South Dakota Water Research Institute
Annual Technical Report
FY 2001

Introduction

Research Program

Lipid Geochemistry of Waters and Sediments in a Prairie Pothole Hydrologic System

Basic Information

Title:	Lipid Geochemistry of Waters and Sediments in a Prairie Pothole Hydrologic System
Project Number:	2001SD1381B
Start Date:	5/1/2001
End Date:	4/30/2002
Funding Source:	104B
Congressional District:	First
Research Category:	Not Applicable
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Descriptors:	organic geochemistry, lipids, dissolved organic carbon, Big Sioux aquifer,Groundwater
Principal Investigators:	James A. Rice

Publication

Problem and Research Objectives

The Big Sioux aquifer is a shallow groundwater system that supplies water to many municipalities and rural, domestic wells in eastern South Dakota. The aquifer has large storage capacity and very rapid recharge characteristics (1).

Until recently, water quality studies of the Big Sioux aquifer, and the Big Sioux Basin, have focused on the inorganic constituents of the waters. We have conducted a geochemical baseline survey of the aquifer's organic constituents that has shown that dissolved organic carbon (DOC) levels within the aquifer are low, averaging 7.7 mg DOC/L (2). However, we have found that DOC levels in wetlands, lakes and rivers that are hydrologically connected to the aquifer can be as much as 30 times higher. The relatively low levels of DOC in the system suggest that it may be a sensitive indicator of the groundwater's quality. Thus it is vital that the organic geochemistry of this system be understood and modeled.

While we are currently investigating the nature of the humic component of the DOC in the aquifer, and the flux of organic carbon between hydrologic domains (e.g., between surface water and the groundwater, or between soil water and the ground water), the effect of selective sorption of the lipid component (compounds such as fatty acids, fatty alcohols, hydrocarbons, etc.) on the chemical characteristics of the groundwater's DOC to subsurface and aquifer material as it moves from one hydrologic domain to the other, is unknown. This is particularly important since we have shown that natural sorbents such as sand, aluminum oxides and clay minerals can selectively sorb different chemical components of a water's DOC (3, 4, 5).

This proposal addresses two major priorities identified by the Water Resources Research Institute's Regional Competitive Grants Program in their solicitation. First, this study addresses the issue of ground and surface water quality. It fills a significant gap in the knowledge of the water quality of the Big Sioux aquifer by quantifying the DOC flux through the system and identifying sorptive reactions with subsurface materials that control lipid concentrations and geochemistry in the aquifer system. Second, it will investigate the relationship and connections between surface water and groundwater DOC and how the lipid components of the DOC contribute to the movement of organic carbon through each hydrologic domain. Since many organic contaminants (such as pesticides, herbicides, PCBs, or PAHs) rapidly and intimately associate with the organic coatings on mineral surfaces, knowledge of the lipid geochemistry will provide information that may be important in predicting organic contaminant fate and transport in this system. This study will provide a missing portion of the geochemical understanding of organic carbon movement that is necessary to manage this resource, protect the groundwater's quality from degradation from anthropogenic organic substances, and if one day needed, facilitate its remediation.

The comprehensive objectives of this project are to: 1) identify the solvent extractable organic compounds (ie, lipids) present in the water and sorbed to the sediments and aquifer materials using gas chromatography mass spectrometry; 2) perform sorption/desorption experiments using representative lipids (natural and model compounds) and sediment and aquifer materials (minerals isolated from cores and reference mineral specimens) to quantify the binding of lipids to mineral surfaces; 4) assess the importance of sorption to mineral surfaces as mechanism for controlling lipids in the aquifer, and; 5) identify the nature and mechanism of lipid binding to the sediment and aquifer material particle-surfaces suing solid-state NMR and small-angle x-ray and light scattering.

This report covers the first year of what has been proposed as a three-year study whose goal is a comprehensive understanding of the lipid geochemistry of the Big Sioux Aquifer. Completing Objective 1 was the focus of this project year.

Methodology

This site consists of self-contained, permanent/semi-permanent pothole wetland around which we have installed a field of 17 nested groundwater wells. We have recently developed a hydrologic model for this site using MODFLOW (6). The site's geology and hydrology are described in detail by Sumption (6). Sediment cores were collected from the pothole using a stainless-steel corer. Organic-matter-free mineral components was isolated from the sediments using a sequential removal procedure described Malekani *et al.* (7). They have shown that their procedure does not alter the mineral structure or surface.

Portions of the cores will extracted with chloroform. The extract will be concentrated by rotary evaporation. All solvents will be capillary GC grade. Lipid identification was performed using GCMS.

Principal Findings and Significance

A number of interesting lipid compounds were identified (such as saturated and unsaturated fatty acids, and ether-based lipids) in the extracts of the sediment cores. These compounds are potential candidates for use as sorbates in the objectives in the second project year (project Objectives 2 and 3).

It was also observed that the sediment environment is highly reducing; and becomes so within a few millimeters of the sediment water interface. The redox potential is so negative that elemental sulfur was observed in the GC mass-spectra that were recorded. The reducing conditions are almost certainly due to the high organic matter content of the sediment

Student Support

	2001/2002	Total
Undergraduate	1	1
Masters	1	1

References

1. The Big Sioux Aquifer Water Quality Study, State of South Dakota, Pierre, SD, 1987, 338 p.

2. 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.

3. Vander Vorste, E.*; Rice, J. A., Selective sorption of natural organic matter by mineral surfaces II. Clay minerals, 34th Midwest Regional Mtg., Am. Chem. Soc., October 1999, Quincy, IL, abstract no. 150.

4. Williams, M.*; Rice, J. A., Selective sorption of natural organic matter by mineral surfaces I. Silica and alumina, 34th Midwest Regional Mtg., Am. Chem. Soc., October 1999, Quincy, IL, abstract no. 148.

5. Williams, M.*; Rice, J. A., Selective sorption of natural organic matter by mineral surfaces. Chemical changes after sorption on sand and alumina, Am. Chem. Soc., 219th San Francisco, CA, March 2000, abstract CHED 755.

6. Sumption, A., 2000, MS Thesis, South Dakota State University.

7. Malekani, K.; Lin, J. S.; Rice, J. A., 1997, The effect of sequential organic matter removal on the surface morphology of humin, Soil Science, 162: 333-342.

