eastern SD Water Conference, Brookings, SD, Nov 2-3, 2009. **(This poster won 2nd place in the student poster competition.)**
- Basnet, N*, **Burckhard, S.R**., and Emmons, P.J., 2009, Development of Climate Scenarios for Precipitation for Aberdeen, South Dakota, Poster presented at the Eastern SD Water Conference, Brookings, SD, Nov 2-3, 2009.

Problem and Research objectives

Problem statement:

The use of groundwater as a public water supply had increased from 26 percent in 1950 to 40 percent for 1985. The water use percentage of groundwater has remained at 40 percent through 2000 (USGS, 2000). Starting in 2000, various regions across the United States, especially in the Western United States, saw a decrease in precipitation causing drought conditions (US Drought Monitor, 2000). As these conditions have persisted, concerns have been raised regarding public and private water supplies. Many cities across the Western United States are developing plans for sustainable water supply alternatives to address concerns about climate changes and economic factors (Dorris, 1989). The proposed GIS based watershed scale model can be used to predict amounts of shallow aquifer recharge expected from different storm events. Eventually, this GIS model will be combined with a Decision Support System that utilizes fuzzy logic to map various management scenarios. The intended users of this DSS are local water resources managers who are trying to predict the optimal manner in which to use surface and groundwater drinking water sources.

Objective:

The objective of this project is to modify an existing GIS based rainfall-runoff model and use that model to develop a robust data set for shallow alluvial aquifer recharge in stream beds as a function of time and storm event size.

Methodology

Based on the work plans for the project, the following list of objectives were proposed to accomplish the overall objective.

1. The first objective is to update and refine an existing MODFLOW groundwater flow model developed for the Aberdeen, SD, area by Emmons (1990). This portion of the project is being finished as part of a previously funded USGS 104b grant.
2. The second objective is to modify an existing GIS based Decision Support System model developed previously by Paulson and Burckhard (2002). Evaluation of the results from this model will be made to the results from the MODFLOW simulations as MODFLOW is well accepted in modeling groundwater flow.
3. The third objective is to simulate various wet and dry climate cycle scenarios for 10, 20, and 50 years into the future to assess the availability of water resources.
4. The fourth objective is to utilize the results from the climate modeling scenarios to develop a series of management alternatives for the well field and associated reservoir system.
5. The fifth objective of this project is to examine the transferability of the Neural Network based Fuzzy Cognitive Decision Support System model to the Sioux Falls, SD area. Analyses will be performed to assess the DSS behavior utilizing historical data.
6. Sensitivity analysis to assess the quantity and quality of data necessary to achieve meaningful management results from the model will be performed.

The first objective of the study was to modify and existing MODFLOW model for the Elm aquifer. Mr. Pat Emmons worked on this part of the project. In order to accomplish the second objective, the format for the proposed datasets was studied, which was part of the third objective. Data was acquired for precipitation, evaporation, and streamflow from the SD Climate Office and from the USGS. These data were processed into annual cumulative amounts for each year of data then analyzed statistically. The data from the Aberdeen, SD, climate station was evaluated statistically then further evaluated to define 8-year periods that would correspond to Dry, Moderately Dry, Average, Moderately Wet, and Wet scenarios consisting of eight continuous water years of real data. In the analysis of Aberdeen’s data, there were found to be discrepancies between the scenarios found by the USGS in their study of flooding in NE SD. The discrepancies between the time periods were studied further by looking at the relationship between the identified climate scenarios, streamflow, and precipitation records and the climate scenarios identified by the USGS in their NE SD study. Further analysis of precipitation and streamflow records from different locations within the state of SD was performed to verify the earlier results. At this time, a more robust dataset of climate records is being processed to create the climate records required by the GIS based model. There were insufficient groundwater data records to develop climate scenarios.

Additional work is ongoing on the climate scenarios and water management models as well as the later objectives not accomplished at this time.

Principal findings

The principal findings of this study were as follows.

- The climate scenarios identified by the USGS in their NE SD study do not correspond to the identified climate scenarios found for Aberdeen, SD, nor for Sisseton, Watertown, Huron, or Brookings. The climate scenarios identified by the USGS relied heavily on a water balance approach which may not be appropriate for all water management scenarios.
- The climate scenarios identified by the USGS also did not correspond to those identified by studying evaporation records from the Brookings, SD, weather station. The lack of long term evaporation data is one area of concern for further study.
- Streamflow and precipitation are strongly correlated, as can be expected from rainfall-runoff relationships. Graphs of cumulative streamflow and precipitation with time show correlations between precipitation events and streamflow. Additionally, analysis of streamflow records can be used to identify climate scenarios as well as precipitation records and vice versa in order to obtain more complete climate records.
- Cumulative precipitation, for long term records, was normally distributed and could be interpreted using normal distribution statistics.
- The climate scenarios created by using cumulative annual water year records greatly over- and under-estimated the 8-year cumulative amounts for Wet and Dry scenarios as the real 8-year Wet scenario included average and above average years as well as a few wet years as classified by statistically evaluating the annual data.
- Climate scenarios developed from evaporation records do not correspond with those developed from precipitation records.
- Climate scenarios developed from one weather station do not always correspond to the climate scenarios developed for another station. Further analysis of the differences and similarities for the stations noted a pattern similar to one found by the USGS and SD DOT for climate areas to use in creating flow equations to predict streamflow in ungaged watersheds.

Significance of findings

The results of the climate scenario studies showed that there are identifiable differences across the state of SD such that a simplistic view of precipitation or evaporation based climate scenarios is insufficient in order to properly identify whether a time period is wet or average. Correlations between precipitation and streamflow were identified and these correlations can now be implemented in the next phase of the project.

Simulating the Soil Erosion from Land Removed from CRP

Basic Information

Title:	Simulating the Soil Erosion from Land Removed from CRP
Project Number:	2008SD135B
Start Date:	3/1/2009
End Date:	2/28/2011
Funding Source:	104B
Congressional District:	SD First
Research Category:	Water Quality
Focus Category:	Water Quality, Models, Sediments
Descriptors:	
Principal Investigators:	Todd P. Trooien, David E. Clay, Thomas Schumacher, Dennis Todey

Publication

1. Sishodia, Rajendra P., 2010, Simulating the Soil Erosion from Land Removed from CRP, MS Dissertation, Agricultural and Biosystems Engineering, South Dakota State University, Brookings, South Dakota, 65 pages.

Simulating the soil erosion from land removed from CRP

Rajendra P. Sishodia, Graduate Assistant, Agricultural and Biological Engineering Department, University of Florida, Gainesville, Florida-32611

Todd P. Trooien, Professor, Agricultural and Biosystems Engineering Department, South Dakota State University, Brookings, SD-57007

Abstract: A survey of South Dakota Conservation Reserve Program (CRP) contract holders indicated that large areas of land in the CRP could be returned to grain production in the next few years. The objective of this study was to use an erosion prediction model to estimate increased soil erosion due to the change of landuse from CRP to grain production. Single storm runoff and sediment yield data collected from a continuous corn field were used for Water Erosion Prediction Project (WEPP) model evaluation. For sediment yield prediction WEPP performance was considered "very good" (NSE = 0.95 and RSR = 0.23), so further model calibration was not performed. This model was then used to predict annual soil loss for different crop rotations including CRP. WEPP results indicated that the simulated change of landuse always increased the annual soil loss. The least increase was indicated when adopting no-till and the highest increase was indicated for soybean spring chisel plow. For the monitored watershed simulated sediment yield increased by 4.9 to 5.5 tons/ha per year while changing the landuse from CRP to continuous corn spring chisel plow or corn-soybean spring chisel plow. Furthermore, for a slope higher than 4% at the monitored site, these two management practices yielded in soil loss greater than the tolerance limit (T ≈ 11 ton/ha). Results suggest that for a slope of more than 4% at the Brookings location, other management options resulting in smaller soil loss should be considered.

(KEY TERMS: CRP; landuse; model performance; simulation; WEPP)

The Conservation Reserve Program (CRP) was established by the Food Security Act of 1985 and was reauthorized in subsequent years. The purpose of CRP is to help agricultural producers safeguard environmentally sensitive land by providing funding for long term resource conserving land cover crops. It is a voluntary program for agricultural landowners in which producers can enroll their land for 10 to15 years. While enrolling in CRP, the producer agrees to plant and maintain approved vegetative cover on the enrolled land which provides various environmental benefits like reduced soil erosion, establishment of wild life habitat and improvement in water and air quality. In past years CRP has helped a great deal in reducing soil erosion and improving water quality. At the end of fiscal year 2008, 14.01 million ha (34.6 million acres) were enrolled in CRP (USDA-FSA CRP summary, 2008). FSA estimated soil erosion reductions from those 14.01 million ha of CRP to be nearly 450 million tons per year as compared to the 1982 level, with wind erosion and water erosion (sheet and rill) each contributing nearly equally to the total (USDA-FSA CRP summary, 2008).In an another estimate when comparing CRP vs. crop production, CRP was nationally estimated to reduce the amount of soil erosion by around 400 tons annually; 71 million tons by water erosion and 335 tons by wind erosion (FAPRI-UMC Report #01-07).

In 2008, 526,100 ha (1.3 million acres) were enrolled in CRP in South Dakota. From 2008 to 2010, CRP contracts totaling nearly 182,340 ha (450,570 acres) expired in South Dakota and from 2011 to 2013 another 186,320 CRP contract ha (460,414 acres) are scheduled to expire (USDA-FSA CRP monthly summary, January 2010). Some of these acres might be re-enrolled in CRP depending upon the CRP funding available, CRP lease rate (premium) and crop production economics. According to a survey conducted on South Dakota CRP contract holders, it is indicated that more than 50% of these expiring CRP acres are likely to be converted to other uses including crop production (Janssen et al., 2008). According to the survey around 60% of land not re-enrolled in CRP would likely be converted to crop production. This increase in area of land under crop production might result in increased soil erosion, impaired water quality and have other adverse environmental effects in the state.

There are various erosion prediction models available like Soil and Water Assessment Tool (SWAT), Water Erosion Prediction Project (WEPP), Revised Universal Soil Loss Equation (RUSLE2), Agricultural Non-Point Source Pollution Model (AGNPS) and Environmental Policy Integrated Climate (EPIC) to estimate soil erosion and water quality impairments. SWAT is generally used for large complex watersheds and it requires a variety of input data. Also it is not designed to simulate detailed single event flood routing. Empirical erosion prediction models like USLE cannot estimate sediment deposition and sediment delivery to offsite channels or streams. Also models based on USLE like RUSLE are unable to estimate runoff and spatially distributed erosion in a hillslope or watershed. WEPP is a process based, continuous simulation model and can be used to predict single storm soil loss in addition to annual soil loss. The WEPP model can compute spatial and temporal distributions of soil loss and deposition, and it provides estimates of soil erosion at various points in the watershed or hillslope to help in effective conservation planning (Flanagan and Nearing, 1995). WEPP has been shown to be a better predictor of soil loss than EPIC and ANSWERS (Bhuyan et. al. 2002). So WEPP was chosen to work with because we had single storm runoff and sediment yield observations and also because it is one of more widely used model for erosion prediction in conservation planning by related agencies like USDA.

The objectives of our study were to:

- Evaluate or calibrate an erosion prediction model, WEPP, with measured runoff and sediment yield data from a small watershed and
- Use the evaluated or calibrated model to estimate the soil loss from land converted from CRP to other crop production.

Material and Methods

The WEPP watershed model is an extension of hillslope model which is used to predict sediment yield from small watersheds (Flanagan and Nearing, 1995). The WEPP hillslope model requires climate, soils, management and slope profile information files in order to predict runoff and soil loss from a hillslope. In addition the WEPP watershed model requires the watershed to be delineated into hillslopes and channels need to be identified. Single storm simulation mode was used to calibrate/evaluate the WEPP using the collected single storm runoff and sediment yield data for the watershed. Afterwards this evaluated/calibrated model was used to predict annual soil loss from different management practices including CRP for different soils, slopes and locations.

Data Collection. Two research sites were selected for runoff and sediment yield data collection. The site in Brookings County, South Dakota is located at 44º 20' 34" N, 96º 48' 09" W. The field is under continuous corn management. Detailed description of soils, management and topography is provided in the WEPP input files section. The Brookings site had three watersheds but only the middle watershed was instrumented to collect data because of instrument limitations. Another site, approximately 60 km. south of Brookings, South Dakota, was also monitored. No storms occurred during the monitoring period so that site would not be discussed further.

Four runoff events were recorded at the eastern South Dakota site. The field was instrumented with ISCO samplers, stage recorders and rain gauge. H flumes were already installed at the field outlet as a part of different research at the site. Samples were taken after every 30 minutes once the sampling was started for first event and after every 15 minutes for the other three events. Runoff samples were analyzed in Water Quality Laboratory, Agricultural and Biosystems Engineering Department, SDSU for Total Suspended Solids (TSS) following the procedure outlined in Standard Methods for the examination of Water and Wastewater (Eaton et al., 2005). Time vs. Stage graphs prepared by stage recorders were used later on to calculate total TSS for different storm events.

WEPP Input files: Climate File. WEPP model uses CLIGEN (Nicks et al., 1995) to generate weather/climate data for over 2500 locations in USA. The CLIGEN is a stochastic weather generator which produces daily time series estimates of precipitation, temperature, solar radiation and other weather parameters for a geographic location based on average monthly measurements for the period of climatic record, like means, standard deviations and skewness. Brookings, South Dakota station was selected from the CLIGEN database for single storm WEPP simulations. To run the single storm simulations, the WEPP climate file requires four storm/event parameters: amount of rainfall, duration of the storm, maximum intensity of rainfall and percentage duration to peak intensity. For the Brookings county watershed these data were taken from the SDSU Climate and Weather website (http://climate.sdstate.edu) for SDSU, Brookings weather station which is 3.5 km from the watershed (Table 1). This weather station records precipitation every five minutes.

After model evaluation, annual simulations were performed for four different locations in Eastern South Dakota: Brookings, Vermillion, Aberdeen and Eureka. The coordinates of these locations are 44° 18' 23'' N 96° 47' 17'' W, 42° 46' 52'' N 96° 55' 37'' W, 45° 27' 53'' N 98° 29' 11'' W and 45° 46' 9'' N 99° 37' 19'' W respectively.

Watershed delineation and slope profile. In order to develop hillslope and channel configuration for Brookings watershed we used GeoWEPP and contour and slope maps of watershed prepared in ArcMap. GeoWEPP is a Geo-Spatial interface for WEPP which utilizes digital geo-referenced information such as Digital Elevation Model (DEM), soil map and land cover information to predict sediment yield and runoff from watersheds (Renschler et al., 2002). GPS data of Brookings County watershed were used to prepare Digital Elevation Model (DEM) of the watershed in ArcMap. NRCS, USDA Data Gateway website (http://datagateway.nrcs.usda.gov/) was used to acquire soil map for Brookings watershed. Considering the channel and hillslope network prepared by GeoWEPP and the actual field runoff observations the watershed was divided into ten hillslopes and five channels. The factor that when the hillslope length exceeds 100 m WEPP tends to over predict soil loss (Baffaut et al., 1997) was also considered while preparing watershed structure. WEPP background image for the watershed was taken from Google Earth and was scaled in WEPP watershed model for ease in watershed delineation. This watershed is nearly flat at outlet having around one percent slope in farthest south and around two percent slope at top north side.

