South Dakota Water Research Institute

Annual Technical Report

FY 1998

Introduction

Research Program

During the tenure of the Regional Competitive Grant Program, only one project was funded in South Dakota. A synopsis on this project, titled "Geochemistry of Dissolved Organic Carbon in the Big Sioux Basin, Eastern South Dakota", by principal investigator Dr. James A. Rice, follows. The change to a Regional Competitive Grant Program reduced the number of research projects conducted at the SD WRI. However, other research at the SD WRI continued, including the second phase of a project to document water quality improvements resulting from construction of animal waste managment systems on feedlots located in eastern South Dakota. A synthesis of the "Literature on Factors Affecting the Revegetation of Shallow Lakes: A Case Study of Heron Lake" was revised based on reviewers' comments, received final approval and was published. A proposal for $534,018 titled "Best Management Practices for Land Application of Manure to Reduce Loadings of Surface Water Resources" was submitted to the EPA 319 program through the Non-Point Source Task Force and the SD Department of Environment and Natural Resources (SD DENR). This proposal was not funded. In addition, a proposal for $30,460 titled "A Literature Review of Phosphorus Accumulation in Soils and the Impact on Runoff Water Quality" was submitted to the SD DENR for consideration for 605b funding. This proposal is scheduled to be funded in December, 1999.

Basic Project Information

Basic Project Information	
Category	**Data**
Title	Geochemistry of Dissolved Organic Carbon in the Big Sioux Basin, Eastern South Dakota
Project Number	C-01
Start Date	10/01/1997
End Date	09/30/2000
Research Category	Biological Sciences
Focus Category #1	Geomorpological and Geochemical Processes
Focus Category #2	Groundwater
Focus Category #3	Surface Water
[illegible]	South Dakota State University

Lead Institution	South Dakota State University

Principal Investigators

Principal Investigators			
Name	**Title During Project Period**	**Affiliated Organization**	**Order**
James A. Rice	Professor	South Dakota State University	01

Problem and Research Objectives

The Big Sioux Basin is a hydrologic system which covers most of eastern South Dakota. Almost all studies have focused on the inorganic constituents of the basin's surface- and ground-waters. In 1989-1990 we conducted a geochemical baseline survey of the organic constituents of the basin's groundwater that showed that dissolved organic carbon (DOC) levels are low, averaging 7.7 mg DOC/L (Rice & Viste, 1994). Aquifer recharge is primarily by downward percolation of surface water which makes the aquifers susceptible to contamination by anthropogenic and autochthonous organic substances present in the overlying materials. To begin to explore the relationship between the surface- and ground-water DOC concentrations, we recently established that DOC levels in wetlands, lakes and rivers in the basin that are hydrologically connected to the aquifers can be as much as 30 times higher (Hendrix, 1997). An investigation into the chemical nature of the DOC in the basin's aquifers, its relationship to the organic matter in the predominate soil type in the region, and to several potential anthropogenic inputs of organic carbon into the groundwater is also near completion (Hendrix, 1997). However, the flux of organic carbon between hydrologic domains (eg., between surface water and the groundwater, or between the soil and the groundwater), and the effect of sorption of components of the DOC to subsurface and aquifer materials on the chemical characteristics of the groundwater's DOC as it moves from one hydrologic domain to the other are unknown. This study will be provide a broad-based understanding of the movement of DOC through hydrologic systems developed in alluvial and glacially-derived materials. It will provide a detailed description of the organic geochemistry of DOC in the Big Sioux Basin and an understanding of the mechanisms that control and affect the composition of DOC as it is transferred from surface-water to groundwater. The geochemical model of DOC transport from surface waters to the groundwater in the basin should capable of extension to other, similar systems in the North Central Region. The hypothesis which drives this proposal is that selective sorption of surface-water DOC substantially alters the composition of the DOC which is actually introduced into the groundwater during aquifer recharge. The specific objectives of this proposal are to: (1) monitor the fluctuations in the dissolved organic carbon (DOC) concentration of the Big Sioux aquifer and connected wetland and surface water areas in the Big Sioux Basin; 2) use this data to create an estimate of the organic carbon flux into and through the aquifer; 3) perform sorption/desorption experiments using subsurface and aquifer material to quantify the binding of organic carbon to mineral surfaces; (4) assess the importance of sorption to mineral surfaces as a mechanism for controlling DOC composition and concentration in the aquifer, and; 5) identify the controls on organic carbon binding to mineral surfaces in subsurface and aquifer materials.