Arsenic Remediation of Drinking Water: Phase II

Basic Information

Title:	Arsenic Remediation of Drinking Water: Phase II
Project Number:	2001SD1541B
Start Date:	5/1/2001
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Research Category:	Not Applicable
Focus Category:	Treatment, Toxic Substances, Water Quality
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Principal Investigators:	Arden D Davis, David J. Dixon, Cathleen J. Webb

Publication

1. Pogany, Michael, 2001, Natural adsorbate removal of arsenic for improved water quality: Final technical report, Research Experiences for Undergraduates, National Science Foundation Summer Program, South Dakota School of Mines and Technology.
2. Davies, Laura, 2001, Pelletization of limestone fines for use as an arsenic adsorption medium: Final technical report, Research Experiences for Undergraduates, National Science Foundation Summer Program, South Dakota School of Mines and Technology.

INTRODUCTION

This research represents Phase II of an on-going project to investigate removal of arsenic from drinking water. Arsenic is harmful to human health in relatively small amounts. The United States Environmental Protection Agency (EPA) recently announced the lowering of arsenic's maximum contaminant level (MCL) to 10 parts per billion (ppb) by 2006. This reflects the harmful nature of arsenic, especially inorganic arsenic. The lower MCL will affect water suppliers and users in many regions of the United States. Figure 1 shows counties with water supplies that will be affected by the new arsenic MCL; darker areas have higher arsenic concentrations (Focazio et al., 2000).

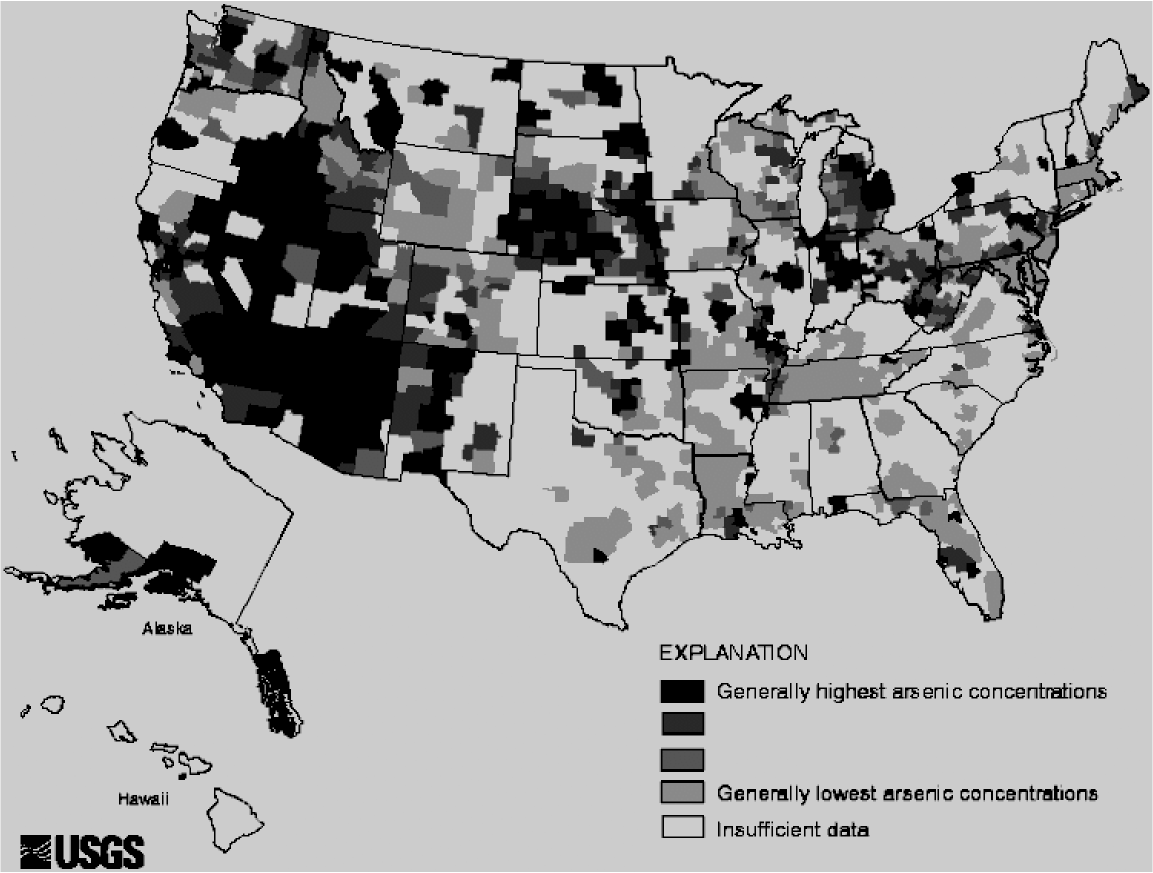

Figure 1. Counties in the U.S. with elevated arsenic concentrations (from Focazio et al., 2000).

The cost of current arsenic removal technologies is quite high (Frey et al., 1998). For example, the American Water Works Association (AWWA) has estimated the cost of decreasing the arsenic standard to 10 ppb in South Dakota at $8.25 million. Generally, larger water systems have the financial resources necessary to meet the expenses and technical demands involved. Smaller suppliers and private well users are likely to be unable or unwilling to implement current arsenic removal methods. Using limestone to precipitate arsenic out of solution could be an inexpensive, viable alternative.

This report, representing Phase II of arsenic removal research, included batch experiments, column experiments, Toxicity Characteristic Leaching Procedure tests, sintering and pelletizing of material, and scanning electron microscopy. In Phase I work, a significant literature review has been conducted on arsenic's uses, history, background exposure, toxicity, and distribution. Experiments investigated the ability of limestone to remove arsenic from a solution of arsenic and deionized water, hereafter referred to as standard solution. Procedures and results are summarized below.

BATCH EXPERIMENTS

The majority of batch experiments performed in this research were conducted by using Minnekahta Limestone from a quarry in Rapid City, South Dakota. Limestone was provided by Pete Lien and Sons, Inc., in coarse rock size (2-4 cm). The limestone then was crushed with a rock crusher and sieved to three uniform particle sizes:

1)	8 mesh	>2.362 mm	~2 mm
2)	16 mesh	2.362-1.18 mm	~1-2 mm
3)	35 mesh	1.18-0.425 mm	~0.5 mm

The 0.5 mm fines were the predominant adsorbent used in the batch experiments as well as in the later pelletization process. The smaller particle size increased the allowable surface area per gram of adsorbent (m^2/g).

Batch experiments were conducted according to the methods described in Appendix A. Experiments included different limestone types, different pH pre-adjustment, and introduced interferences from Cl^- and SO_4^{2-} ions.