Soils file. Soils information for Brookings County watershed was obtained from Web Soil Survey, NRCS, USDA web site (http://websoilsurvey.nrcs.usda.gov/app/). Though the Brookings County watershed is very small, it has three different kinds of soil types in it (Table 2). WEPP has a soil file database for different soils found in USA but it didn’t have all types of soils we have in the Brookings County watershed, so the required soil files were downloaded from MS Access database of Soil Data Mart, USDA, NRCS (http://soildatamart.nrcs.usda.gov/).

For the sake of simplicity in watershed delineation and analysis approximately 32% of north side of Brookings watershed, which originally contained two different types of loam soil, was assumed to have only one kind of loam soil association (Barnes Buse Loam), while around 13% of the area in East side of watershed was assumed to have other kind of loam soil (Fordville Loam) and remaining 55% of the area was designated as McIntosh Badger Silty clay loam soil. Annual simulations were also performed for different soils usually found on CRP lands at four different locations in this region of South Dakota along with existing soils at Brookings watershed. Altogether six different soil sets were simulated across four different locations in Eastern South Dakota. The soil types usually found on CRP lands in South Dakota were adapted from FAPRI-UMC Report #01-07 ("Estimating Water Quality, Air Quality, and Soil Carbon Benefits of the Conservation Reserve Program").

Management files. Brookings county watershed is under continuous corn management. Continuous corn fall MB plow file in the WEPP management database was used for single storm simulations. This file was modified for tillage and other management parameters as SDSU farm uses chisel plow in fall instead of MB plow. Date of planting and harvesting, date of different tillage operations and implements used were modified in default WEPP file to simulate actual field conditions. For single storm WEPP simulations, the initial conditions database in continuous corn management file was also adjusted for all four events. To perform continuous simulations for annual runoff and sediment yield prediction for different management practices default WEPP files for different managements were used. Commonly used continuous corn, soybean, corn-soybean, winter wheat, alfalfa along with CRP (brome grass) rotations were simulated in WEPP. For existing continuous corn management file, initial conditions file was modified to represent conditions on January 1st.

Channel Input file. Channels slope was decided based upon the contour and slope map of the area prepared with the DEM of the watershed in ArcMap (Table 3). Friction slope calculation method was selected to be Modified EPIC (Ascough et al., 1997). Channel was assumed to have uniform slope through the whole length having equal slope conditions at top and bottom of length. For all managements, Manning's roughness coefficient of 0.03 was taken for bare soil (Chow, 1959). Total Manning's roughness coefficient allowing for vegetation of 0.1 was used for all managements except for CRP (bromegrass and bluegrass) for which 0.3 was used (Knisel 1980). Since there is no temporal updating of channel erodibility values with time, like for hillslopes, average annual channel erodibility value of 75% of baseline hillslope rill erodibility was used and channel critical shear stress value of 125% of baseline hillslope critical shear stress was used for both annual and single storm simulations. Other parameters were also adjusted to simulate actual field conditions.

Model Performance Evaluation. To evaluate model simulation results Nash Sutcliffe Efficiency (NSE), Root Mean Square Error (RMSE)-observation standard deviation ratio (RSR) and percent bias (PBIAS) were calculated based on the recommendations by Moriasi et al (2007).

NSE determines relative magnitude of residual variance compared to measured data variance (Nash and Sutcliffe, 1970). It indicates the variance of prediction from a 1:1 line.

The RMSE is commonly used as an error index statistic and lower RMSE values indicate better model performance. RSR is a model evaluation statistics developed by Moriasi et al, 2007 which combines error index and standard deviation as recommended by Legates and McCabe (1999). RSR is the ratio of RMSE to standard deviation of observed data. The value of RSR ranges from zero to a large positive value. Lower RSR values indicate better model performances while a value of zero is considered as optimal model performance. RSR values < 0.7 are generally considered as satisfactory (Moriasi et al, 2007).

PBIAS value measures the average tendency of predicted data to be smaller or larger than observed data. Zero value of PBIAS indicates optimal model performance while positive values indicates model under estimation bias and negative values indicates model over estimation bias. PBIAS values ≥ ±25 are considered unsatisfactory for runoff prediction and a value ≥ ±55 is considered unsatisfactory for sediment yield prediction (Moriasi et al, 2007) (Table 4).

Initial Single Storm WEPP Simulations. For single storm simulations WEPP climate files were prepared as described in climate section for Brookings site for all four storms and for soils file default WEPP files were used for dominant soil types found in each hillslope. Soil parameters like interriil erodibility, rill erodibility, critical shear stress and effective hydraulic conductivity were left unchanged in default WEPP soil files. Initial saturation was adjusted based on the moisture measurements in the field. Channel erodibility values were taken as 75% of baseline hillslope rill erodibility and critical shear stress value was taken as 125% of baseline hillslope critical shear stress value to represent an average condition.

Annual Continuous WEPP Simulations**.** CLIGEN version 4.3 in WEPP was used to generate 50 year weather/climate data for four locations across South Dakota including Brookings, Aberdeen, Vermillion and Eureka. These climate files were then used to run annual continuous simulations for 50 years for different management practices including CRP (bromegrass and bluegrass) for different slopes and soils. Altogether six different types of soil sets were simulated for different management practices over 2 to 12% slope range for four locations.

Results

WEPP Evaluation/Calibration. The results indicate that WEPP predicted only one event producing sediment yield and it didn't predicted any sediment yield from other events at all (Table 5). The NSE, RSR and PBIAS values were in the unsatisfactory range for runoff prediction by WEPP and the high positive PBIAS value indicates that model under predicted the runoff (Table 6). For sediment yield prediction the NSE, RSR and PBIAS values were in satisfactory range. In fact a high NSE value, close to one, indicates very good model performance for the sediment yield prediction. A positive PBIAS value indicates little underestimation of sediment yield by WEPP. Because the NSE, RSR and PBIAS values were in satisfactory range for sediment yield prediction, indicating adequate soil loss prediction by WEPP, no model calibration was performed.

Annual Soil loss estimation for different management practices. After satisfactory model evaluation this uncalibrated WEPP was used to estimate soil loss for different agricultural management practices including CRP management practice for different soils, slopes and locations in Eastern South Dakota.

The results of continuous annual simulations for different management practices at different soils, slopes and locations indicates increased soil erosion while changing simulated landuse from CRP to other management practice(Figure 2). The least increase in the soil loss occurs while adopting no till option and the highest increase in soil loss is indicated when adopting spring chisel for soybean or corn-soybean rotation. The smaller amount of soil loss in the no-till option and greater soil loss for the spring chisel plow indicates the effect of tillage on soil loss. Soil loss also increases while increasing watershed slope for almost all managements and soils excluding some exceptions. With increasing slopes higher energy is available to flowing water because of high velocity thereby increasing its soil erosion potential. The annual simulation results for different soils at the Brookings location indicates the highest amount of soil erosion for a Poinsett soil and the least soil loss for soils existing at the Brookings watershed (McIntosh, Barnes and Fordville) for all managements and slopes. Analysis of the results-, at the Brookings location for three different soils sets, indicates the effect of hydraulic conductivity on soil loss. Lower hydraulic conductivity of the Poinsett soil might have caused this higher soil loss, though interrill erodibility and critical shear stress values indicates better erosion resistivity than Renshaw soil but this effect seems to be offset by very low effective hydraulic conductivity. For a McIntosh, Barnes and Fordville soil set soil loss is smaller because of lower rill erodibility and higher effective hydraulic conductivity values than the Poinsett soil. At the Aberdeen location also, instead of lower erodibility and higher critical shear stress, soil loss is higher for a Forman soil as compared to the Ulen soil because of comparatively very low effective hydraulic conductivity.

The simulated soil loss increases by 5-6 times when changing the landuse from CRP to continuous corn spring chisel plow or corn-soybean spring chisel plow (Table 7). Also, this percentage increase in soil loss increases with increasing slope while changing simulated landuse at Brookings location. Table 7 also indicates that the soil loss for slopes greater than 4% is greater than the soil loss tolerance limit ($T \approx 11$ ton/ha [4.45 tons/acre]) for these two crop management practices. It suggests that these management practices are not sustainable economically on slopes more than 4%. Other management practices, such as the soybean spring plow and corn fall MB plow, also produced higher soil loss than the T value for slopes more than 4%. Management options such as alfalfa, no-till and winter wheat are better practices for higher slopes in terms of soil erosion because these management practices have soil loss values less than the T value.

When increasing the tillage intensity, either for corn, soybean or corn-soybean, increase in the soil loss is substantial depending upon the slope and management. The amount of soil loss is comparatively higher for the Vermillion location and lower for Eureka but the percent increase in soil loss while switching simulated management practice is similar for all the four locations. While comparing similar tillage options for different crops, continuous corn management has less soil loss than soybean. It might be because of corn residue in the field which improves soil structure and causes less erosion as compared to soybean (Laflen and Colvin, 1981, Bradford and Huang, 1994). Alfalfa and winter wheat are also some better options than soybean, continuous corn, and corn-soybean in terms of relative amount of erosion. Comparing the relative amount of soil loss for different management practices, no-till or other options involving less tillage resulted in less soil erosion than spring chisel or fall MB plow or options involving increased tillage intensity.

In annual WEPP watershed simulations there is no temporal updating of channel erodibility parameters during the year, whereas, for the hillslopes the erodibility parameters are updated based on other variables such as rainfall. Average values of channel erodibility and critical shear stress need to be estimated for annual and single storm simulations. Since the channels in our watershed are not permanent and do not have water all the time, using an average erodibility value for all the runoff events during the year (for single storm simulations) might lead to erroneous results. For annual simulations these values can be calibrated but for single storm simulations it might not be possible because each single runoff event would have a unique value of these parameters associated with it. Also while doing annual simulations it was observed that some combinations of channel parameters produce undesirable effects in sediment yield prediction. When channel width is higher these effects are more pronounced; an example is reduced simulated soil loss for greater slope for some management practices. This effect can be observed more prominently for continuous corn management existing at the Brookings site with a McIntosh, Barnes and Fordville soil set at Eureka location.

The sediment yield and runoff for the four locations for each management practice indicates that generally runoff and soil loss increases as we move from Eureka to Vermillion (North to South) in this region of South Dakota i.e. runoff and soil loss follows this general trend: Vermillion > Brookings > Aberdeen > Eureka. The average annual precipitation follows the same trend in this region and increases as we move from Eureka to Vermillion (North to South) (Table 8). So this increased amount of soil loss and runoff may be attributed to increased amount of precipitation for these four stations.

Conclusions

On the basis of model performance statistics (NSE, RSR and PBIAS), uncalibrated WEPP performance was “very good” for sediment yield prediction for a Brookings County watershed. WEPP simulations of the Brookings County watershed with existing soils (McIntosh, Barnes and Fordville) indicated at least 5 to 6 times increase in the annual sediment yield while changing the landuse from CRP to the continuous corn spring chisel or corn-soybean spring chisel plow. The percent increase in the soil loss while changing the simulated landuse is the lowest for existing slope (1.42%) and it increases as the slope increases with a 20 to 25 times higher soil loss at 12% slope. For the Brookings watershed having existing soils and slope the sediment yield increased by 4.9 to 5.5 tons/ha per year (1.9 to 2.2 tons/acre per year) while switching the simulated landuse from CRP to continuous corn spring chisel plow or corn-soybean spring chisel plow.

The least increase of 0.5 ton/ha per year (0.2 tons/acre per year) was indicated for no till practice at the Brookings site (Corn-soybean no till).

If the slope is greater than 4%, continuous corn and corn-soybean spring chisel plow resulted in soil loss greater than the soil loss tolerance limit (T ≈ 11 ton/ha [4.45 ton/acre]), indicating unsustainable landuse. Therefore, for a slope of more than 4% at the Brookings location other management options producing smaller soil loss such as alfalfa, winter wheat or no-till should be considered. Assuming 6-8% is the average slope for general CRP enrolled lands, the increased soil loss at the Brookings site would be somewhere between 12-20 tons/ha while switching simulated landuse from CRP to continuous corn spring chisel or corn-soyaben spring chisel plow. This is a huge increase in the soil loss and might have adverse impacts on water quality in state.

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Table 1 WEPP Climate File Input Parameters for Single Storm Simulation at the Brookings County Watershed

Date	Rainfall (mm)	Duration (min)	Max/Peak Intensity (mm/hr)	Percentage duration to peak intensity (%)
6/27/2009	19	180	33.53	13.88
7/7/2009	18.5	35	67.06	14
7/9/2009	9.4	110	9.14	36.36
7/14/2009	10.7	15	67.06	50

Table 2 Percentage Area of the Brookings County Watershed Covered By Different Soils

Site	Soil types	Percentage of area covered	Total area of watershed (ha)
Brookings County	Fordville Loam	22	2.19
	Barnes-Buse Loam	27	
	Mcintosh Badger Silty Clay Loam	51	

Table 3 Channel editor file parameters for the Brookings watershed

Channel ID	Slope (percent)	Length (m)	Width (m)
C1	1.4	55.2	0.2
C2	1.1	68.4	0.4
C3	1.4	81.3	0.2
C4	1.1	88.9	0.3
C5	1.1	43.1	1.5

Table 4 Performance Ratings for Various Model Evaluation Statistics (Moriasi et al, 2007)

Performance rating	NSE	RSR	PBIAS	
			Stream flow/runoff	Sediment yield
Very good	0.75<NSE≤1	0 ≤ RSR ≤ 0.5	PBIAS≤±10	PBIAS≤±15
Good	0.65<NSE≤0.75	0.5 < RSR ≤ 0.6	±10≤PBIAS<±15	±15≤PBIAS<±30
Satisfactory	0.50<NSE≤0.65	0.6 < RSR ≤ 0.7	±15≤PBIAS<±25	±30≤PBIAS<±55
Unsatisfactory	NSE≤0.5	RSR > 0.7	PBIAS≥±25	PBIAS≥±55

Table 5 Initial WEPP Predicted and Observed Runoff and Sediment Yield at the Brookings Watershed

Date	Rainfall (mm)	WEPP Predicted sediment yield (Kg)	Observed sediment yield (Kg)	WEPP Predicted runoff (m^3)	Observed runoff (m^3)
6/27/2009	19	0	0.08	0	5.79
7/7/2009	18.5	21.8	24.26	24.86	116.4
7/9/2009	9.4	0	2.94	0	45.8
7/14/2009	10.7	0	2.22	0	7.98

Table 6 Calculated NSE, RSR And PBIAS Values for Initial Runoff and Sediment Yield Prediction by WEPP

	NSE	RSR	PBIAS
Runoff	-0.32	1.15	85.88
Sediment Yield	0.95	0.23	26.1

Table 7 Soil Loss at the Brookings Watershed Having Existing Soils for Different Management Practices and Slopes

Slope	1.42%	2%	4%	6%	8%	10%	12%
Bromegrass	0.9	1.2	1.1	1.2	1.4	0.9	1
Corn spring chisel plow	5.8	8.2	11	13.3	15.3	17.7	20.5
Corn-soybean spring chisel plow	6.4	9.3	13.6	17.4	21.1	24.2	28.7

Table 8 Average Annual Precipitation (Mm) as Produced by WEPP Output File for Four Stations in SD (50 Year Climate File)

Station	Eureka	Aberdeen	Brookings	Vermillion
Average Annual Precipitation	431	484	542	634

Acidic Leaching Tests to Determine Arsenic Mobility from Concrete-Encapsulated Limestone Waste

Basic Information

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1. Davis, A.D., C.J. Webb, D.J. Dixon, J.L. Sorensen, and S. Dawadi, 2007, Arsenic Removal From Drinking Water By Limestone-Based Material: Mining Engineering, Volume 59 (Number 2) pages 71-74.
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Final Technical Report

South Dakota Water Resources Institute
U.S. Geological Survey 104b Program

Acidic Leaching Tests to Determine Arsenic Mobility from Concrete-Encapsulated Limestone Waste

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Introduction

Arsenic contamination of drinking water is a major problem facing many areas of the United States and the world. Limestone-based technology for arsenic removal from water is an innovative and promising method. The technology offers the potential for low-cost disposal of waste product after arsenic removal, either in an ordinary landfill or by encapsulation in concrete. There is a need for an inexpensive remediation technology for the removal of arsenic in drinking water that can be applied to small rural water systems.