Methodology

This project involves a combination of field and laboratory studies to assess the flux of DOC between surface and groundwaters within the study site. An detailed hydrologic description of the study site is being prepared. DOC levels are regularly monitored to determine the flux of organic carbon through the site. Periodic bulk water samples are fractionated into hydrophobic and hydrophilic organic acids, bases,

and neutral compounds to evaluate seasonal changes in the nature of the DOC. This same fractionation scheme will be used to assess the compositional affect of of selective sorption of DOC components to mineral surfaces as surface water DOC percolates down into he groundwater. Finally, a model will be constructed to describe the flux of DOC through the system.

Principal Findings and Significance

HYDROLOGY Using the intensive study site developed the first year of the project, weekly water level measurements of 18 observation wells have been made. Soil cores taken when the wells were drilled were logged and classified to provide a stratigraphic description of the study site. This information has been used to define the boundary areas of the hydrologic model that is being created using MODFLOW. The primary goal of the final year of this project is to complete this model and couple it to DOC levels in the system. DOC FLUX A large of enough database of DOC measurements now exists to begin to describe trends in groundwater and surface water DOC levels. Data collected thus far show that groundwater DOC levels peak in the fall and show little effect of spring snowmelt infiltration. This information will be input into the hydrologic model created in MODFLOW to provide an estimate of DOC flux through the system. SORPTION TO MINERAL SURFACES Using DOC isolated from the surface waters at the intensive study site, and mineral materials (silica, alumina, kaolinite and montmorillonite), study of the sorption of the DOC components to the mineral surfaces has revealed that hydrophobic and hydrophilic acids (as defined by XAD-8/XAD-4 sorption fractionation) selectively sorb to the mineral surfaces. Removal of these components, compared to the original DOC isolate is not quantitative, but in all case more than 75% of these fractions are removed. There is very little, if any, sorption of either hydrophobic or hydrophilic neutral or base fractions to these surfaces. Fluorescent spectra of the original surface water isolate reveal two distinct fluorescent signals, one of these is essentially completely absent after sorption experiments and in the ground water. Chemical characterization, primarily using solution-state 13C NMR, is being completed to further characterize the components being sorbed to the minerals surfaces to better understand the role of mineral surfaces in controling DOC composition as surface water percolates through the unsaturated zone to recharge the aquifer. REFERENCES Rice, J.A. and Viste, D.A., 1994, Major Sources of Groundwater Contamination Point and Nonpoint Contamination in a Shallow Aquifer System IN Groundwater Contamination, U. Zoller (ed.), Marcel Dekker, p. 21-35. Hendrix, K., 1997, Comparison of DOC in Low-DOC and High-DOC Wells of the Big Sioux Aquifer by PYMS, MS Thesis, South Dakota State University, Brookings, SD.