Comparison Between Different Limestone Samples

Currently, little is known about the chemical kinetics or mechanism responsible for the adsorption of arsenic by limestone. These mechanisms were explored during this phase of the research project. Chemical compositions of different limestone formations could be responsible for improved arsenic removal. Therefore, three different sources of limestone were tested for their respective removal efficiencies at variable mass quantities. The three limestone sources included:

1) Minnekahta Limestone from the Pete Lien and Sons quarry at Rapid City, South Dakota. Material was crushed and sieved to 35 mesh ~0.5mm (SEM average particle size ~4-15 μm).
2) Minnekahta Limestone from the Pete Lien and Sons quarry. This was waste rock dust from industrial rock crusher (10-25 μm).
3) Pahasapa (Madison) Limestone sample acquired from SDSM&T chemical storage. The sample dates from 1938 and was taken from "a formation near the Rimrock Highway below the old white schoolhouse." This location is west of Rapid City, South Dakota.

Batch experiments were conducted with 100 ppb arsenic standard solutions with each limestone, varying the amount of adsorbent used. Figure 2 depicts the removal efficiencies of these samples.

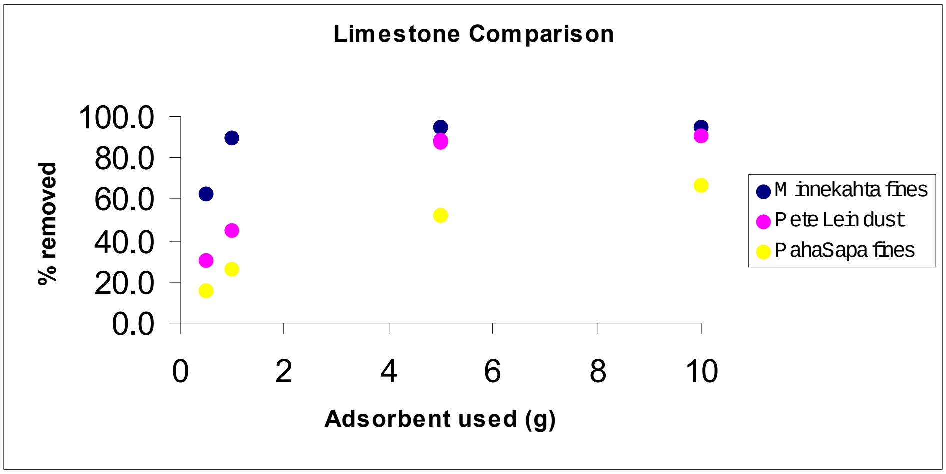

FIGURE 2. Removal efficiencies of various limestone samples.

Removal down to the detection limit of 5 ppb was achieved in the Minnekahta sample at 5.0 g. The removal efficiency therefore was greater than 95%.

Experiments on pH Dependence

In early phases of this work, the pH of the arsenic solution was pre-adjusted to approximately 8.0. This was done primarily to simulate "real-world" ground-water and surface-water pH values. However, pH values of sites with high arsenic concentration are not always within this range. For example, acidic mine drainage (AMD) can have pH values in the ranges of 1 to 5. Therefore, the effectiveness of arsenic removal was explored in the acidic and basic range of pH conditions. A batch experiment was conducted to simulate pH conditions in the range of $4 \leq pH \leq 10$. Ten grams of limestone (1-2 mm) were agitated with a 100 ppb arsenic solution at varying pH values. Samples were studied at every 0.5 pH unit for the range $4 \leq pH \leq 6$ and $8 \leq pH \leq 10$, and then compared with work from Phase I of this project (Davis and Webb, 2001), in which the pH range varied between 6 and 8. Figure 3 shows the results of pH dependence.

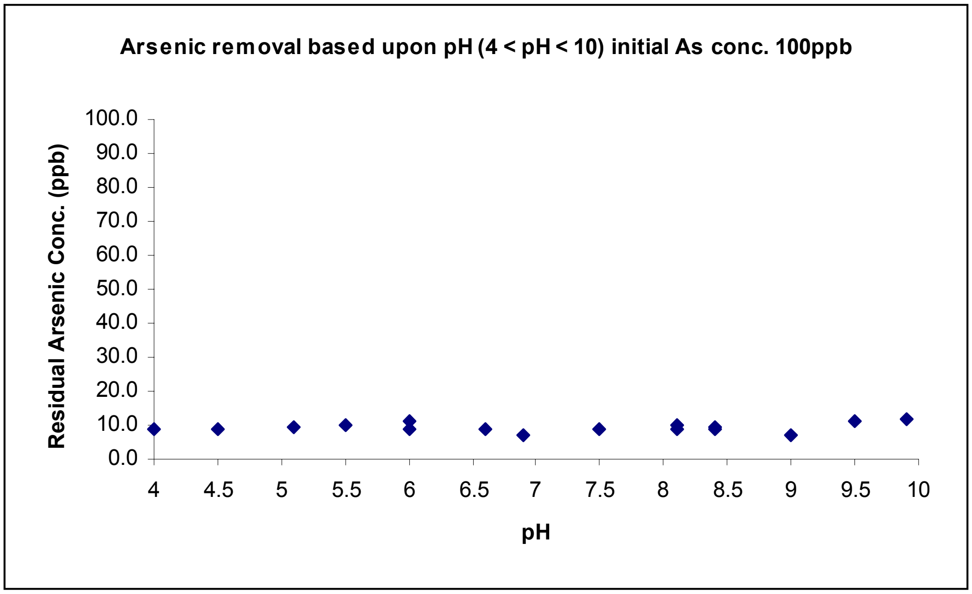

FIGURE 3. Residual arsenic concentration versus initial pH value.

Results indicate that the initial pH of the arsenic solution has very little impact upon the arsenic removal. One possible reason could be that the buffer, created by the carbonate ion present in the limestone, negates the dependence of initial pH upon arsenic removal.

Introduced Interference Study

Field water quality issues such as high total dissolved solids (TDS) and dissolved trace elements are usually absent in the laboratory setting, where all solutions are typically prepared using distilled-deionized water (DI-H_20), or water that has undergone some type of reverse osmosis or nanofiltration. All solutions prepared to this point of the research had previously used deionized water.

Concentrations of chlorides and sulfates in ground and surface water can be in the 3 to 30 ppm range or greater, which could interfere with the adsorption process. A batch experiment was conducted to explore these possible interferences and their effects upon arsenic removal. Solutions of 100 ppb arsenic were prepared with interferences as listed below and reagent grade NaCl and $NaSO_4$ were used for interference solution preparation.

S1 100 ppb As + 5 ppm Cl^- + 1.0 g Limestone
S2 100 ppb As + 5 ppm Cl^- + 5.0 g Limestone
S3 100 ppb As + 10 ppm SO_4^{2-} + 1.0 g Limestone
S4 100 ppb As + 10 ppm SO_4^{2-} + 5.0 g Limestone

The chloride in the samples was precipitated before analysis by using 0.1M $AgNO_3$. The addition of $AgNO_3$ to the samples was to try to precipitate any chlorides before inductively coupled plasma – mass spectrometry (ICP-MS) analysis. Because of problems associated with this method, samples were analyzed by graphite furnace – atomic absorption (GFAA). The samples then were compared to the standard solutions. Results are shown in Table 1, below.