Arsenic is a persistent and bioaccumulative toxin. Long-term exposure has the potential to cause heart arrhythmia, nerve damage, vascular damage, bone marrow depression, anemia, and leucopenia, as well as cancer of the lung, liver, skin, and bladder. The maximum contaminant level for arsenic, formerly 50 parts per billion (ppb), was lowered to 10 ppb in 2006 because of links to cancer. In South Dakota, it has been estimated that 15 to 20 water supply systems will not be in compliance with this mandate. Current removal technologies are expensive and their implementation will cause economic pressures for rural communities with high levels of arsenic in their drinking-water supplies.

Project Information

Limestone-based material has previously demonstrated the potential to remove arsenic and other metals from drinking water. Limestone is widely available, with suppliers in South Dakota and other states of the U.S. Earlier research by the principal investigators, using limestone particles and manufactured limestone-based granules as an adsorbent for drinking water treatment, has shown that the efficiency of the arsenic-removal process can be improved by increasing surface area while maintaining flow-through rates needed for adsorption technologies. Research by the authors also has shown that the waste product passes the Toxicity Characteristic Leaching Procedure (TCLP) test. Disposal of arsenic-enriched waste is critical for commercial viability of removal technologies. Low-cost disposal of waste in an ordinary landfill gives the method an advantage that could help communities meet the new maximum contaminant level for arsenic. The ability to recycle the waste material by encapsulation in concrete or mortar would add a significant economic benefit, reducing overall costs. Other methods of arsenic removal suffer from the disadvantage of higher waste-disposal costs because of the potential for leaching of arsenic from the waste product.

This project investigated acidic leaching of arsenic from limestone waste after encapsulation in concrete or mortar. The work focused on leaching with simulated rainwater and mild sulfuric acidic solutions typical of shale soils that contain minerals such as pyrite. The tests help demonstrate the potential for recycling of the waste material, thereby decreasing overall costs of limestone-based technology. In laboratory tests with limestone-based material, arsenic-contaminated water was combined with limestone material. The waste material then was removed, encapsulated in mortar, and tested for leaching potential under acidic conditions such as rainwater and weak sulfuric acid solutions.

Objectives

The objectives of this work were to:

1) Determine adsorption of arsenic by using limestone-based material as the treatment medium.
2) Remove the limestone waste material and combine the product in mortar. Prepare mortar cubes with the material.
3) Conduct leaching tests with simulated rainwater and mild sulfuric acid solutions, and analyze the leachate for arsenic concentrations.

When arsenic is removed from water by limestone-based material, the process is believed to be either adsorption or the precipitation of hydrated calcium arsenate. Hydrated calcium arsenate has an extremely low solubility as compared to limestone. The proposed research could help answer a critical research question: when arsenic is removed from water by limestone, is the arsenic merely adsorbed on the surface of the limestone, where it could be released after dissolution of the limestone, or is it bound as a low-solubility calcium arsenate and thus unavailable for release even if the limestone base dissolved?

The research presented in this report focused on improving the economic advantages of disposal of limestone-based material by recycling the waste product in concrete. Overall goals include application as a pilot study at a wellhead with naturally occurring arsenic contamination, and commercial viability of the technology. Two of the principal investigators have extensive experience with arsenic removal by limestone, and the third investigator is a recognized expert in the fields of cement and concrete.

The leaching tests in this work were designed to determine the stability of the waste material and the potential for mobility of contaminants in wastes. Infiltrating water and acidic liquids that come into contact with the waste could potentially leach toxins from the material. The U.S. Environmental Protection Agency’s D List indicates the maximum concentration of arsenic for toxicity characteristic is five parts per million (ppm). Previous work by the researchers has shown that waste product from limestone-based material, after arsenic removal, is considered benign and suitable for disposal in a landfill. Results from that previous research showed final arsenic concentrations ranging from 8 to 24 parts per billion (ppb). Testing was needed for encapculated waste in concrete or mortar, however. We see the potential for recycling of the limestone waste product and its adsorbed arsenic in concrete, but testing has been needed to determine long-term stability of the encapsulated waste under mildly acidic conditions typical of weathering. The proposed research helps demonstrate the viability of this approach.

Methods

This project investigated leaching potential and stability of concrete-encapsulated limestone waste product after arsenic removal. The tests help demonstrate the potential for recycling of the waste material, thereby decreasing overall costs of limestone-based technology. In laboratory tests, arsenic-contaminated water was combined with limestone-based material in batch tests. The limestone waste material then was removed, encapsulated in mortar, and tested for leaching under acidic conditions to determine its potential for recycling in concrete. The work could give limestone-based technology a distinct advantage for use in small rural water systems.

A stock As(V) solution was used to prepare influent solutions of water. Four one-liter bottles were filled with 1000 grams of 0.5 to 1 mm sized Minnekahta Limestone, and four 500-mL bottles were filled with 500 grams of 0.5 to 1 mm sized Minnekahta Limestone. The prepared solutions were introduced into the bottles, which were shaken several times a day.

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After batch testing, the solution was drained and samples were analyzed for final arsenic concentrations. From the difference between the initial and final concentrations, the mass of arsenic adsorbed on the limestone was determined.

The waste material then was removed and encapsulated in mortar cubes of 2 in x 2 in x 2 in. After curing, the mortar cubes were broken into pieces of approximately 1 to 2 cm, and placed in acidic solutions ranging from simulated rainwater to weak sulfuric acid. The pH values were 5.6 (simulated rainwater), 4 (prepared with HCl), and 2 (prepared with sulfuric acid). The leachate then was tested for arsenic concentrations.

Principal Findings and Significance

During initial phases of the work, arsenic was removed from prepared solutions of water by limestone. Table 1 (below) shows the mass of arsenic removed during this part of the laboratory work.

Table 1. Arsenic removal by limestone during laboratory testing.

	Bottle 1	Bottle 2	Bottle 3	Bottle 4	Bottle 5	Bottle 6	Bottle 7	Bottle 8
Initial arsenic concentration [mg/L]	7.100	7.230	0.713	0.760	7.100	7.230	0.713	0.760
Initial volume of the solution[L]	0.640	0.640	0.640	0.640	0.350	0.350	0.350	0.350
Initial mass of As in solution[mg]	4.544	4.627	0.456	0.486	2.485	2.531	0.250	0.266
Final arsenic concentration [ml/L]	1.890	3.640	0.038	0.038	4.040	4.380	0.078	0.047
Final volume of the solution[L]	0.375	0.445	0.425	0.420	0.202	0.210	0.180	0.215
Final mass of As in solution[mg]	0.709	1.620	0.016	0.016	0.816	0.920	0.014	0.010
% of the final to the initial concentration	26.620	50.346	5.330	5.000	56.901	60.581	10.940	6.184
Removal [%]	**73.380**	**49.654**	**94.670**	**95.000**	**43.099**	**39.419**	**89.060**	**93.816**
Mass of As removed [mg]	**3.835**	**3.007**	**0.440**	**0.470**	**1.669**	**1.611**	**0.236**	**0.256**
Percentage mass of the removed As[%]	**84.403**	**64.994**	**96.461**	**96.719**	**67.160**	**63.651**	**94.374**	**96.201**

The limestone waste then was used in acidic leaching tests. Samples of leachate were sent to MidContinent Testing Laboratories in Rapid City, South Dakota, for analysis. Results of the leaching tests are shown in Table 2.

Table 2. Results of acidic leaching tests.

Sample	L-1	L-2	L-3 (dup)	L-4	L-5	L-6 (dup)	L-7	L-8
pH	5.6	5.6	5.6	4	4	4	2	2
As (mg/L)	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005

As shown in Table 2, the arsenic concentrations in leachate were less than the limit of detection of 0.005 mg/L for all samples. This indicates that measurable leaching did not occur under the acidic conditions used during testing.

Use of Cover Crops to Minimize Loss of Plant Nutrients to Water Resources

Basic Information

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"Use of Cover Crops to Limit Nutrient Runoff from Agricultural Field"

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ABSTRACT

Manure can be an important source of plant nutrients for crop production and may improve soil quality. Management practices such as methods of applying manure, timing of manure application, tillage, cover crop use and their interactions with landform and climate play an important role in nutrient losses from agricultural fields. Our research objective was to determine the effect of cover crop on nutrient loss in simulated rainfall runoff with manure use. A field study was designed to compare cover crop (rye) used after corn with and without (liquid swine) manure at ~59,325 L ha^{-1}. Sixteen 4 m^2 steel frames were used to define individual plots. Treatments were randomly assigned so that each replication had one manure treatment under cover crop, one non-manure under cover crop, one manure treatment without cover crop and one non-manure treatment without cover crop. Two rain simulations (the first defined as "dry" and the second "wet") were conducted during May 2010 and sub-samples analyzed for nitrate nitrogen (NT), total suspended solids (TSS), total Kjeldahl nitrogen (TKN), total phosphorus (TP) and total dissolved phosphorus (DP) from the run-off of each plot. Significant treatment effects and mean comparison were done with $LSD_{(0.10)}$. Runoff under manure treatments had significantly ($LSD_{0.1}$) higher concentrations of NT, TSS, TP and DP in both runoff runs. The dry run loads of NT, TSS and DP were significantly higher in the manured treatments while NT was found significantly greater in the wet run. With both dry and wet runs the concentration and load of NT was significantly lower in runoff water with the cover crop compared to no cover crop treatment. In addition TKN concentration under the wet run was lower with the cover crop treatment.

INTRODUCTION

Manure can be an important source of plant nutrients for crop production. Land application of manure is a common practice in North America and around the world. Manure can improve soil quality by increasing organic matter, infiltration, soil productivity and minimizing surface run-off. The increasing number of concentrated animal feeding operations (CAFOs) creates more challenges for producers to effectively manage land application of manure. Nutrient losses to water bodies from applied manure have led to concerns by producers, consumers and environmental scientists. A relatively small (agronomically) amount of nutrients reaching water bodies can significantly impair water quality and may lead to eutrophication. Land applied manure contributes a significant amount of nitrogen and phosphorus to the Gulf of Mexico and are the major nutrients causing hypoxia. Approximately 14 % of the total nitrogen and 48 % of the total phosphorus that reached the Gulf was from manure sources (Goolsby et al., 1999). Over enrichment of N and P in aquatic ecosystems may cause toxic algal blooms, loss of aquatic vegetation, loss of bio-diversities, and degradation of coral reefs.

Implementation of proper practices and conservation measures may mitigate agricultural non-point N and P loss to water sources. Incorporating cover crops into the crop rotation when manure is applied could minimize nutrients loss in runoff. Cover crops can reduce surface sealing, improve infiltration, reduce erosion, improve soil fertility and serve as excellent sinks for NO_3 (Meisinger et al., 1991). Due to timeliness, manure is often applied after small grain harvest, which also lends itself to more cover crop growth (i.e. higher nutrient uptake). The management strategy of using cover crops when manure is applied on small grain stubble could be developed as a best management practice to minimize nutrient runoff and leaching losses in South Dakota and over the Midwest region. Cover crops have been shown to scavenge and reduce nitrogen loss (Hamlett and Brannan, 1991; Gallaher, 1997; Delgado et al., 2001 and 2007; Parkin et al., 2006; Singer et al., 2007; Camberdella et al., 2010) and phosphorus loss (Sharpley and Smith, 1991; Burwell et al., 1975; Kleinman et al., 2005; Vliet et al., 2002) either in runoff or drainage water when manure has been applied to the field. Numerous studies indicate cover crops are effective in capturing soil nutrients and reducing loss to both surface and sub-surface water resources. However, few of these studies have been conducted in the Northern Great Plains where cover crop growth after corn can be limited due to lack of growing season once the corn is harvested. The possibility of incorporating rye into a corn-soybean rotation as a manure management option is needed.

The overall objective of this study is to determine the effect of cover crop growth on loss of manure applied nutrient under simulated rainfall. The overall goal of the project is to develop alternative best management practices (BMPs) for manure management.

MATERIALS AND METHODS

A research site was established at the Southeast Research Farm near Beresford, South Dakota in 2009 on a silty clay loam (Egan soil series) just south east of the office building. The research design consisted of a split plot with four replications using cover crop as the main plot and manure as the split. The crop rotation was corn-soybean-spring wheat with no tillage. A winter rye cover crop was broadcast seeded on July of 2009 in standing corn. After corn harvest, liquid hog manure was injected on 1st December 2009 at a rate of ~59325 L ha^{-1}(6345 gal $acre^{-1}$) with analysis given in Table 1. The rye cover crop was well established in spring of 2010. Sixteen (16) 4.0 m^2 runoff plots were established in April 2010 as described previously with four plots on rye cover crop and manure, four on rye cover crop with no manure, four on no cover crop with manure and four on no cover crop and no manure.

The rainfall simulator used for this study was constructed according to the NPRP (National Phosphorus Research Project, 2001). A single nozzle (TeeJet™ ½ HHSS50WSQ) was used in this study and based on the design of Miller (1987) which covered the 4.0 m^2 plots. The nozzle was placed approximately 305 cm (10 feet) above the ground to provide adequate terminal velocity of rain drops before reaching the soil surface, residue or cover crop canopy. During the simulation, a 3 x 3 meter aluminum frame enclosed with tarps was used to minimize wind drift. The nozzle, wiring and associated plumbing were attached to the aluminum frame. Pressure gauges were adjusted to achieve a target rainfall rate of 7.0 cm hr^{-1} (2.7 in hr^{-1}) following standard protocol of NPRD. However, actual rainfall achieved was 6.48 cm hr^{-1} (2.55 in hr^{-1}). Two rain simulations were performed from April 30 to May 10, 2010. The first was termed as a dry run under existing soil moisture conditions, the second was termed a wet run, was conducted the following day (at least 12 hours later) after completion of the dry run.

Natural rainfall was collected during summer 2009 to spring 2010 to use as the main water source for this study. Natural rain water contains low concentrations of flocculative cations as compared to well water and lessens the influence of soil flocculation during runoff. The concentrations of ortho-phosphate and TKN were very low for the collected rain water (data not reported).