Descriptors

Dissolved organic carbon, geochemistry, surface-groundwater relationships, soil-water relationships, groundwater recharge

Articles in Refereed Scientific Journals

Book Chapters

Dissertations

Water Resources Research Institute Reports

Conference Proceedings

Williams, M., J.A. Rice, Selective Sorption of Natural Organic Matter by Mineral Surfaces I. Silica and Alumina, "IN" 34th Midwest Regional Meeting, American Chemical Society, October 1999, Quincy, IL, Abstract No. 148. Vander Vorste, E., J.A. Rice, Selective Sorption of Natural Organic Matter by Mineral Surfaces II. Clay Minerals, "IN" 34th Midwest Regional Meeting, American Chemical Society, October 1999, Quincy, IL, Abstract No. 150. Williams, M., J.A. Rice, Selective Sorption of Natural Organic Matter by Mineral Surfaces. Chemical Changes After Sorption on Sand and Alumina, TO BE PRESENTED at American Chemical Society 219th Meeting, San Francisco, CA, March 2000.

Other Publications

Information Transfer Program

South Dakota Water Resources Institute Program Report - Base Grant Water is one of the most important resources in South Dakota. Together with the state's largest industry, agriculture, it has and will continue to play an important role in the economic future of the state. Enhancement of the agricultural industry and allied industries, the industrial base and, therefore, the economy of South Dakota all depend on compatible development of our water resources. The South Dakota Water Resources Institute (SD WRI) base grant program, with support from state funds, was used to develop and maintain working relationships with local, state and federal agencies to enhance management of water resources in South Dakota. Information Transfer Program/Publishing The education and information transfer roles are an important part of the SD WRI programs. Information was provided to the public, researchers, resource managers and agencies through SD WRI staff. This included responding to questions received from the general public, other state agencies, livestock producers and County Extension Agents concerning water quality issues related to stream monitoring, surface water ground water interactions, livestock poisoning by algae, lake protection and management, fish kills and other issues related to water quality. The SD WRI Water Quality Laboratory also provided important testing services to livestock producers and other rural water users. The waters in many areas of South Dakota have high sulfates, and other dissolved solids that can be detrimental to livestock health and productivity. Water Resources Institute staff also continued to provide interpretation of analysis and recommendations for use of water samples submitted for analysis for other uses, such as irrigation, lawn and garden, farmstead, and heat pump. SD WRI staff continue to update and improve information available to individuals with water quality problems. Educational materials concerning the effects of poor water quality and solutions available are given a high priority. Due to enactment of more stringent controls on agricultural discharges, SD WRI staff have seen a substantial increase in inquiries regarding agricultural practices and their effect on water quality. In response to this, two new package analyses (land application of waste and rural runoff) were added to the Water Quality Lab's list of services. Information transfer to individuals concerned with these issues is becoming an important component of the Institute's Information Transfer Program. SD WRI staff also have created web pages for the Institute as well as the Water Quality Lab to provide up-to-date information to the public about current issues in water quality. EPA is moving toward national regulations for land applications of waste in response to the fact that non-point source discharges of phosphorus, and in some instances nitrogen, are a primary cause of serious eutrophication problems in streams, lakes and wetlands in some agricultural areas where large animal concentrations are present. South Dakota regulations for the application of animal waste are based upon the nitrogen needs of the crop. This results in excessive phosphorus applications (i.e. relative to the phosphorus needs of the crop), and it is likely that eutrophication problems will increase in South Dakota as a result. Information is needed about non-point losses of phosphorus in runoff as affected by land applications of livestock waste. This will provide a basis for the state to develop reasonable regulations that protect the water quality of streams and lakes without placing undue hardships on livestock producers. SD WRI staff have initiated a review of available literature to identify research that is applicable to this problem and to identify research needs.