TABLE 1. Introduced interference results.

Sample #		**Gram Quantity**		**% removal**	
S1	5ppmCl	1	>	94.8	AgNO3 added
S2	5ppmCl	5	>	94.8	AgNO3 added
S3	10ppmSO4	1		79.0	AgNO3 added
S4	10ppmSO4	5	>	95.0	AgNO3 added
S5	standard with 5ppm Cl	(96 ppb)		standard	
S6	standard w/10ppm SO4	(100 ppb)		standard	
S7	standard with 5ppm Cl	(90 ppb)		standard	AgNO3 added
S8	standard w/10ppm SO4	(81 ppb)		standard	AgNO3 added

Results from this study indicate little or no appreciable effect of introduced species on arsenic removal. The addition of Cl^- appeared to slightly enhance the removal of arsenic for sample S1. Typically, the removal of arsenic with one gram of adsorbent is about 80 to 90%, which, as demonstrated here, is below detection limits (> 94.8% or 5 ppb). This experiment could be repeated with the introduction of additional species such as nitrate or phosphate, or using waters high in dissolved species and introduced arsenic.

Alternative Materials Testing

Although the limestone material was effective for arsenic removal, alternative materials also were tested for their adsorptive abilities. The primary motivation for this batch experiment was to find alternative materials that potentially could be used for a pellet binding material or a doping agent to improve removal efficiency. A commercial anion exchange resin also was explored to compare to an equivalent limestone sample. Alternative materials chosen for experimentation are listed below. Table 2 lists results of the batch experiment.

1) 5.0 g WyoBen Bentonite 200 mesh (Mills, Wyoming	+100 ppb As
2) 5.0 g activated charcoal ~200mesh	+100 ppb As
3) 5.0 g $CaSO_4$ (gypsum) anhydrous powder	+100 ppb As
4) 5.0 g iron [III] oxide powder	+100 ppb As
5) 5.0 g Dowex® anion exchange resin	+100 ppb As

TABLE 2. Alternative materials testing. Initial arsenic concentration 100 ppb.

	Material	Grams	% removal
S1	Bentonite	5	non-filterable no results
S2	Charcoal	5	95.7
S3	CaSO4	5	66.3
S4	Fe2O3	5	98.4
S5	Dowex	5	68.7

The results above should be viewed with caution. Although the ICP-MS was used for these arsenic determinations, it was later determined through standard solution confirmation that results might have been biased because of chloride interference. A second sample run on GFAA was not possible because sample volumes were not sufficient for determination. Results should be considered with this possible interference in mind.

CONTINUOUS FLOW EXPERIMENT

An adsorption column has been used in earlier phases of this research and will ultimately be explored further. Prior work had focused on gravity feed arsenic removal with vertical columns. Concentrated arsenic solutions were added in numerous volumes in the top of the column, and samples were taken from the bottom. Pore volumes were recorded and residual arsenic recorded until column breakthrough. Another application of the column concept in this phase of the work used a continuous flow reactor vessel.

The reactor was a cylinder with an input tube directing water into the bottom of the vessel. Limestone (1.0 kg of 1-2 mm Minnekahta fines) was placed in the bottom of the vessel, and a standard arsenic solution was forced up through the rock. In the middle of the vessel was a PVC reservoir (1½" pipe, ~5 in. length) that acted as a "flushing mechanism." When full, the water was directed out of the reactor through a tube. This tube was connected directly to the arsenic reservoir (1.0 L Nalgene bottle). An exit tube from the arsenic reservoir was connected to a centrifugal pump, which was driven by an ordinary ½" variable-speed drill. The exit or dump tube was connected to the input on the reactor vessel.

The speed control was variable and the flow rate was controlled with a clamp. For this experiment, the flow rate was set at ~1.0 L/min to allow adequate circulation in the system. The setup was run for 24 hours with 3.0 L of 100 ppb arsenic solution, and small aliquots were taken at set time intervals to determine the effectiveness of the method. Figure 4, below, shows the results of the continuous flow reactor.

A unique result was demonstrated in the analysis of the continuous flow reactor. The arsenic in the system has reached a "quasi" equilibrium, or saturation with the limestone adsorbent. It also shows that a majority of arsenic removal in the system occurred within the first few hours. Although not completely successful (with respect to total arsenic removal), the data indicates a process that removes a majority of the arsenic relatively quickly. This is a positive outcome, and applications to a large-scale process should be explored further.

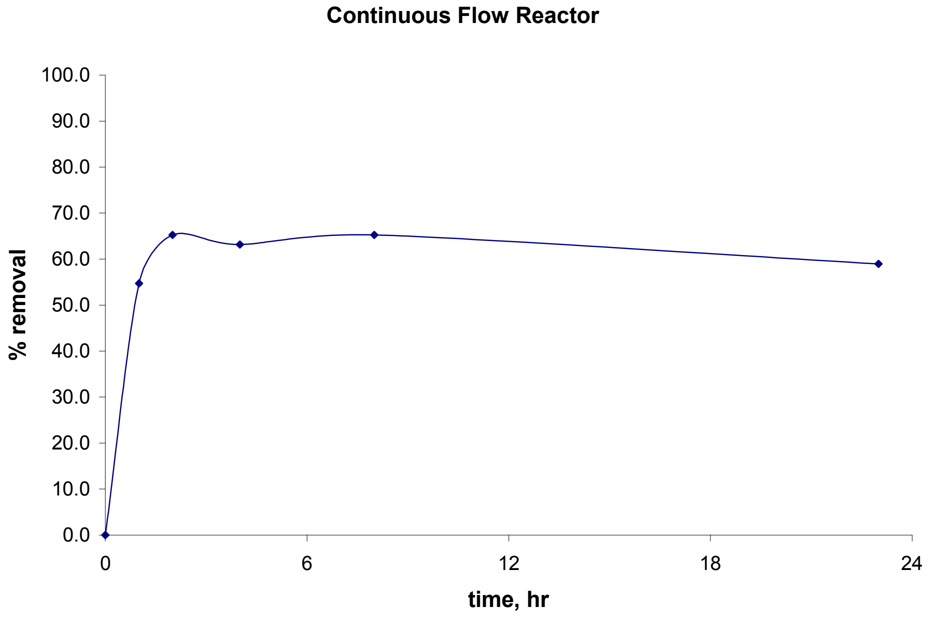

FIGURE 4. Continuous flow reactor arsenic removal with respect to time.