Run-off for each side of the framed plots (left and right) was collected separately. Runoff water collected in a trough container was frequently vacuumed using a wet vacuum and routed by plastic pipe to a 19 liter container. Water was collected for 30 minutes after the beginning of the runoff. A sub-sample from each runoff was taken for further analysis that included the nutrients listed in table 2 and total suspended solids. Each runoff volume, analysis concentration and load (volume x concentration) was calculated from each sub plot. To determine actual rainfall rate, 12 rain gauges, 6 on each sub-plot termed "left" and "right" were uniformly set and the rainfall simulator was run for five minutes before starting each simulation. The rainfall simulation resumed until runoffs started from each sub-plot and continued for another 30 minutes.

The following formula was used to calculate runoff rate for 30 minute.

Runoff rate cm hr^{-1} = (V/A) T

Where,

V= Volume of water cm^3 collected as runoff in 30 minutes

A= Area of plot 20,000 cm^2, and

T= time of runoff collection i.e. 0.5 hr

The time for runoff to occur was recorded in minutes.

Table 1: Manure characteristics used for cover crop study, Beresford, SD.

[1]Date	[2]TM	[3]TDM	[4]AM	[5]TN	[6]TP	[7]TK
	Cover crop rainfall runoff study, Beresford site (swine manure)					
			---------------------Kg ha^{-1}----------------			
December	95.4	4.64	148	240	152	110

[1]Date= Application dates; [2]TM= Total moisture percentage; [3]TDM= Total dry matter percentage; [4]AM= Ammonium nitrogen; [5]TN= Total nitrogen; [6]TP= Total phosphorus; [7]TK= Total potassium.

Runoff sub-samples were taken in a 250 ml sub-sample and filtered to determine total dissolved phosphorus (DP) using 0.45µm membrane filter under constant vacuum. A 50 ml, 200 ml, and 1000 ml sample were acidified with 2 drops of 10% H_2SO_4 and stored in a cooler with ice packs and refrigerated before being delivered to Olsen Analytical Services Laboratory, SDSU. Samples were analyzed for ammonia nitrogen (AM) (snowmelt only), nitrate nitrogen (NO_3 –N), total suspended solids (TSS), total kjeldahl nitrogen (TKN), total phosphorus (TP) and total dissolved phosphorus (DP) concentrations (mg L^{-1}) as per table 2. Concentrations for each sub plot were multiplied by their respective runoff volumes to estimate total mass loads.

Table 2: Different parameters analyzed and methods used for their analysis

Parameters Analyzed	Methods used
Water samples	
AM[1]	EPA[2] 350.2 method
NT[3]	SM[4] 4110 B method
TKN[5]	EPA 351.3 (Nesslerization) method
TSS[6]	SM 2540 D method
TP[7]	SM 4500 B & E method
DP[8]	SM 4500 B & E method
Manure N, P and K	Method 3.3 for N, method 5.2 & AOAC[9] 931.01 for P and method 5.2

[1]AM= Ammonium nitrogen; [2]EPA=Environmental protection agency; [3]NT= Nitrate-nitrogen; [4]SM= Standard methods for the examination of water and waste water; [5] TKN= Total Kjeldhal nitrogen; [6] TSS= Total suspended solids; [7]TP= Total Phosphorus; [8]DP= Total Dissolved Phosphorus; [9]AOAC=Association of official agricultural chemists

Soil samples were taken two weeks after runoff completion at the Brookings site and one month after rain simulation at the Beresford site. Samples were taken to a 5 cm depth using a 2 cm diameter stainless steel soil probe. Ten to twelve soil cores were taken at random inside each sub plot, composited and air dried. The Beresford site also included samples from outside the plot area to a depth of 5 cm and 5-15 cm. Soils were crushed, sieved (2 mm screen) and analyzed for Olsen phosphorus (in duplicate) using the SDSU soil testing lab procedures (Skroch et al., 2006).

An ANOVA (SAS) procedure was used to determine significant effects for the simulated rainfall runoff study. Mean separation of treatment effects (where appropriate) was conducted using Fisher LSDs at p=0.10.

RESULTS AND DISCUSSION

Site characteristics

Initial gravimetric soil moisture content at 15 cm before rainfall simulation ranged between 18 to 25% (gravimetric). No difference was found in the initial soil moisture percentage between cover crop treatments as well as the manure treatments (data not reported). Soil moisture was much above average for October, 2009 and somewhat higher than average just before the onset of rain simulation on April 30, 2010. The 4 cm of precipitation about one week prior to soil moisture measurements may have masked any soil water usage by the cover crop. Rye cover crop growth in the fall was rather limited because of shade from standing corn and cool temperatures. Rye spring growth obtained 20-40 cm in height. Plots had at least 50% of the surface area covered with rye. Corn residue left in the field from the previous year was estimated at ~10 ton ha^{-1}.

Runoff and nutrient loss

Mean rainfall RO ranged from 14.9 to 18.6 liters (L) and 38.6 to 48.5 L in the dry and wet run respectively during the runoff period (Table 3 and 4). The average volume of rain applied ranged from 84-270 L and 70-112 L in the dry and wet runs respectively. The estimated amount of runoff water captured in the runoff ranged from 3% to 31% and 32 to 82 % in dry and wet run, respectively (data not reported). Runoff volume (RO) was about two fold greater in the wet run compared to dry run presumably due to the higher antecedent soil moisture for the wet run (Table 3 and 4).

Manure application effects (manure vs. no manure)

As expected, manure application significantly increased the measured runoff parameters from the dry run except the runoff volume (RO), and the TKN and TP loads (Table 3). In the wet run, all runoff nutrient measurements (parameters) increased with manure, although not all differences were significant (Table 4). In general manure addition increased the concentration and runoff load of soluble and total nutrients lost in runoff which agrees with studies by (Kleinmen et al., 2005; Camberdella et al., 2009; Kovar et al., 2010). Presumably the higher nutrient load is because of the additional nutrients from manure, but increased TSS losses may have been due to increased soil disturbance and exposure caused by the knifing (incision made in soil surface) application of the manure. Non-manured plots were not knifed.

Cover crop effects

The addition of the cover crop significantly decreased dry run NT concentration and load, although most nutrient parameters trended downward with this dry run treatment (Table 3). The wet run results showed similar trends (Table 4). Lower NT values may reflect a lower soil nitrate level because of N uptake with the rye growth. Soil nitrate concentrations and cover crop nutrient uptake were not measured before runoff commenced in this study. However, nitrogen uptake for rye is generally about 10-15 times greater than P uptake at this growth stage (Singer et al., 2008) indicating higher removal rates of N compared to P. This may explain why runoff P values were not influenced by cover crop (Table 3 and 4). Singer et al., (2007 and 2008) reported increased uptake of nitrogen (N), phosphorus (P) and potassium (K) by cover crops with manure applications. Cover crop growth has lowered nitrogen loss in surface runoff (Sharpley and Smith, 1991; Vliet et al., 2000). Less nitrogen loss to sub-surface drainage with cover crop has also been shown by Meisinger (1991, Parkin et al., 2006; Kasper et al., 2007).

Table 3: Nutrients in rainfall runoff and rainfall runoff load (dry run) as influenced by cover crop and manure application, Beresford, SD, 2010

Treatments	Concentration in Runoff						Runoff load[1]				
	RO[2]	NT[3]	TKN[4]	TSS[5]	TP[6]	DP[7]	NT	TKN	TSS	TP	DP
	(L)	---------------------- mg L^{-1} -------------					----------------- Kg ha^{-1} --------------------				
[8]M- C-	17.6	0.74	1.75	85	0.29	0.16	0.12	0.15	7.19	0.028	0.017
[9]M- C+	18.6	0.29	1.93	109	0.31	0.15	0.05	0.16	8.21	0.030	0.018
[10]M+ C+	17.4	1.00	2.02	129	0.39	0.18	0.18	0.16	11.47	0.034	0.017
[11]M+ C-	14.9	2.64	2.67	225	0.83	0.18	0.14	0.20	15.69	0.049	0.015
Manure (n= 16)	16.8	1.82*	2.35*	178*	0.18*	0.61*	0.15*	0.18	14.0*	0.015	0.041*
No manure (n= 16)	18.1	0.48	1.84	97	0.16	0.30	0.045	0.16	7.71	0.017	0.028
[12]$LSD_{0.1}$	3.6	0.47	0.34	49	0.014	0.25	0.05	0.04	5.10	0.003	0.012
Cover crop (n= 16)	18.0	0.64*	1.97	120	0.16*	0.35	0.06*	0.16	9.84	0.017	0.032
No cover crop (n= 16)	16.3	1.65	2.21	151	0.17	0.56	0.13	0.18	11.44	0.015	0.038
$LSD_{0.1}$	3.61	0.47	0.34	49	0.014	0.25	0.05	0.04	5.10	0.003	0.012
Source of variation	---------------------ANOVA Pr>F[13]------------------						-----------------ANOVA P>F----------------				
Manure (m) (1)	0.36	<.00	0.01	0.01	0.02	0.05	0.007	0.38	0.06	0.35	0.09
Cover crop (c) (1)	0.42	0.00	0.24	0.23	0.28	0.18	0.04	0.15	0.59	0.45	0.40
m x c (1)	0.74	0.02	0.05	0.04	0.42	0.13	0.25	0.34	0.39	0.97	0.23
[14]MSE (19)	35.04	0.59	0.31	6515	0.00	0.18	0.009	0.004	69.84	0.000	0.0004

Dry run= Rainfall applied at the existing soil moisture condition of the field; [1]Calculated as runoff volume/area x concentration; [2]RO= Simulated rainfall run-off (Liters); [3]NT= Nitrate-nitrogen; [4]TKN= Total Kjeldhal nitrogen; [5]TSS= Total suspended solids; [6]TP= Total Phosphorus; [7] DP= Total dissolved Phosphorus; [8]M- C- = No manure no cover crop; [9]M- C+ = No manure cover crop; [10]M+ C+ = Manure cover crop; [11]M+C- = Manure no cover crop; [12]LSD= Least significant difference and is a function of the size and the MSE of the group comparison. Therefore, LSD values for both cover crop and manure comparison are the same due to a balanced design and equal number of observations; [13]Pr>F = Probability that tabular F-ratio exceeds F-ratio calculated by analysis of variance. Values less than 0.10 are considered significant; [14]MSE = Mean square error; data in parenthesis are df of MSE for each parameter; *Indicates LSD values significant at the 0.1 probability level.

Table 4: Nutrients in rainfall runoff and runoff load(wet run) as influenced by cover crop and manure application, Beresford, SD, 2010

Treatment	Concentration in Runoff						Runoff load[1]				
	RO[2] (L)	NT[3]	TKN[4]	TSS[5]	TP[6]	DP[7]	NT	TKN	TSS	TP	DP
		---------------------- mg L^{-1}------------------					--------------------- Kg ha^{-1}-------------------				
[8]M- C-	38.7	0.42	1.63	74	0.26	0.13	0.06	0.32	15	0.51	0.027
[9]M- C+	42.5	0.27	1.61	80	0.28	0.13	0.03	0.33	14	0.05	0.030
[10]M+ C+	42.2	0.55	1.50	84	0.30	0.15	0.10	0.31	17	0.06	0.030
[11]M+ C-	39.2	1.26	2.03	121	0.36	0.17	0.20	0.39	24	0.07	0.034
Manure (n= 16)	40.7	0.82*	1.76	103*	0.16*	0.33*	0.16*	0.35	20.28	0.032	0.066
No manure (n= 16)	40.6	0.24	1.62	77	0.13	0.27	0.05	0.32	14.84	0.028	0.055
[12]$LSD_{0.1}$	5.55	0.30	0.18	24	0.02	0.04	0.05	0.06	5.95	0.007	0.014
Cover crop (n= 16)	42.3	0.36*	1.55*	82.72	0.142	0.29	0.07*	0.32	15.79	0.030	0.060
No cover crop (n=	38.9	0.70	1.83	97.44	0.154	0.31	0.14	0.36	19.33	0.031	0.061
$LSD_{0.1}$	5.55	0.30	0.18	24	0.02	0.04	0.05	0.06	5.95	0.007	0.014
Source of variation	---------------------ANOVA Pr>F[13]----------------------						--------------ANOVA Pr>F------------------				
Manure (m) (1)	0.98	0.003	0.18	0.08	0.02	0.02	0.003	0.50	0.13	0.33	0.21
Cover crop (c) (1)	0.30	0.06	0.01	0.30	0.36	0.45	0.04	0.31	0.32	0.90	0.85
m x c (1)	0.89	0.27	0.02	0.14	0.52	0.10	0.30	0.24	0.40	0.42	0.28
[14]MSE (19)	82.4	0.24	0.08	1540	0.001	0.005	0.007	0.01	94.85	0.001	0.005

Wet run= Rainfall applied after 12 hours of dry run (nearly at field capacity); [1]Calculated as runoff volume/area x concentration; [2]RO= Simulated rainfall run-off (Liters); [3]NT= Nitrate-nitrogen; [4]TKN= Total Kjeldhal nitrogen; [5]TSS= Total suspended solids; [6]TP= Total Phosphorus; [7] DP= Total dissolved Phosphorus; [8]M - C - = No manure no cover crop; [9]M - C + = No manure cover crop; [10]M + C + = Manure cover crop; [11]M + C - = Manure no cover crop; [12]LSD= Least significant difference and is a function of the size and the MSE of the group comparison. Therefore, LSD values for both cover crop and manure comparison are the same due to a balanced design and equal number of observations; [13]Pr>F = Probability that tabular F-ratio exceeds F-ratio calculated by analysis of variance. Values less than 0.10 are considered significant; [14]MSE = Mean square error; data in parenthesis are df of MSE for each parameter; *Indicates LSD values significant at the 0.1 probability level.

Interaction effects

There was a significant interaction effect of manure application and cover crop treatment for the NT, TKN and TSS concentration parameters in the dry run (Table 3). Cover crop lowered runoff nutrient or TSS concentrations in runoff to a much greater extent when manure was applied. Without manure, the cover crop had little effect. Cover crop growth may have lowered the higher soil NT levels that resulted from manure application. Therefore less soil NT was available for runoff. Where no manure was applied, soil NT may have been similar (low) regardless of cover crop presence. Plant nitrogen uptake by the cover crop was not measured. The cover crop may have provided a physical barrier from the simulated raindrops and protected TKN and TSS materials from leaving in runoff water. Without the manure addition there may have been less soluble solids, TKN and less exposed soil and hence little effect from the cover crop treatment.

In the wet run, there were significant interactions for the TKN and TP concentration parameters (Table 4). The interaction for TKN and TP would be similar for the above explanation for dry run TKN.

CONCLUSIONS AND RECOMMENDATIONS

Nutrient concentration at the soil surface, intensity of soil-manure interaction and runoff volume play an important role in nutrient loss in snowmelt runoff. Manure application trended to increase nutrient loss (concentration and loads) from simulated rainfall. This study did not address nutrient losses associated with commercial fertilizers. Future research is needed to compare losses from manure and fertilizer based systems. Cover crop growth trended to reduce nutrient loss more under manure system compared to a non-manured system.

Best management practices (BMPs) implications for manure use.

- Incorporation of cover crops in South Dakota crop rotations which utilize manure will be useful to limit nutrient losses to water resources.