This effort by the SD WRI will likely influence how animal wastes are managed in South Dakota in the future. South Dakota is currently developing Total Maximum Daily Loads (TMDL's) for numerous water bodies. TMDL's are an important tool for the management of water quality. The goal of a TMDL is to ensure that waters of the state attain water quality standards and provide designated beneficial uses. A TMDL is defined as "the sum of the individual waste load allocations for point sources and load allocations for both nonpoint source and natural background sources established at a level necessary to achieve compliance with applicable surface water quality standards". In other words, a TMDL limits the total pollution load of any given water body to the TMDL it can bear and still remain healthy. TMDL's are required on waters that do not attain water quality standards or assigned beneficial uses. The SD WRI Water Quality Lab is providing laboratory support for two TMDL projects in eastern South Dakota, including the Central Big Sioux River Watershed Assessment Project, being conducted by East Dakota Water Development District, and the Bachelor Creek project, being conducted by the SDSU Biology Department. Involvement in several South Dakota Water Festivals continued, with two staff members serving as presenters at two festivals, and two staff members serving on the Big Sioux Water Festival planning committee. Statewide, these Water Festivals were held at six locations and provided approximately 375 South Dakota elementary teachers and 7,400 students with an enhanced understanding of the role of water in the environment and our dependence on water.

USGS Internship Program

Student Support

Student Support					
Category	**Section 104 Base Grant**	**Section 104 RCGP Award**	**NIWR-USGS Internship**	**Supplemental Awards**	**Total**
Undergraduate	2	4	N/A	N/A	N/A
Masters	N/A	1	N/A	N/A	N/A
Ph.D.	N/A	N/A	N/A	N/A	N/A
Post-Doc.	N/A	N/A	N/A	N/A	N/A
Total	N/A	N/A	N/A	N/A	N/A

Awards & Achievements

South Dakota Water Resources Research Associate David German received special recognition from the SDSU Dean of Agriculture and Biological Sciences for work with an interdisciplinary group of scientists that identified research needs in the area of animal waste management, and developed a package of proposals to meet those research needs in the state of South Dakota.

Publications from Prior Projects

Articles in Refereed Scientific Journals

Clay, S.A., T.B. Moorman, D.E. Clay, and K.A. Scholes. 1997. Sorption and Degradation of Alachlor in Soil and Aquifer Material. J. Environ. Qual. 1335-1353. Clay, D.E., S.A. Clay, and T. Moorman. 1996. Dissolved Organic Carbon and Nitrate Temporal Variability in a Shallow Aquifer. Water Research 30: 559-568.

Book Chapters

Dissertations

Hendrix, Karyn. 1997. Characterization of the Dissolved Organic Carbon Isolated from the Big Sioux Aquifer, Eastern South Dakota. MS Thesis, Chemistry Department, South Dakota State University, Brookings, South Dakota. 109 pp.

Water Resources Research Institute Reports

Berry, Charles R., David German. 1998. Revegetation of Shallow Lakes: A Case Study of Heron Lake. Minnesota Waterfowl Association, Minneapolis, MN. Bischoff, John, David German. 1998. Pesticides in Eastern South Dakota Rivers: 1994-1996, Evaluation of Event and Baseflow Loading. DRAFT. South Dakota Water Resources Institute, South Dakota State University, Brookings, South Dakota. German, David. 1998. "Water Quality in South Dakota Lakes", 1998 ASAE/CSAE intersectional meeting, South Dakota State University, Brookings, South Dakota. German, David R. 1997. South Dakota Lake Protection Water Quality Report. 1997. South Dakota Water Resources Institute Report to the South Dakota Department of Environment and Natural Resources, South Dakota State University, Brookings, South Dakota.

Conference Proceedings

Zhuojing, L, S.A. Clay, and D.E. Clay. 1999. Spatial Variation in Atrazine Field Dissipation and Laboratory Mineralization and Their Relationship to Weed Control "in" Proceedings of 4th International Conference on Precision Agriculture, St. Paul, Minnesota. pp. 879-884. Clay, S.A., D.E. Clay, Z. Liu, and S.S. Harper. 1996. The Effect of Ammonia on Atrazine Sorption and Transport, "in" Herbicide Meatbolites in Surface Water and Groundwater, ACS Symposium Series, Washington, D.C., 630:117-124.

Other Publications

Presentations: German, David. 1998. "Water Quality in South Dakota Lakes", presented to SDSU Agricultural Engineering Seminar class, Brookings, South Dakota.