PLATE-AFFIXED BATCH REACTOR

Initial difficulties encountered with binding of material in the pelletization process (described below) prompted investigation of affixing methods for the limestone. This included the use of a silicone sealant/adhesive to affix sulfonated biomasses to Plexiglas plates for cadmium removal of aqueous solutions. A 100% silicone rubber sealant (food grade) DAP (Dow Chemical Corp.) was spread on a Plexiglas plate and limestone was attached as evenly as possible to the glued surface. The plate was allowed to dry overnight, and then was rinsed in DI-H_20, to remove any non-affixed limestone. It is believed that approximately < 1.0 g of adsorbent actually adhered to the plate. The plate then was submerged in 400 mL (600 mL beaker) of 100ppb arsenic solution and placed upon a magnetic stir plate. Figure 5 shows the setup.

FIGURE 5. The plate affixed batch reactor.

The stir rate was sufficient enough to produce continuous surface motion. The batch reactor then was covered with plastic wrap and allowed to stir for 48 hours. An aliquot was taken for elemental analysis. Results are shown below in Table 3.

TABLE 3. Plate affixed batch reactor results (48hrs.).

Sample #	**Residual Arsenic ppb**	**% removal**
Standard	89	
S1	66	25.8

The plate-affixed batch reactor result indicates modest arsenic removal. Assuming that one gram of adsorbent was affixed to the plate, it removed a considerable amount of arsenic compared to the volume of solution (400 mL). The plate reactor method could be explored further by submerging additional plates (three or more) simultaneously, and exploring the application of recycling of the adsorbent plates for arsenic removal.

PELLETIZATION AND ARSENIC REMOVAL

A long-term goal of this research project is to develop a marketable product for arsenic removal in domestic drinking water supplies that are contaminated with arsenic concentrations exceeding U.S. EPA drinking water quality regulations. Pelletization of limestone fines is a step toward the overall goal because it could improve adsorption efficiency and handling. Various methods of pelletizing and sintering limestone and other materials are described in sections below.

This research also explored binders including bentonite clay, cement, and gypsum as possible agents to bind limestone particles into pellets. The attempts of these "natural binders" was to find a binding agent that could be added to the limestone, mixed with water, and pelletized under low pressure.

Several pellets of different percentage compositions of limestone and selected binders were attempted with nominal success. Pellets of satisfactory structural integrity were obtained (bentonite was the most successful binder), but dissolution was observed when pellets were subjected to water submersion. Portland cement (Hills Materials Mortar Reddi-Mix, Rapid City, South Dakota) was a poor binder of limestone. Because cement is partially the product of limestone decomposition, it is likely that a chemical reaction occurred between cement and limestone in slurry, degrading the structural integrity of the concrete.

Ball-Milling Procedure

In order to begin research on the pellitization process of limestone, fines were prepared from limestone rocks. To do this, limestone rocks were crushed with a rock crusher. Then they were put through a sieve and separated, with the following grain diameters: fines greater than 2.362 mm in diameter, fines between 2.362 mm in diameter and 1.18 mm in diameter, fines between 1.18 mm in diameter, and 0.425 mm in diameter, and fines with a diameter less than 0.425 mm. For the ball-milling procedure, the fines with a diameter less than 0.425 mm were used.

In preparation for ball-milling the fines, a ceramic container was rinsed with water, approximately one cup of the fines to be ball-milled, and ceramic beads. This container was placed on a bottle roller for six hours. These rinse fines were filtered out with de-ionized distilled water. Next, the container was refilled, first with the ceramic beads and fines and then with de-ionized distilled water, leaving approximately one inch of air at the top of the container before putting the lid on and placing it onto the bottle roller for six hours. When this was complete, the fines were separated and dried.

Sintering

Sintering was used to make pellets for an adsorption column. Sintering essentially welded the limestone fines together, creating a stronger pellet that would hold together in water yet contain pore spaces for water to flow through. Sintering was performed at high temperatures just below the melting point of the limestone. Sintering decreased surface energy by decreasing the surface area present as the fines welded together. This improved the mechanical and physical properties of the limestone fines, in this case increasing strength and preventing disintegration in water. Previous research indicated that 850^{o} C would be a good temperature at which to begin sintering trials on the limestone fines.

Trials P5, P6, and P7

Initial trials, P5, P6, and P7, were unsuccessful. These pellets were heated to approximately 820° C for about one hour. Each pellet showed signs of decomposition. The pellets were white and crumbly. To test for problems, the pellet was dissolved in water. It had a very basic pH, leading to the conclusion that calcium carbonate had decomposed in the heating process to become calcium oxide or lime.

Trial P8

Trial P8 provided the first successful experiment in pellet preparation. Twenty grams of limestone fines and three milliliters of de-ionized H_2O were combined using a hydraulic press with a pressure of 10,000 lb/in^2 for one minute. The pellet then was placed in an oven and heated to a temperature of 570° C over a four hour and fifty-two minute time period. The pellet was then cooled in a CO_2 environment for 24 hours. This procedure produced a noticeably harder and stronger pellet. P8 also was placed in water to see if it would disintegrate. It held its shape and remained hard. Pellets similar to P8 were produced for later comparison experiments to test the arsenic adsorption abilities of this pellet.

Trials P9 and P11

Trials P9 and P11 explored whether the pellet could be strengthened at temperatures lower than 500° C. Although heating the pellets to 430° and 300° C made them harder, when compared to P8, they broke more easily and disintegrated in water more readily.

Trials P10, P12, P13, and P14

Trials P10, P12, P13, and P14 were unsuccessful. They involved the use of a polyethylene glycol (PEG) in combination with the limestone, held together using paraffin wax. Originally, the plan was to heat the pellet enough to volatilize the wax and then heat it to a slightly higher temperature, allowing sintering to occur. However, these pellets crumbled after heating, leading to the conclusion that the wax had not been completely volatilized during the heating process. Trial P12 had to be cancelled in the heating process because it released large amounts of smoke and vapor when heated to about 200°C and there was concern about a fire. It was hypothesized that the wax caused the problems; therefore, successive polymer trials were completed by using water and pressure to produce pellets rather than using waxes for binding.

Trials P21a, P22a, P23a, P24a, P25a, P26a, and P27a

Trials P21a, P22a, P23a, P24a, P25a, P26a, and P27a explored the temperature limit for sintering by heating to a temperature of 630° C. This temperature appeared to be too high for successful pelletization. All the pellets looked very much like the calcium oxide results from P5, P6, and P7.