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Measurement of Human Pharmaceutical Compounds (HPC) in Surface Water

Basic Information

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Measurement of Human Pharmaceutical Compounds (HPC) in Surface Water

We successfully developed and evaluated the performance of methodology for the identification of Human Pharmaceutical Compounds (HPCs) following the laboratory procedures identified for that purpose by the Waters OASIS. Water samples have been filtered using a 0.7 um glass fiber filter which has been properly conditioned. Hydrophilic – lipophilic – balance (HLB) solid – phase extraction (SPE) cartridges were utilized to prepare the samples resulting in sample clean up and concentration prior to analysis. HPCs concentrated in sample extracts have been separated, identified, and quantified using reversed – phase, high – performance liquid chromatography / electrospray mass spectrometry (HPLC/ESI – MS) using a selected ion monitoring (SIM) operated in appropriate detector mode as determined during the methodology development.

Initially we screened for ethynyl estradiol, norgestrol, oxandrolone, estrone, and equilenin which previous studies in the Brookings and Sioux Falls areas had identified in the Big Sioux River. First year methodology development resulted in successful laboratory determination for norgestrol and estrone and unscuccessful determination for mestranol (a form of the ethynyl estradiol).

We have shown that, although the methodology published by Waters Corp. seems very straight forward, the electrospray detection mode is actually very important, and the elution peak timing makes simultaneous detection of multiple compounds in surface water very difficult (i.e. norgestrol, estrone, and equlenin). Work continued throughout the second year to develop methodology which would allow simultaneous detection of estrone and norgestrol in a single injection. The table below summarizes the findings of the research. The Ethynyl estradiol was purchased in the mestranol form and detection was not possible using the proposed methodology. Additional methods were also been attempted unsuccessfully to date for identification of mestranol.

Compound	LCMS LLQ[a]	LLD in RW[b]	Avg. Method Recovery[c]	Calculated Levels in River Water samples	Detection Mode
Estrone	0.1 ppm	0.008 ppb	52%	1.2 ppb	ES-
Norgestrel	0.5 ppm	0.03 ppb	67%	3.0 ppb	ES+
Equilenin	0.5 ppm	0.02[d] ppb	---	1.1ppb[d]	ES-
EthynylEstradiol	NA	NA	NA	NA	ES-

[a] Lowest Limit of Quantification (LLQ) with injection volume of 15 µl of analytical standard in acetonitrile.
[b]Lowest Limit of Detection (LLD) in 500 ml of river water (RW) after extraction and concentration to 1 ml, using a 15 µl aliquot for injection, and calculating amounts based on average recovery.
[c]Average recovery based on spiking 500 ml of nanopure water with (name the amount) of compound of interest and concentrating sample in the same manner as field samples.
[d]LLD and calculated levels in river water assuming 100% recovery from spiked samples.

Following determination in river water, samples were collected at the Sioux Falls WWTP after primary and secondary treatment as well as upstream and downstream of the treatment plant during 2010. Analyses was completed in triplicate to develop common statistical parameters along with the ability to evaluate significance of impact of time of day, season, and impact if any of the treatment processes on the concentration of HPC.

Although Equilenin was successfully identified in spiked samples and river water, we were not able to successfully quantify the Equilenin concentrations in the wastewater samples. Wastewater samples in general required more pretreatment (filtration) prior to the solid phase extraction, elution and LCMS identification. Estrone and Norgestrel analysis in the wastewater and stream ranged as follows (all values are ppb):

Compound	Upstream of WWTP	After Primary Treatment	After Secondary Treatment	Downstream of WWTP
Estrone	<1 -1.2	1.4-4.2	1.5-5.1	<1-1.1
Norgestrel	3.4-14.1	0.6-9.4	2.5-6.7	6.9-10.0

Investigation of Arsenic Removal from Water by Microbiologically Induced Calcite Precipitation

Basic Information

Title:	Investigation of Arsenic Removal from Water by Microbiologically Induced Calcite Precipitation
Project Number:	2010SD174B
Start Date:	3/1/2010
End Date:	2/28/2011
Funding Source:	104B
Congressional District:	SD First
Research Category:	Water Quality
Focus Category:	Toxic Substances, Treatment, Water Supply
Descriptors:	
Principal Investigators:	Arden D Davis, Sookie S Bang, David J. Dixon

Publications

1. Davis, A.D., C.J. Webb, D.J. Dixon, J.L. Sorensen, S. Dawadi, 2007, Arsenic Removal From Drinking Water by Limestone-Based Material, Mining Engineering, 59 (2), Pages 71-74.
2. P.K. Chintalapati, A.D. Davis, M.R. Hansen, J.L. Sorensen, D.J. Dixon, 2009, Encapsulation of Limestone Waste in Concrete after Arsenic Removal from Drinking Water, Environmental Earth Sciences, 59 (1) Pages 185-190.

Final Report

South Dakota Water Resources Institute
U.S. Geological Survey 104b Program

Investigation of Arsenic Removal from Water by Microbiologically Induced Calcite Precipitation

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Introduction

Limestone-based material has demonstrated the ability to remove arsenic and other metals from drinking water. The means of arsenic removal is believed to be the formation of a calcium arsenate precipitate on the surface of limestone, but the surface chemistry is not well understood, and the efficiency of the method should be improved if it is to achieve commercial viability. Earlier research by the principal investigators, using limestone particles and manufactured limestone-based granules as an adsorbent for drinking water treatment, has shown that the efficiency of the arsenic-removal process can be improved by increasing surface area while maintaining flow-through rates needed for adsorption technologies. Research by the authors also has shown that the waste product passes the Toxicity Characteristic Leaching Procedure (TCLP) test. Other methods of arsenic removal suffer from the disadvantage of higher waste-disposal costs because of the potential for leaching of arsenic from the waste product.

Microbiologically induced calcite precipitation is a process that uses bacteria to create an environmentally friendly calcium carbonate cement. In this process, a common soil bacterium, Sporosarcina pasteurii, is fed a solution of urea and calcium chloride. The bacteria hydrolyze urea, forming carbon dioxide and ammonia as end products. In the presence of water, the ammonia reacts to form ammonium hydroxide, which raises the pH, creating a basic environment with an abundance of carbonate ions. These react with calcium ions to induce precipitation of calcium carbonate, commonly known as limestone.

This project investigated arsenic removal from water by microbiologically induced calcite precipitation, which shows great promise for improving the efficiency of arsenic removal by using bacterial enhancement to increase the reaction rate. If bacteria are involved in the formation of a calcium arsenate precipitate during arsenic removal by limestone-based material, it would constitute a major advance in the field. The work could be extended to aquifer remediation, industrial applications such as waste streams, and mine drainage water.

Project Information

This project investigated arsenic removal from water by microbiologically induced calcite precipitation, which shows great promise for improving the efficiency of arsenic removal by using bacterial enhancement to increase the reaction rate. If bacteria are involved in the formation of a calcium arsenate precipitate during arsenic removal by limestone-based material, it would constitute a major advance in the field, with the added benefit of encapsulation of arsenic within precipitated calcium carbonate.

If successful, the work could be extended to aquifer remediation, industrial applications such as waste streams, and mine drainage water.

Objectives

The objectives of this research were to:

1) Develop and test a process for arsenic removal from water during microbiologically induced calcite precipitation, by using a solution with a relatively low (approximately 100 parts per billion) concentration of dissolved arsenic.
2) Investigate the efficiency of the process by determining arsenic removal rates during bacterially enhanced calcite precipitation.
3) Determine levels of tolerance of Sporosarcina pasteurii for dissolved arsenic in solution, by testing solutions with different arsenic concentrations ranging from 10 parts per billion to 1 part per million or greater.

During earlier phases of this on-going research, laboratory research has indicated that arsenic is effectively removed from water by limestone-based material, including manufactured limestone-based granules as well as material with a limestone base and an additional arsenic-removal medium. Previous work has been aimed primarily at improving the efficiency of limestone-based material in removing arsenic by increasing surface area while maintaining flow-through of the media.

When arsenic is removed from water by limestone, the process is believed to be the precipitation of hydrated calcium arsenate, which has an extremely low solubility as compared to limestone. The proposed research could help answer a critical research question: are bacteria involved in the formation of a calcium arsenate precipitate during arsenic removal by limestone-based material?

The research focused on improving the economic advantages of limestone-based arsenic removal by increasing its efficiency. Dissolved arsenic in water has a known affinity for limestone. Microbiologically induced calcite precipitation shows great promise for improving the efficiency of arsenic removal by using bacterial enhancement to increase the reaction rate. Overall goals include application as a pilot study at a wellhead or mine site with naturally occurring arsenic contamination, and commercial viability of the technology. Two of the principal investigators have extensive experience with arsenic removal by limestone, and the third investigator is a recognized expert in the field of microbiologically induced calcite precipitation.

Methods

This project investigated arsenic removal by microbiologically induced calcite precipitation. The tests, if successful, would help demonstrate the potential for increased efficiency through microbiological applications of arsenic removal, potentially decreasing the overall costs of limestone-based technology. In laboratory tests, a prepared solution containing dissolved arsenic was used along with a common soil bacterium, Sporosarcina pasteurii, which was fed a solution of urea and calcium chloride. As the bacteria hydrolyze urea, carbon dioxide and ammonia form as end products. The ammonia reacts with water to form ammonium hydroxide, which raises the pH, creating a basic environment with an abundance of carbonate ions. These react with calcium ions to induce precipitation of calcium carbonate.

After formation of the precipitate, the solution was tested to determine the amount of arsenic removal. In subsequent tests, levels of tolerance of Sporosarcina pasteurii for dissolved arsenic were determined. The proposed work could give limestone-based technology a distinct advantage for use in applications ranging from aquifer remediation to mine runoff.

Procedures are described in detail below.

The first step in the process was a bacteria toxicity assay to determine whether the presence of arsenic would inhibit the normal growth cycle of S. pasteurii. The bacteria were originally grown in a BPU media. The concentration chosen for the study was 1×10^7 cells. After the primary inoculation, bacteria were drawn out and emplaced into flasks with varying levels of arsenic concentration, from 25 ppb to 200 ppb. The flasks were inoculated at 4^o C overnight. The cell concentrations were tested at 4-hour intervals for a 36-hour period.

The second step in the process is a batch test at two levels of arsenic concentration. The batch tests are set up with two types of matrix; a limestone matrix and a sand matrix. In previous studies, the bacteria precipitated calcite in the presence of clean quartz sand. Eight Nalgene bottles, 500 mL in size, were used for the process. Four of the bottles were filled with 300 grams of sand, and four of the bottles were filled with 300 grams of limestone. The limestone grains from the Minnekahta Limestone formation had been crushed to a grain size of approximately 0.5 to 1.0 mm. After the material was measured, the bottles were sterilized via autoclave. The bacteria were inoculated separately in a BPU media. Prior to adding the bacteria to the bottles with the limestone and sandstone, the arsenic-enriched media with urea and $CaCl_3$ was added.

The bottles were set up as follows:

a) 200 g limestone with 210 mL of urea and CA media with arsenic concentration of 100 ppb
b) 200 g limestone with 210 mL of urea and CA media containing bacteria with arsenic concentration of 100 ppb
c) 200 g limestone with 210 mL of urea and CA media with arsenic concentration of 500 ppb
d) 200 g limestone with 210 mL of urea and CA media containing bacteria with arsenic concentration of 500 ppb
e) 200 g quartz sand with 210 mL of urea and CA media with arsenic concentration of 100 ppb
f) 200 g quartz sand with 210 mL of urea and CA media containing bacteria with arsenic concentration of 100 ppb
g) 200 g quartz sand with 210 mL of urea and CA media with arsenic concentration of 500 ppb
h) 200 g quartz sand with 210 mL of urea and CA media containing bacteria with arsenic concentration of 500 ppb

In the testing, 10 mL of the media were drawn from each bacterial inoculation and sent to Midcontinent Laboratories to test arsenic concentration immediately prior to placing the media in the Nalgene bottles with the sand and limestone. After the 10mL were drawn, the media, bacteria, and sand or limestone matrix were mixed thoroughly by shaking and left to sit for seven days, the expected duration of bacterial life. Every 72 hours a 10 mL sample was retrieved from each bottle and taken to the laboratory to test for arsenic concentration. The samples were drawn through sanitized pipettes from the media above the sand or limestone to exclude any limestone or sand fines from being included in the sample. After the 7-day period was complete, the full bottle was filtered first through a 0.11 cm filter and secondly through a 0.45 micrometer filter to remove any fines before the final sample was taken to the lab. The fluid remaining after filtration was measured and the solids were weighed and spread in boxes to dry after standing overnight.

Laboratory facilities at South Dakota School of Mines and Technology were used in the work.

Principal Findings and Significance

After the first part of the project was completed, involving testing of the bacterial resistance to arsenic, the data were plotted on a graph of time versus cell concentration, shown in Figure 1. The bacteria exhibit a typical growth curve with no significant difference regardless of arsenic concentration. The results indicate that all levels of arsenic concentration in the media were not harmful to bacterial growth and life.

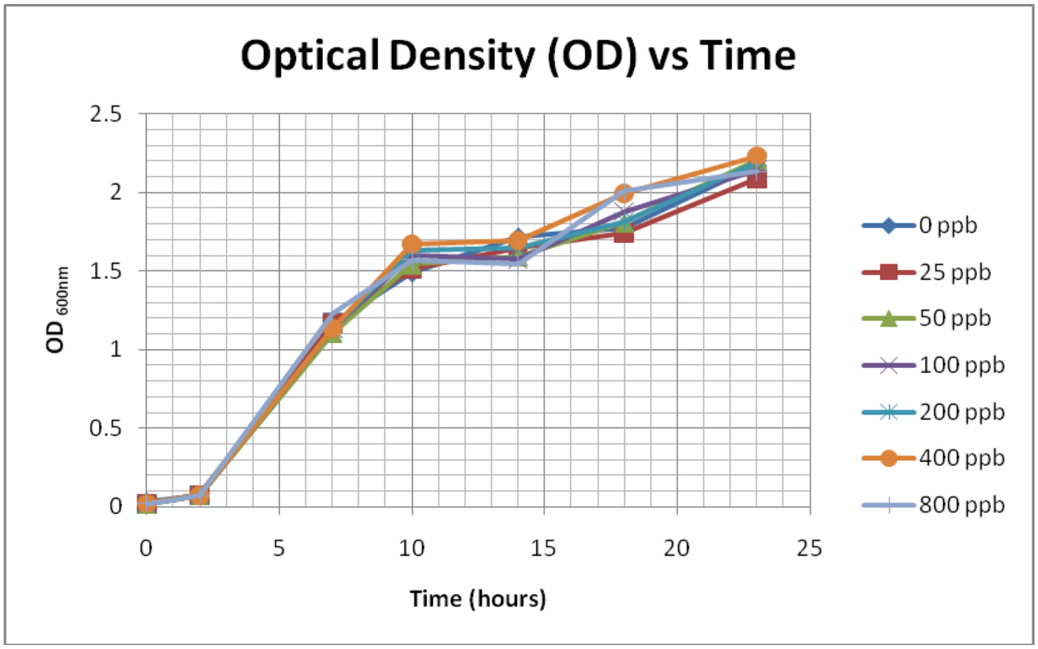

Figure 1. Bacterial growth curve of S. Pasteurii in the presence of arsenic at increasing concentrations.

In the second phase of the project, the batch tests produced a variety of results. The original samples showed arsenic concentrations of 200 ppb and 1000 ppb, respectively, indicating that the original arsenic concentration was miscalculated. However, for the purposes of the testing, the higher levels of arsenic concentration did not create a problem. The limestone with the arsenic enriched urea and CA media at a concentration level of 200 ppb showed arsenic removal of 79.7% percent and the limestone with the same mixture and an arsenic concentration level of 1000 ppb showed arsenic removal of 74.2% percent. The values for arsenic concentration at each of the sample times for samples beginning at 1000 ppb are shown in Figure 2; values for arsenic concentration at each of the sample times for samples beginning at 200 ppb are shown in Figure 3. At each concentration level, the limestone and media combination had the best total arsenic removal; the limestone, media, and bacteria combination showed the worst levels of arsenic removal. The sand matrix without bacteria performed better than the sand matrix with bacteria at both concentration levels as well.

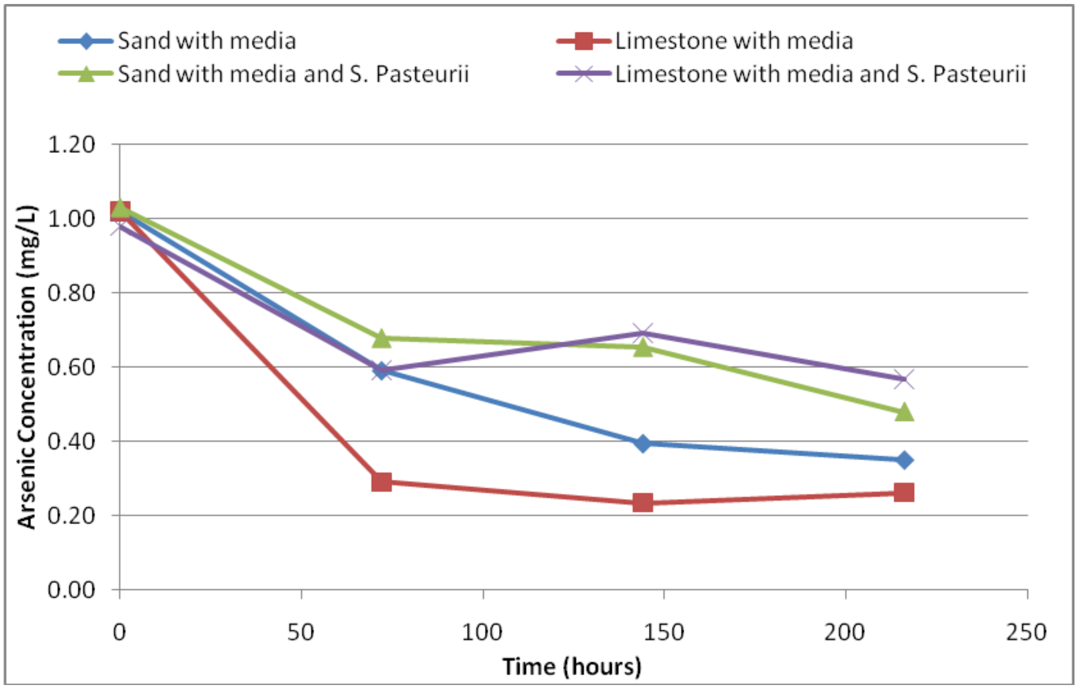

Figure 2. Arsenic concentration vs. time for samples beginning at 1000 ppb arsenic.

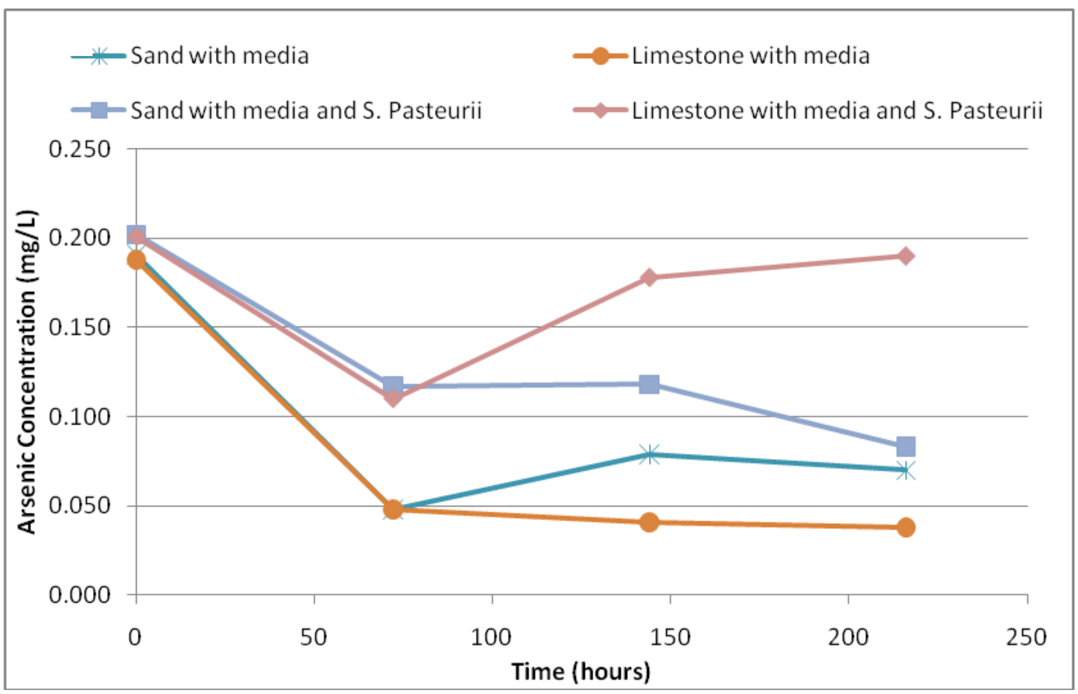

Figure 3. Arsenic concentration vs. time for samples beginning at 200 ppb arsenic.

The bacterial toxicity tests indicated that the bacteria were not affected by low levels of arsenic concentration. The S. Pasteurii experienced a normal growth curve even with the influence of arsenic levels from 25 to 800 ppb.

The batch tests indicated that the presence of the bacteria did not enhance the removal of arsenic as much as expected. In all setups, the presence of bacteria resulted in a lower arsenic removal than the same setup with no bacteria. The limestone with bacteria had the lowest arsenic removal, with a removal rate of 30 percent versus 60 percent. The poor removal rate could indicate an interaction between the limestone and the bacteria that inhibited arsenic removal. In previous testing, crystalline calcite did not perform as well as amorphous calcite, presumably because of less surface area on the smooth faces of crystals. The process of arsenic removal using the limestone at a microbial level is poorly understood, so it is difficult to determine exactly what factor limited the arsenic removal. In previous testing, crystalline calcite did not perform as well as amorphous calcite, presumably because of less surface area on the smooth faces of crystals. The presence of phosphorus in the urea and CA media might have also inhibited the arsenic removal. The phosphorus could have taken the place of the arsenic on the surface of the limestone.

Information Transfer Program

Results of this research will be presented at a conference such as the Western South Dakota Hydrology Conference.

Student Support

A graduate student, Tessa Krueger, was supported by this research during spring semester, 2010, and fall semester, 2010, while working toward her Ph.D. degree in Geology and Geological Engineering at South Dakota School of Mines and Technology. A second graduate student, Deborah Brewer, was supported by this research during fall semester, 2010, and part of spring semester, 2011, while working toward her M.S. degree in Geology and Geological Engineering at South Dakota School of Mines and Technology.

An undergraduate student, Jason Koch, also was supported by this research.

Awards and Achievements

It is expected that the results of this work will be incorporated in a Master of Science thesis or a Ph.D. dissertation.

A patent for the limestone-based arsenic removal process was filed (SDSM 1036037). The application number is 11/284,440. In May, 2010, South Dakota School of Mines and Technology received a Notice of Allowance from the U.S. Patent and Trademark Office, stating that the application has been examined is allowed for issuance as a patent. The inventors have filed for a second patent for removal of heavy metals.

The patent that was received, and the new patent application for removal of heavy metals, are listed below.

U.S. Patent:

Webb, Cathleen Joyce, Arden Duane Davis, and David John Dixon, “Method and composition to reduce the amounts of arsenic in water,” United States Patent 7,790,653, 7 September 2010.

Provisional U.S. Patent Application:

Webb, Cathleen Joyce, Arden Duane Davis, and David John Dixon, “Method and composition to reduce the amounts of heavy metal in water,” United States Patent and Trademark Office, Provisional application for patent, SDSM-1064434, Serial no. 61/393,806.

Related Publications

Davis, A.D., Webb, C.J., Dixon, D.J., Sorensen, J.L., and Dawadi, S., 2007, Arsenic removal from drinking water by limestone-based material: Mining Engineering, v. 59, no. 2, p. 71-74.

Chintalapati, P.K., Davis, A.D., Hansen, M.R., Sorensen, J.L., and Dixon, D.J., 2009, Encapsulation of limestone waste in concrete after arsenic removal from drinking water: Environmental Earth Sciences, v. 59, no. 1, p. 185-190.

Protein-Based Mechanisms of Uranium Detoxification in Subsurface Bacteria

Basic Information

Title:	Protein-Based Mechanisms of Uranium Detoxification in Subsurface Bacteria
Project Number:	2010SD175B
Start Date:	3/1/2010
End Date:	2/28/2011
Funding Source:	104B
Congressional District:	SD First
Research Category:	Biological Sciences
Focus Category:	Radioactive Substances, Toxic Substances, Groundwater
Descriptors:	
Principal Investigators:	Rajesh Kumar Sani, Rajesh Kumar Sani

Publications

There are no publications.

Final Report for award # 3F3479
Start date - 3/1/10
End date -2/28/11

Title: Protein-based mechanisms of uranium detoxification in subsurface bacteria

Principle Investigator:
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Problem and Research Objectives:

Uranium (U) is the primary radioactive metal contaminant in subsurface environments at the Department of energy (DOE) sites. Many activities associated with mining, extraction, and processing of U for nuclear fuel and weapons, as well as with the processing of spent fuel, have generated substantial quantities of waste materials contaminated with U and other radionuclides. In many cases, past practices relating to the handling and storage of such waste materials have resulted in extensive contamination of the subsurface e.g., at the Field Research Center, (TN), Hanford site (WA) (Ilton et al. 2008; Riley and Zachara, 1992). In western South Dakota, historical U-mining operations have lead to extensive contamination of surface and groundwater, soils, and sediments. At the Edgemont Uranium Mill Site, previously located in downtown Edgemont, South Dakota (prior to reclamation during the 1980's), regional sediment and groundwater sites were extensively impacted by U milling and mining operations, and have since been remediated as part of the uranium mill tailings program of the DOE. We (July 2008) collected soil samples from Edgemont and North Cave Hills, SD, and found high concentrations of U (9 and 6 U mg/kg dry soil, respectively; Rastogi et al. 2009). It has been shown that U chemical toxicity is of great ecological risk. It has also been stated that depleted U is a teratogen, and can be toxic to many human body organs including kidney, brain, liver, and heart (Hindin et al. 2005; Craft et al. 2004, and references therein). Besides the detrimental effects of U to human health, U is carcinogenic and toxic to other organisms and microorganisms.

The most common form of U in subsurface groundwater is U(VI), which is present either as the uranyl cation (UO_2^{2+}) or as anionic carbonate complexes, $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$. These oxidized species of U are highly soluble, thus mobile in groundwater. The fate and transport of U in groundwater depend significantly on the activity of indigenous subsurface bacteria including sulfate reducing bacteria (SRB). Indigenous SRB can immobilize U via enzymatic reduction using various proteins, thus providing a mechanism for removal of U from groundwater. SRB, however, are subject to U toxicity (Sani et al. 2006). Therefore, for efficient treatment of waters containing uranium by SRB either *in situ* or *ex situ*, there must be sufficient knowledge of uranium detoxification mechanisms by SRB. Thus, the response of SRB to U has important implications for understanding U reactivity, fate, and transport in the environment. U protein-based detoxification mechanisms in SRB at molecular level are poorly understood and were focused in the proposed research. The main objectives of the research were to

i) Isolation and identification of induced proteins from *Desulfovibrio desulfuricans* G20 under U(VI)-stressed conditions

ii) Elucidation of U detoxification mechanisms

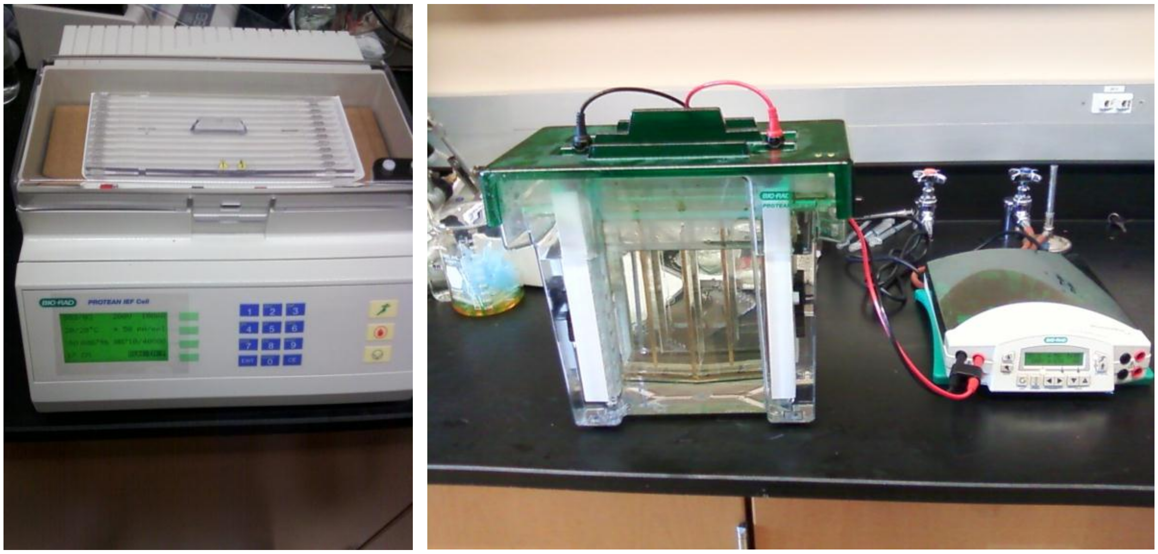
Methodology and Principal Findings:

Growth of SRB with uranium:

Our model SRB (*Desulfovibrio desulfuricans* G20 - hereafter simply written as G20) was grown in a medium (MTM, Sani et al. 2001a) developed in our laboratory and designed to study metal toxicity. MTM contains lactate and sulfate as electron donor and acceptor, respectively. For U(VI) exposure experiments, late-log phase grown G20 cells were harvested and washed as described previously (Sani et al. 2003). Washed G20 cells (about 5 mg/L cell protein) were used to inoculate a set of serum bottles containing 100 mL of MTM supplemented with 0, 45 or 90 μM U(VI). These U(VI) concentrations were selected on the basis of our published results (Sani et al. 2006). To determine the decrease in aqueous U(VI) concentrations, samples (0.2 mL) were withdrawn using a needle and syringe, and were measured immediately after filtration (0.2 μm) with an existing kinetic phosphorescence analyzer. Aliquots at log-phase (cell protein concentration about 20 mg/L) were collected and centrifuged. Pellets were used to extract membrane and soluble protein fractions as described below.