Trials P16a, P16b, P17a, P17b, P18a, P18b, P19, and P20

Trials P16a, P16b, P17a, P17b, P18a, P18b, P19, and P20 involved experimentation with pellet shape and less pressure during pellet formation. This technique used more water to hold the pellets together and hand pressure to roll the pellets into a spherical shape. These pellets were placed in the oven for heating to a temperature of 500^o and 550^o C. Then the pellets were cooled in a CO_2 environment. These pellets were strong and did not disintegrate when placed in water. They were not as strong as the pellets produced using the hydraulic press, but they retained strength. It was hoped that these pellets could be made more porous, enabling them to adsorb arsenic better. Further trials, making pellets in a similar manner, were conducted to test the ability of these pellets to adsorb arsenic.

Trials P21b, P22b, P23b, P24b, P25b, P26b, and P27b

Trials P21b, P22b, P23b, P24b, P25b, P26b, and P27b were experiments to compare different compositions of limestone, limestone and bentonite, and limestone and polymer. All pellets were prepared in the same way using the hydraulic press providing 10,000 lb/in^2 for one minute. Pellets were placed in the same oven and heated to 530^o C over a time period of approximately six hours. The pellets were placed in a vacuum CO_2 chamber upon removal for approximately 24 hours. A sample then was taken from each of these pellets for SEM analysis. The pellets all were chiseled so that the mass size for each would be 2.42 g. These pellets were placed in a static batch test with 100 ppb arsenic contaminated water to test their adsorption abilities. During this batch experiment, P23b and P24b disintegrated in the water, so the five percent and ten percent bentonite compositions did not hold together.

Trials P29 a, b, c through P35 a, b, c

Trials P29 a,b,c through P35 a,b,c attempted to repeat the comparison experiment using the different compositions of limestone, limestone and bentonite, and limestone and polymer. This time, however, more de-ionized water was added and spherical pellets were formed with hand pressure. However, there was experimental interference with all of the “c” trials of this experiment. Therefore, the results of this part of the experiment could not be determined. Pellets P33, P34, and P35 disintegrated in water. Once again, as observed earlier, these pellets did not seem as strong as the ones created by using a hydraulic press.

Trials P36 a, b, c, d through P38 a, b, c, d

Trials P36 a,b,c,d through P38 a,b,c,d involved a comparison of the amount of heating time in the oven. Three different pellets, composed of limestone, two weight percent bentonite, and two weight percent PEG, were made by using the hydraulic press and applying 10,000 lb/in^2 for one minute. The oven containing these pellets then was heated to 500^o C. The “a” pellets were removed after one hour, the “b” pellets were removed after one hour and thirty minutes, the “c” pellets were removed after two hours, and the “d” pellets were removed after two hours and thirty minutes. All pellets were cooled in a CO_2 environment. Batch experiments explored the adsorption capabilities of these pellets. For regular limestone after one hour, the pH was very basic and specific conductance was high. It was concluded that decomposition was still occurring even though there were no visible signs of it. PEG seemed to retard decomposition because this did not occur until the two-hour mark with these pellets. The results of this experiment were very encouraging. Although arsenic does not adsorb as readily as with un-sintered fines, a significant amount of arsenic was adsorbed on these pellets. It had been feared that less would be adsorbed on these pellets because the decreased surface area available for adsorption, as compared to other pellets and the fines.

Trials P39 and P40

Trial P39 and P40 involved a comparison of a pellet made with a hydraulic press (at 10,000 lb/in^2) and a pellet made with hand pressure to create a spherical shape. At the time of this experiment, it was not known that heating the oven to 500° C for more than one hour would lead to decomposition. Therefore, the results of the batch experiment showed high pH and specific conductance readings. The results of this experiment were interesting because it appeared that the pellet prepared with a hydraulic press adsorbed arsenic much better than the one prepared with hand pressure.

Results of Sintering Experiments

Several pellets prepared by research assistants appeared to be of such structural integrity that arsenic removal testing was required to determine their removal effectiveness. As mentioned above, numerous variations of binder materials including water, bentonite, PEG (polyethylene glycol), were used.

Variations of temperatures as well as sintering time were used systematically to determine the best overall binder and removal efficiency. Variations are described in Table 4, as well as arsenic removal efficiencies. All arsenic solutions were prepared at 100 ppb, unless otherwise noted.

TABLE 4. Static pellet arsenic removal experiments.

Sample #	Time at 500C Time (hr)	final pH	TDS	Description	% removal
P21	1	9.4	70	Pelletized Limestone	54.8
P22	1	9.3	70	Limestone + 2% Bentonite	35.6
P25	1	9.2	60	Pelletized Limestone	> 93.2 *
P26	1	8.9	60	Limestone + 2% PEG	> 93.2 *
P27	1	8.9	60	Limestone + 5% PEG	> 93.2 *
P36 S1	1	8.8	80	Pelletized Limestone	26.0
P36 S2	1.5	10.4	210	Pelletized Limestone	29.0
P36 S3	2	10.8	410	Pelletized Limestone	43.0
P36 S4	2.5	11.3	440	Pelletized Limestone	35.0
P37 S5	1	10.0	100	Limestone + 2% Bentonite	11.0
P37 S6	1.5	10.1	100	Limestone + 2% Bentonite	**
P37 S7	2	10.9	270	Limestone + 2% Bentonite	30.0
P37 S8	2.5	10.7	190	Limestone + 2% Bentonite	24.0
P38 S9	1	9.67	80	Limestone + 2% PEG	7.8
P38 S10	1.5	9.72	90	Limestone + 2% PEG	21.1
P38 S11	2	9.74	100	Limestone + 2% PEG	8.9
P38 S12	2.5	10.44	180	Limestone + 2% PEG	40.0

* This experiment should be replicated to ensure the validity of the data.

** Arsenic concentration increased from 100 ppb to almost 1 ppm, an obvious anomaly of the data set.

As expected, the static pellet results were mixed. Excluding P25-P27, the removal efficiencies of the pellets are typically below 40%. This is attributable to the decreased exposed surface area and reduced porosity of the pellets.

Interesting observations of the data are the final pH and total dissolved solids (uS/cm). Observed final pH of limestone batch experiments typically ranged from 8.5 to 9.5. Values of pH in the pellet experiments, above, indicate that some pellets have undergone partial decomposition to lime CaO, which is strongly basic in solution ($9.5 < \text{pH} < 13$). The high TDS recorded for the pellets also indicates dissolution of lime, increasing the pH.

Sintering time appears to play a significant role in the pelletization process, especially relating to limestone decomposition. There were no significant differences among physical strengths of the pellets tested. This indicates that although heating is necessary for pelletization and sintering, limiting the heating time is desirable.

Of the two binders tested, polyethylene glycol (PEG) appeared to resist the decomposition of limestone more effectively than bentonite, with respect to time. The binders also seemed to slightly hamper the removal characteristics of the limestone. It is possible that the addition of a doping compound such as Fe_2O_3 or $MgCO_3$ could be used to increase the arsenic removal of the pellets.