Protein extraction:
For membrane and soluble protein fractions from U(VI)-exposed and U(VI)-free control cultures, mid-log phase cells were suspended in 10 mL of 20 mM sodium phosphate buffer (pH 7). The suspended cells were lysed using a BeadBeater. Unbroken cells were removed by centrifugation (36,000×g, 4°C, 20 min). Membrane protein fraction was separated from the soluble fraction by ultracentrifugation (100,000×g, 4°C, 60 min). The pellets were resuspended in 20 mM Tris (pH 7.5) and washed two times with the same buffer. The soluble fractions containing protein was precipitated with ice-cold acetone (about 80%, v/v), incubated for 2 h at -20°C, and centrifuged at 14,000 × g, 4°C, 30 min. Both soluble and membrane proteins were resuspended in isoelectric focusing buffer containing 9.5 mM urea, 3.6% CHAPS, and 0.01%, w/v bromophenol blue. The protein samples were stored at -20°C until analysis. Protein concentrations were determined using the Coomassie method as described previously (Sani et al. 2001b). Soluble and membrane protein fractions were also isolated using the ProteoPrep™ universal extraction kit (Sigma) according to manufacturer's directions.

Two-dimensional gel electrophoresis and protein pattern analysis: The concentrated total protein samples were subjected to 2-D gel electrophoresis. Precast IPG Strips with a non-linear gradient from pH 3 to 11 (BioRad, Hercules, CA) were rehydrated overnight with 150-250 µg of protein in 9 M urea, 4% CHAPS, 1% dithiothreitol, 2% carrier ampholytes pH 3-11, and 0.002% w/v bromophenol blue. The first dimension separation was carried out in a Protean II system (BioRad, Hercules, CA) for a total of about 65 kVh according to the manufacturer's instructions. Typically for 17 cm IPG Strips were run at 500V for 1 min and were followed at 3500V for approx. 16-18 hours (see figure). Phosphoric acid (0.08 M) and NaOH (0.1 M) were used as anode and cathode solutions, respectively. After isoelectric focusing, the strips were first



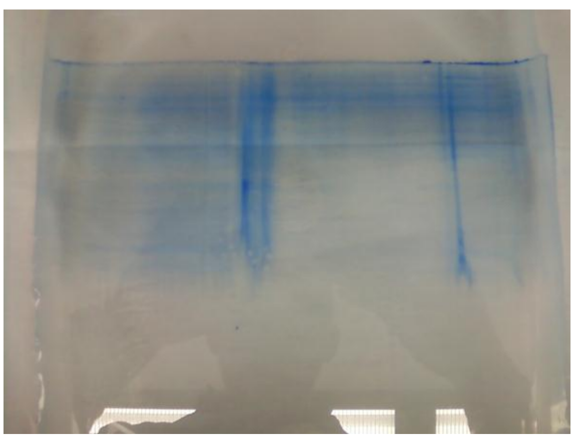
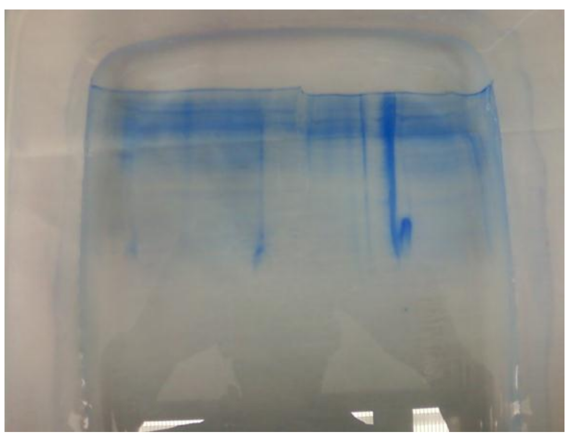
Two-dimensional gel electrophoresis

incubated for 10 min in an equilibration buffer (50 mM Tris-HCl, 2% SDS, 30% glycerol, 1% DTT, 6 M urea, pH 6.8). The same solution, without DTT, but with 2.5% iodoacetamide and 0.01% bromophenol blue, were used for another 15 min equilibration period.

The second dimension separation was carried out using a vertical sodium dodecyl sulfate-polyacrylamide gel electrophoresis with 12.5% acrylamide resolving gels and 1 cm stacking gel (4%) according to our previously developed protocol (Chakraborti et al. 2000). Separation was performed in two steps: 12.5 mA per gel was applied during the stacking period and 25 mA was used for the separation period. Gels were stained using Coomassie brilliant blue.

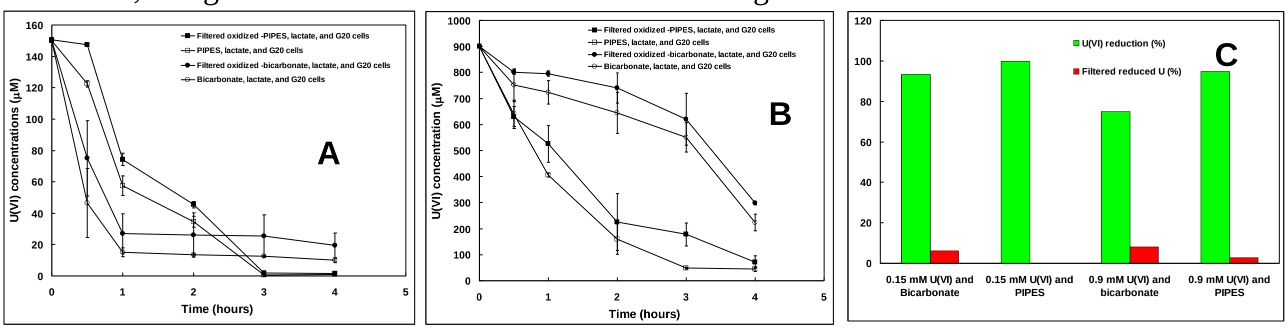
Results: The growth rates of the bacterium (G20) on the MTM with 0, 45, 90, or 140µM uranium (VI) were studied. From these results it was clear that U(VI) in all the mentioned concentrations inhibited the growth of the G20, while the cultures without U(VI) grew with grater rates and no lag times. It was, however, seen that in all the cultures, as soon as the lag phase ended, the cultures grew like U-free treatments. The rates of reduction of U(VI) to U(IV) were recorded. From these results it was observed that there was a considerable reduction in the U(VI) concentration for the cultures growing with 45 and 90µM U(VI) compared to 140µM U(VI). On the basis of these above mentioned results, cells were harvested for proteins at the end of the 12th day of incubation.

The protein from the cultures was extracted at the end of 12th day of incubation using the above mentioned protocols. The protein samples were loaded on IPG strips (13cm, non linear, pH 4-11), and was incubated overnight to allow the complete absorption of the proteins on the IPG strip. At the end of the incubation period, the IPG strips were put on the Iso Electric Focusing (IEF) tray and subjected to the first dimension electrophoresis (IEF) on the IEF cell (Biorad). At the end of IEF electrophoresis, the second dimension gel (SDS-PAGE) was prepared and the IPG strips were transferred to the SDS-PAGE gel. The gel was run on Protean II (Biorad) system. At the end of the gel run, the gel was stained with Coomassie reagent. However, no bands were obtained on the SDS-PAGE gel after staining.

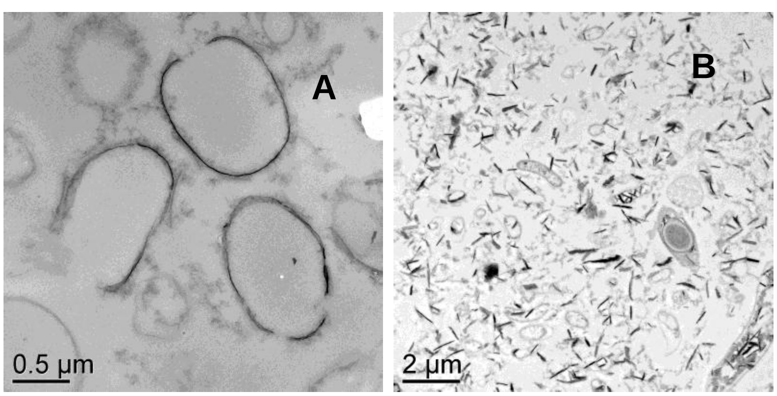
All the steps were rechecked and experiments were performed repeatedly. Still no bands were seen on gels. The protein concentration was checked before adding the proteins on the IPG strips. It was decided to increase the protein concentration before it was loaded on the IPG strips. In order to increase the protein concentration, the G20 cells were concentrated by centrifugation and then subjected to protein extraction. The protein concentration increased approximately 3 folds than the previously used concentration. The same procedures were repeated, but ending with the similar results. The protein concentration was further increased to approximately 10 times compare to the very first protein concentration, and 2-D gel electrophoresis was performed. This resulted visualization of proteins in the gels using Coomassie staining. However, discrete bands of proteins were not obtained (a continuous smear was obtained - figure). To resolve the smear problem, we are currently optimizing the concentration of acrylamide (e.g., 15, 17 or 20%) and loading protein concentrations. Mr. Rajneesh Jaswal (graduate student, chemical and biological engineering) is currently working in troubleshooting the problems.

When Mr. Rajneesh Jaswal was working on troubleshooting the problems related to 2-D gel, undergraduate students (Emily Squillace, Sunday Ogunsanya, and Antoinette Winckel) were working to evaluate the uraninite (UO_2) nanoparticles produced by *Desulfovibrio desulfuricans* G20 (our model organism) under non-growth conditions (where only cells, electron donor and electron acceptor were used) in the presence of lactate or pyruvate and sulfate, thiosulfate, or fumarate, using ultrafiltration and HR-TEM. Under non-growth conditions with initial



The effects of bicarbonate or PIPES buffer (each at 30 mM and pH 7) on 150 or 900 μM U(VI) reduction under nongrowth conditions by *D. desulfuricans* G20 (OD 600 nm = 0.45). Symbols show the mean of duplicate analyses. Error bars indicate the standard deviation.

concentrations of 0.15 and 0.9 mM U(VI) in PIPES or bicarbonate buffer, only 0-8% bioreduced U existed in a mobile phase (Figures A, B, and C).



Transmission electron microscopic images of *Desulfovibrio desulfuricans* G20 culture treated with **A)** 0.15 mM U(VI) **B)** 0.9 mM U(VI) under non-growth conditions in medium containing bicarbonate buffer (30 mM, pH 7).

TEM results showed (see figure) that with higher U(VI) initial concentration (0.9 mM), significant amount of reduced U resided intracellularly as well in aggregate form out side the G20 cells. For the successful application of U bio-stabilization, it is vital to understand the governing factors that control the redox behavior of these extracellular bioreduced uraninite species (28-65%) with respect to U fate, transport, and long-term stability. The data are useful i) to evaluate factors that influence the long-term stability of biogenic U(IV) under sulfate-reducing conditions that have been shown to develop in natural and biostimulated environments and ii) to develop mathematical models needed to predict stability of bioreduced U in groundwater systems.

Summary and conclusions:

G20 cultured in MTM media, were harvested in their late-log phase after 12 days incubation. Proteins were isolated and run on the 1st and 2nd dimension of electrophoresis under various conditions (including acrylamide, protein loading concentrations). Mr. Rajneesh Jaswal (graduate student) is still working on troubleshooting these problems. In addition, this project has provided training of students at postdoctoral, doctoral, and undergraduate levels on uraninite particles transport potential under non-growth conditions. All students received training in not only hands on 2-D gel electrophoresis but also in basic microbiological techniques and research methodologies, and gained knowledge on issues of U contamination in environments. The project has played a critical role in dissertation of a Ph.D. student (Mr. Rajneesh Jaswal).

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2. Sani RK, Emily Squillace, Gursharan Singh, Mufutau Lasisi, Ravi Kukkadapu, Brent Peyton, Timothy R Ginn. Identification of Iron Sulfides during Reoxidation of Uraninite Under Sulfate Reducing Conditions. 2010 AIChE Annual Meeting. Salt Lake City, UT.

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Information Transfer Program Introduction

The Information Transfer Program includes public outreach, interpretation of laboratory analysis results, active participation in the annual Dakotafest, steering committee representation and active involvement in the Big Sioux Water Festival and in the Eastern South Dakota Water Conference, interactions with extension agents and local, state and federal agencies, participation and presentation at regional and national conferences, youth education, adult education and university student training and education. Publications, such as pamphlets, educational materials, reports and peer-reviewed journal entries, are made available in paper format and electronic through the Institute's website and are designed to support the mission of the Institute.

PUBLIC OUTREACH Public outreach and dissemination of research results are cornerstones of the South Dakota Water Resources Institute's (SDWRI) Information Transfer Program. Information Transfer takes many forms, including interactive information via the Internet, pamphlets and reports, direct personal communication, hands-on demonstrations and through presentations and discussions at meetings, symposia and conferences is used to ensure effective transfer of water resources information to meet the needs different audiences. The SDWRI Water News newsletter is in its seventh 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 and is distributed via e-mail, as well as a link on the SD WRI homepage (http://sdstate.edu/abe/wri) in PDF format allowing for viewing of past and present issues. Water-related research including updates on present projects, notification of requests for proposals, state-wide water conditions, conferences, as well as information on youth activities are highlights in each issue.

SDWRI's web site has been designed to allow users access to updated links which include publications intended to help diagnose and treat many water quality problems. The site allows the public to stay informed about 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 SDWRI web contains past and present research projects, highlighting the Institute's commitment to improving water quality.

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 provides important testing services to water users across the state. SDWRI 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, fish culture, and land application of waste. Printed publications and on-line information addressing specific water quality problems are relayed to lab customers to facilitate public awareness and promote education.

An extensive library of information relating to water quality 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.

The seven year drought in western South Dakota ended in most areas in 2008 and above normal rain was received in 2010 and 2011. Even with the welcome rain the inherent quality of surface waters in western South Dakota is commonly low, leading to chronic livestock production problems. Drought intensifies this problem for livestock producers in these semi-arid rangelands. During the dry period many dugouts and ponds degraded to the point of causing cases of livestock illness and, in some instances, deaths. Due to above normal rainfall in 2010 fewer cases of severe salt limitations for livestock use was observed. 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.

SDWRI 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, irrigation and drainage. SD WRI continues to provide soil and water compatibility recommendations for irrigation permits to the SD Division of Water Rights.

SDWRI staff assisted in implementing the fifth annual Eastern South Dakota Water Conference held November 9-10, 2010 to provide a forum for water professionals to interact and share ideas. The theme of the 2010 conference was water-energy nexus. Speakers highlighted to importance of the scientific method to determine the state of our water resources. The Eastern South Dakota Water Conference was started in 2006 to serve as a mechanism to educate participants on water resource issues in South Dakota.