Problems Encountered While Making Pellets

An important finding encountered during this research is the decomposition of calcium carbonate at high temperatures. At temperatures above 630^{o} C, the pellets decomposed, releasing CO_2 and converting to calcium oxide (lime). To eliminate this problem, several methods could be tested. The pellets could be heated in a vacuum oven with CO_2 pumped into it. It is believed that the CO_2 environment could prevent the decomposition reaction from occurring. However, this would be expensive and might not be practical for this application. Therefore, future experiments could be conducted to find the maximum temperature to which the pellets could be heated without causing decomposition.

Doping Experiments

Trials P41- P46

Trials P41, P42, P43, P44, P45, and P46 were conducted to examine the addition of other metals to the limestone, in order to increase the adsorption efficiency of the limestone. At the time of these experiments, it was not known that one hour at 500^o C would cause decomposition of calcium carbonate. The pellets were heated at 500^o C for 1.5 hours. After analysis of the samples from this experiment, it was discovered that $MgCO_3$ appears to help the sintered pellets to adsorb arsenic, while Fe_2O_3 appears to hinder the ability of the pellet to adsorb arsenic.

ELEMENTAL DETERMINATIONS

Residual arsenic in batch and column experiments was analyzed with two methods. Samples were sent to Mid-Continent Testing Laboratories in Rapid City, South Dakota, for arsenic analysis by graphite furnace atomic absorption (Varian GFAA). Graphite furnace AA is the preferred method for arsenic determinations, according to EPA methods (Total Arsenic EPA Method 206.2). Typical detection limits by this method are 5 μg/L (5 ppb).

Samples also were sent to the Engineering Mining and Experiment Station (EMES) at South Dakota School of Mines and Technology in Rapid City, South Dakota, for analysis by Inductively Coupled Plasma Mass Spectrometry (Agilent Technologies, HP 4500 ICP-MS). The ICP-MS was explored as an alternative method because of its increased detection limits over GFAA (~X pptr = part per trillion ng/L).

TOXICITY CHARACTERISTIC LEACHING PROCEDURE

The Toxicity Characteristic Leaching Procedure (TCLP) test is a method used to determine the relative stability of a waste component. EPA protocol SW-846 1311 describes the procedure and is available online at *http://www.epa.gov/sw-846/4xxx.htm* (9). The EPA has devised methods such as the TCLP to predict the leaching properties of waste in the landfill/ waste management environment.

Conditions in a landfill are simulated though the preparation of an acidic extraction fluid, based upon the properties of the waste being analyzed. A known quantity of the waste is then bottle-rolled with the prepared extraction fluid for 18 ± 2 hrs. Aliquots of the solution then were withdrawn and acidified with nitric acid prior to elemental analysis.

Two samples of limestone were analyzed with the TCLP test. Prior column work in Phase I of this research provided limestone wastes saturated with arsenic. Solids samples were extracted from column #1 (~ 0.5-1.0 mm sands) and column #4 (0.5-1.0 cm coarse sands). Waste samples (~150 g) were filtered with an 11-cm ceramic Buchner filtration apparatus with 2.0 L of DI-H_20 to remove any interstitial arsenic. The waste then was subjected to the TCLP, and sample aliquots were withdrawn for analysis (GFAA MC testing). Table 5 lists results from the TCLP tests.

TABLE 5. Residual arsenic concentrations from the TCLP.

Sample #	**final pH**	**Residual Arsenic ppb**
Col 1 TCLP	6.4	8
Col 4 TCLP	6.2	< 5.0

The leaching potential of column 4 waste was at or below the detection limit for Total Arsenic EPA method 206.2 by GFAA. Results from this procedure indicate that the waste rock is relatively stable, and could be disposed by normal means in a landfill.

SCANNING ELECTRON MICROSCOPY

A scanning electron microscope (SEM) was used to view materials under high magnification (up to 300,000 X). Several samples of limestone were examined with the SEM to determine particle size and the potential effects of pressure and heat that could occur during the sintering and pelletization process.

Limestone samples that were used in the arsenic removal process also were examined, but little or nothing was visible that could relate to surface bonding or interactions. At the ppb level, it is very difficult if not impossible to find any arsenic formation or complexes on the surface of limestone. Figure 6 shows an image of the limestone fines under SEM at 1000x. Note that although particle size is variable, there appears to be a semi-homogenous particle distribution.

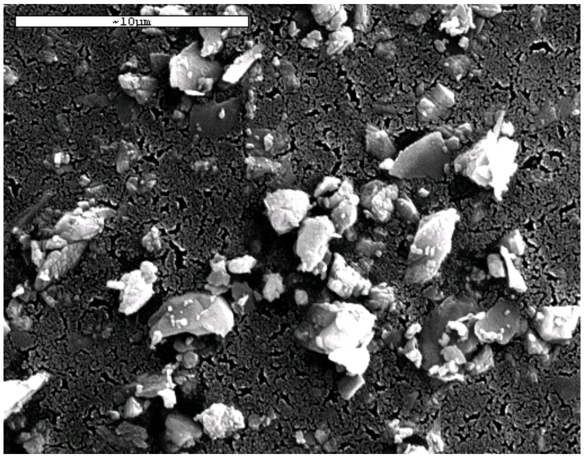

FIGURE 6. Limestone fines at 1000x.

CONCLUSIONS AND RECOMMENDATIONS

Findings from this work have several implications for continuing research on arsenic removal from drinking water. Minnekahta Limestone has been shown to be effective in the removal of arsenic from aqueous solutions, as demonstrated by batch experiments. The composition of the limestone appears to be a controlling factor in the removal of arsenic. The isolation of specific compounds within the limestone will provide insight into unlocking the responsible mechanism or processes for arsenic removal.

The starting pH of the solution played an insignificant role in arsenic removal ($4 \leq pH \leq 10$), and post treatment pH values remained predominantly in the range of $8.0 < pH < 9.5$. A pH value of 8 is reasonable for drinking water quality. The characteristic pH values for surface-water and ground-water supplies are within the range of 6 to 8; therefore this technology will be applicable to domestic water treatment.

Results from the introduced interference studies indicate that additional chloride and sulfate species in solution did not appear to affect the arsenic removal properties of the limestone. Although "real world" water conditions can include high total dissolved solids, introduced chlorides and sulfates, in the ppm level, were of no consequence in this study. If necessary, high TDS concentrations could be reduced through the addition of a flocculent such as activated alumina before arsenic remediation.