The goal of the 2010 Eastern South Dakota Water Conference held November 9-10, 2010 in Brookings, SD was to bring together federal, state, and local governments, along with university and citizen insights. The event, in its fifth year, and included speakers and presenters from South Dakota State University (SDSU), South Dakota School of Mines and Technology, The Day Conservation District, South Dakota Department of Water and Natural Resources, North Dakota State University and many others. In addition to the conference, a poster competition for college students was held. Eleven student posters were presented. First prize of $200 went to Ammar B. Bhandari from the Department of Plant Science at SDSU and a $100 second prize awarded to Sai Sharanya Shanbhogue in the NDSU Department of Civil Engineering.

Alexandra Davis opened the conference with a plenary presentation from the Colorado Division of Water Resources. Carter Johnson a distinguished professor of ecology from SDSU delivered the banquet keynote address on “South Dakota’s Prairie Farm: An Experiment in Economic and Ecological Sustainability”. Information on the conference is available at this link:
http://www.sdstate.edu/abe/wri/activities/ESDWC/2010.cfm.

The call for abstracts and speakers was released in July 2010. SDWRI program assistant Denise Hovland registered conference attendees through a website where participants could review the conference timeline and pre-register and pay for the conference.

SD WRI is chairing the organizing committee for the 2011 Eastern South Dakota Water Conference to be held on October 13, 2011. Mike Wireman, National Groundwater Expert from the US Environmental Protection Agency in Denver, CO will be the keynote speaker addressing nitrate contamination in eastern South Dakota. Sessions throughout the conference will be offering information important to a wide array of stakeholders including engineers, industry, public officials, agricultural producers, and conservation groups. Water is an important piece of the economic future of South Dakota, and this conference served as a mechanism to educate participants on this resource.

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 state Non-Point Source (NPS) Task Force, where the SD WRI is represented as a non-core member. The NPS Task Force, which is administered by the SD Department of Environment and Natural Resources, coordinates, recommends, and funds research and information projects relating to non-point water pollution sources. Participation on the NPS Task Force allows SDWRI input on non-point source projects funded through the task force and has provided support for research in several key areas such as soil nutrient management, agricultural water management, biomonitoring, 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. SDWRI 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, state and federal agencies conduct cooperative research with SDWRI or contribute funding for research. Feedback to these agencies is often given in the form of reports and presentations at state meetings, service through committees and local boards, and public 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 SDWRI’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. SDWRI staff members continued to support and participate in Water Festivals throughout the state in FY2011. SDWRI personnel were part of the organizing committee for the 2011 Big Sioux Water Festival where 1000 fourth grade students participated. SDWRI was responsible for coordination of volunteers and helpers, and co-coordinating the exhibit hall. SDWRI also supported water quality education in local schools including classroom presentations and assisting local educators with field trips.

ADULT EDUCATION David German (SD WRI), Dennis Skadsen (Day Conservation District), Dennis Todey (State Climatologist), and Chris Hay (ABE) presented a lake water quality workshop at Outlaw Ranch near Custer, SD and at Enemy Swim Lake. The workshops were made possible with funds through an EPA 319 grant. The idea behind the workshops stemmed from the fact that most water quality events like Water Festivals are usually targeted towards children.

Another reason for doing the workshops was the idea of “teaching the teachers.” Helping adults learn about water quality and providing them with useful information encourages them to teach others in their home community how their behaviors affect the lake. A PowerPoint presentation and sampling equipment assembled at the workshop was available for participants to take home to help encourage them to share what they learned at the workshop. Both workshops offered participants the opportunity to earn continuing education credits and one graduate credit in the education department at SDSU

Several hands-on activities were developed that helped workshop participants share their new-found knowledge of lakes. These activities included “The Lake Game” and demonstrations of lake stratification, photosynthesis and aquatic plants, as well as biomagnification using “mercury cookies.” The group also made their own Secchi discs to monitor the transparency of the lakes they live on. This allows participants to monitor the water quality of a lake and provides an avenue for individuals to take an active part in monitoring their lake.

As part of SDWRI’s outreach to the agricultural community, staff hosted a booth at DakotaFest, a three-day agricultural fair held in August each year near Mitchell, South Dakota, which draws approximately 30,000 people. A large selection of literature regarding water quality is available for distribution and SDWRI staff members field a variety of questions concerning water quality and current research from farm and ranch families. A taste of “good water” versus “bad water” (high in magnesium sulfate) was used to demonstrate that water quality cannot always be determined by visual inspection. Producers also drop off water samples to be taken back to the WQL for analysis.

SDWRI personnel participated in and presented at several regional and national meetings and conferences, including the EPA Region 8 Nutrient and Water Quality Workshop, Water Cycle CoP 2011 Evapotranspiration Workshop and the Western South Dakota Hydrological Conference.

PUBLICATIONS The SD WRI encourages the publication of research results in the form of thesis publications, reports and papers in scientific journals. Providing information over the Internet on current research and completion reports from past projects is a priority. The SDWRI web site (http://wri.sdstate.edu) is used and will be used increasingly to provide information about water resources and to communicate information to the public. The “Research Projects” section of the SDWRI Web site is updated on a regular basis. The site allows the public to stay updated with the activities of the Institute, gather information on specific water quality problems, learn about recent research results and follow links to other water resource related information available on the Web

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.

Information Transfer

Basic Information

Title:	Information Transfer
Project Number:	2008SD132B
Start Date:	3/1/2010
End Date:	2/28/2011
Funding Source:	104B
Congressional District:	SD First
Research Category:	Not Applicable
Focus Category:	Education, None, None
Descriptors:	None
Principal Investigators:	Van Kelley, David R. German

Publications

There are no publications.

FY 09 Information Transfer Program

Public Outreach

Public outreach takes many forms. Assistance to individuals to identify and solve water quality problems is an important component of the Institute's Information Transfer activities. The Water Quality Laboratory which has partnered with Analytical Services provides important testing services to water users across the state. Water Resources Institute staff continue to provide interpretation of analysis and recommendations for suitability of use based on intended use of the water. Samples are submitted for livestock suitability, irrigation, lawn and garden, household, farmstead, heat pump, rural runoff, and land application of waste.

Dakotafest display

The inherent quality of surface waters in western South Dakota is commonly low (due to high levels of dissolved solids, especially sulfates), leading to chronic livestock production problems. Due to dry periods, many dugouts and ponds have degraded to the point of causing cases of livestock illness and, in some instances, livestock deaths. SDWRI makes this issue a priority in its outreach/information transfer efforts by gathering information from a variety of sources and developing fact sheets for distribution to lab customers tailored to specific water quality problems.

Dakotafest, a three-day agricultural show in Mitchell, SD provides SD WRI with another avenue for public contact. A display consisting of photos depicting undergraduate and graduate research projects as well as providing information to producers about irrigation and livestock water quality are used to promote interaction with the public. The demonstration consists of one water cooler containing "good" (fresh) water and one water cooler containing "bad" water (small amount of magnesium sulfate added). The demonstration allows people to taste the two waters while parameters from an actual water quality analysis are discussed, helping them understand that it is not always possible to tell if their water is safe to drink according to taste, appearance, color, and odor.

SD WRI staff routinely respond to questions 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, soil-water compatibility, and irrigation drainage. SDWRI also continues to provide soil and water compatibility recommendations for irrigation permits to the SD Division of Water Rights.

Agency Interaction

SDWRI's 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. A Non-Point Source (NPS) Task Force exists in South Dakota to coordinate and fund research and information projects in this high priority area. 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. TMDL studies and other watershed assessments funded by the Task Force provide an opportunity for information transfer activities in cooperation with the local sponsors of these projects.

Conference Presentations

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

In cooperation with East Dakota Water Development District, Water and Environmental Engineering Research Center, USGS SD Water Science Center, and the USGS-EROS Data Center, SD WRI sponsored the third annual Eastern South Dakota Water Conference (http://wri.sdstate.edu/esdwc) October 22-23, 2008. The purpose of the annual conference is to provide a forum for researchers and policy makers to present research related to South Dakota water resources. In 2009, the conference steering committee will be utilized to strengthen the WRI advisory committee. This group has been invited to help determine research priorities for the USGS 104b institute research program. The committee will meet in February. Involving the steering committee will bring a sharper focus to the institute program and will more widely publicize the program. This will increase the opportunity for collaboration between agencies and universities in the state to develop proposals that meet priorities established for the 104b program.

Youth Education

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 eight sites including Spearfish, Rapid City, Pierre, Huron, Vermillion, Brookings, Aberdeen, and Sioux Falls. SDWRI staff members will continue to support and participate in Water Festivals throughout the state in FY2009. Since 1992, water festivals have delivered a strong water conservation message. In the past 15 years, 85,000 fourth graders have been armed with the knowledge necessary to preserve and protect our state's water supply.


Youth Education

SD WRI will continue other activities to support water quality education in local schools including classroom presentations, and assisting local educators with field trips and seminars on aquatic ecology.

Adult Education


Adult Education

In 2008 SDWRI expanded its education focus to include adults. In cooperation with the EPA's 319 program and the South Dakota Department of Environment and Natural Resources, SD WRI focused on adult education by hosting two basic limnology and stream bioassessment water quality workshops, with 12 science teachers in attendance July 25-27 at Camp Bob Marshall near Custer, SD and 10 science teachers in attendance August 15-17th at NeSoDak Camp near Waubay, SD. Continuing education credits were offered. Two more workshops (NeSoDak and a Black Hills location) are planned for 2009.

University Students:

The Institute currently supports two undergraduates in our mission to train the next generation of water scientists. These students are involved in many different Institute activities, ranging from active participation in on-going research projects to planning and building exhibits for water festivals. The students gain valuable experience in research methods, data collection, and laboratory safety as well as writing proposals and completion reports for their own undergraduate/graduate research projects.


Student Research

WRI staff also provide technical support for graduate students conducting water-related research. Research Associate German assisted graduate student Matt Hubers in completing two seasons of rain simulating on the project titled "Infiltration, Runoff, and Sediment Yield for Two Soils in the Belle Fourche River Watershed" in 2008 and 2007 and will serve on his thesis committee in 2009. Matt is a graduate student in the Animal and Range Science Department advised by Dr. Patricia Johnson. German will also provide technical support to graduate student Daniel Ostrem in collecting field data for the project titled "Evaluation of Performance on Vegetative Treatment Systems." Dan is a graduate student in the Agricultural and Biosystems Engineering Department advised by Dr. Todd Trooien.

Graduate students conducting water-related research are also encouraged to present findings at the Eastern South Dakota Water Conference (ESDWC). In 2008 the following 17 students gave oral or poster presentations at the ESDWC.

2008 Eastern South Dakota Water Conference Student Presentations			
Student	**Type**	**Presentation Title**	**School**
Hannah Albertus	Oral	Surface Water and Sediment Investigation Concerning Abandoned Uranium Mines Within the Slim Buttes Region, Harding County, South Dakota	SDSM&T
Lucas Borgstrom	Oral	Unique Aquatic System of the Coteau Escarpment	SDSU
Erin Dreis	Oral	Environmental Implications Associated with Land Application of Antimicrobial-Containing Manure	SDSM&T
Cari Anne Hayer	Oral	Status of Fishes in South Dakota's Eastern Rivers	SDSU
Matt Hennen	Oral	History and Current Status of Research on Common Carp Cyprinus carpio, an Invasive Species in Eastern South Dakota	SDSU
Andrew Kopp	Oral	Chironomidae Functional Community Characteristics within streams of the Lower Cheyenne River Watershed	SDSU
Cindie McCutcheon	Oral	Relationships Between Water Quality and Mercury Fish Tissue Concentrations for Natural Lakes and Impoundments in South Dakota	SDSM&T
Daniel Ostrem	Oral	Performance of Vegetated Treatment Systems in South Dakota-An Update	SDSU
JoAnne Puetz Anderson	Oral	Eastern South Dakota Soil Temperature Climatology: Eureka, Brookings and Centerville Soil Temperatures from 1982 to 2008	SDSU
Eric Rasmussen	Oral	Problems Associated with Stream Monitoring Protocols for Intermittent, Headwater Streams	SDSU
Ross Vander Vorste	Oral	Hydrologic Connectivity of Intermittent Headwaters with Downstream Reaches	SDSU
Katherine Aurand	Poster	Determination of Environmental Impacts Due to Antimicrobial Usage at Swine CAFOs: a Life Cycle Assessment Approach	SDSM&T
Kristopher Dozark	Poster	Macroinvertebrate Community Responses to Regional Sediment Loads in Two Habitat Types of Oak Lake, a Prairie Pothole in Eastern South Dakota	SDSU
Evan Schnabel	Poster	Potential Water Savings Using ET-Based Landscape Irrigation Control	SDSU
*Claire Garry-Peschong	Poster	A Laboratory Study of Streamflow and Groundwater Recharge	SDSU
*Kendra Hauck	Poster	Development of a Statewide Collection and Database for Aquatic Macroinvertebrates in South Dakota	SDSU
Casey Schoenebeck	Poster	Affects of Nutrient Release on Nutrient Limitation and Phytoplankton Abundance as Influenced by Winterkill Conditions in Glacial Lakes	SDSU
*Undergraduate Students			
SDSU (South Dakota State University)			
SDSM&T (South Dakota School of Mines and Technology)			

Publications

SD WRI is providing information over the Internet. A Web site for the SDWRI and Water Quality Lab (http://wri.sdstate.edu) has been established. The "Research Projects" section of the SDWRI Web site is updated on a regular basis. 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. Information regarding analytical services available at the SDSU Analytical Services Water Quality Laboratory and information that may be used to address water quality problems has been made available on-line.

Distribution of research findings to the public, policy makers and sponsors of non-point source pollution control projects is another important component of the SDWRI 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 develop. SDWRI is committed to making this material readily available to persons within South Dakota as well as in other states. A library is maintained at SDWRI 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. Project PIs are also encouraged to submit articles to referred journals for publication of research findings.

USGS Summer Intern Program

None.

Student Support					
Category	**Section 104 Base Grant**	**Section 104 NCGP Award**	**NIWR-USGS Internship**	**Supplemental Awards**	**Total**
Undergraduate	7	0	0	0	7
Masters	6	0	0	0	6
Ph.D.	2	0	0	0	2
Post-Doc.	0	0	0	0	0
Total	15	0	0	0	15

Notable Awards and Achievements

Ronald Gelderman's project titled 'Use of cover Crops to Minimize Loss of Plant Nutrients to Water Resources' supported Ammar B. Bhandari in his MS thesis work. He won the following awards: 1) He won first place in the poster competition held in conjuction with the 2010 Eastern South Dakota Water Confernce held in Brookings, South Dakota on November 9, 2010. 2: He won an Outstanding Graduate Student Award held at the North Central Extension-Industry Soil Fertility Confernece held in Des Moines, Iowa on November 17, 2010.

Arden D. Davis's project titled 'Investigation of Arsenic Removal from Water by Microbiologically Induced Calcite Prcipitation' received a patent for the limestone-based arsenic removal process. U.S. Patent: Webb, Cathleen Joyce, Arden Duane Davis, and David John Dixon, "Method and Composition to Reduce the Amounts of Arsenic in Water," United States Patent 7,790,653,7 September 2010. Another patent is pending:Webb, Cathleen Joyce, Arden Duane Davis, and David John Dixon, "Method and Composition to Reduce the Amounts of Heavy Metal in Water," United States Patent and Trademark Office, Provisional application for patent, SDSM-1064434, Serial no. 61/393,806.