Industrial large-scale application of the continuous flow reactor or the plate affixed batch reactors could merit consideration. Unless refined, however, the processes described above might not sufficiently reduce the arsenic concentration in solution. Application of limestone fines to a large continuously mixed reactor, followed by filtration, could be an effective application of the small-scale experiments employed in the laboratory.

Pelletization and sintering should be explored further for use of limestone fines in a column application. Several variables must be considered in this process, including time, sintering temperature, limestone composition, and binder properties. Ultimately, the addition of any heating process or binding material adds complexity and cost to the development of a limestone adsorbent. This should be balanced between the overall removal efficiency and the costs as well as the complexity of the process.

The Toxic Characteristic Leaching Procedure indicates that the waste is relatively stable. The leaching potential of the arsenic on the waste rock is low, which is encouraging for considerations of disposal of the rock in a normal waste facility.

REFERENCES

Davis, A.D., and Webb, C.J., 2001, Arsenic remediation of drinking water: Final Technical Report, U.S. Geological Survey and South Dakota Water Resources Institute.

Focazio, M.J., Welch, A.H., Watkins, S.A., Helsel, D.R., and Horn, M.A., 2000, A retrospective analysis on the occurrence of arsenic in ground-water resources of the United States and limitations in drinking-water-supply characterizations: U.S. Geological Survey Water-Resources Investigations Report 99-4279, 27 p.

Frey, M.M., and Edwards, M.A., 1997, Surveying arsenic occurrence: Journal of the American Water Works Association, March, v. 89, no. 3, p. 105-117.

Langmuir, D., 1997, Aqueous environmental geochemistry: Prentice-Hall, Upper Saddle River, New Jersey, 600 p.

Porter, J. L., 2000, Removal of arsenic from ground water for application at the Rosebud Indian Reservation, South Dakota: M.S. thesis, South Dakota School of Mines and Technology, 80 p.

U.S. Environmental Protection Agency, 2001, Drinking water priority rulemaking: arsenic: http://www.epa.gov/safewater/ars/arsenic.html, July **2001**.

U.S. Environmental Protection Agency, 2001, SW846-1311: Toxicity Characteristic Leaching Procedure: U.S. Environmental Protection Agency: http://www.epa.gov/sw-846/4xxx.htm, p.1-4.

U.S. Environmental Protection Agency, 1999, Arsenic in drinking water: http://www.epa.gov/OGWGW/ars.html; 10/19/99.

WaterWorld, 2001, Arsenic rule could cost utilities billions: WaterWorld, July, 2001, http://www.wwinternational.com.

APPENDIX A

Standard Methods for Arsenic Batch Removal Process

Standard Methods for Arsenic Batch Removal Process

Equipment Required

prepared limestone adsorbent

micro-spatula

arsenic standard (1000 ppm)

analytical balance

Burrell wrist action shaker

150-200 mL round bottom flasks w/stoppers

~10% conc. nitric acid (glassware cleaning)

distilled water

distilled-deionized water

disposable plastic cups ~1-2 oz. (sample analysis)

glass vials 3-5 mL (final elemental analysis)

disposable glass micro-pipets

pH meter and buffers 4, 7, and 10

total conductivity meter

30 mL plastic syringe

0.45 µm small volume filtration apparatus

5, 10, 100 mL volumetric pipets

pipet bulb

aqueous NaOH (standardized pH pre-adjustment of arsenic solution)

0.5, 1.0 L volumetric flasks

1.0 L NALGENE storage vessel

rubber gloves

safety goggles

Preparation for Batch Process

In order for elemental arsenic analysis to be reproducible at the part-per-billion (ppb) level, special precautions need to be taken. *All labware used in the procedure must be rigorously washed using the following procedure.*

1) All labware must be triple rinsed with ~10% conc. nitric acid.
2) After acid wash, triple rinse labware with distilled water (d-H_2O).
3) Follow the d-H_2O rinse with a triple rinse of distilled-deionized water (DI-H_2O).

Limestone Sample Preparation

In order to determine the effectiveness of a limestone adsorbent in the batch process, it is often necessary to vary the quantities used. Prior to setup of the batch procedure, weigh out various quantities of crushed limestone. Typical gram quantities could include: 0.5, 1.0, 5.0, and 10.0. Using the analytical balance, carefully weigh out the desired quantity of absorbent using a pre-tared disposable cup and micro-spatula. Measure out all quantities using this procedure.

It is also desired to include a duplicate as well as a blank sample in the batch process. The duplicate sample is prepared to check the process by reproducibility. The blank sample (limestone adsorbent + DI-H_2O) is for quality control of the experiment, a method to detect any cross-contamination. The duplicate and blank samples are prepared at a sample quantity at the middle of the desired experiment. For example, in the gram quantities listed above, the duplicate and blank samples would be prepared at 5.0 g.

Arsenic Solution Preparation

For the experiments performed in this laboratory, a 100 ppb solution was used during testing. Chemical supply companies readily sell arsenic standards for HPLC analysis as 1000 ppm. Two dilutions are necessary for solution preparation. The 100 ppb solution is prepared using the procedure below.

1) The first dilution is made to 10 ppm. Using appropriate volumetric pipets, transfer the amount of arsenic standard required to the respective volumetric flask. For example, if 500mL of 10 ppm was desired

$$(500\text{mL}) * (10 \text{ ppm}) = (X \text{ mL}) * (1000 \text{ ppm})$$

$$X = 5 \text{ mL}$$

The 5 mL of 1000 ppm arsenic solution is transferred to the 500mL volumetric flask using a 5 mL pipet. The flask is then filled with DI-H_2O to the dilution mark and shaken vigorously.

2) The second dilution is made to 100 ppb or 0.1 ppm. Using appropriate volumetric pipets, transfer the amount of arsenic standard required to the respective volumetric flask. For example if 1.0 L of 100 ppb was desired,

$$(1000 \text{ mL}) * (0.1 \text{ ppm}) = (X \text{ mL}) * (10 \text{ ppm})$$

$$X = 10\ mL$$

The 10 mL of 10 ppm arsenic solution is transferred to the 1000mL volumetric flask using a 10 mL pipet. The flask is then filled with DI-H_2O to the dilution mark and shaken vigorously. After the arsenic solution is prepared to 100 ppb, it is then necessary to pH pre-adjust the solution before the batch process.

1) Transfer ~900mL of the 100 ppb arsenic solution to the 1.0 L NALGENE container.
2) Calibrate the pH meter using the buffers required and appropriate methods.
3) Measure the pH of the arsenic solution.
4) The first typical pH measurement of the arsenic solution will be approximately pH = 4.3-5.0.
5) Carefully add NaOH dropwise, to increase the pH to the desired level. For the course of these experiments, the desired range was pH = 7.8-8.3.
6) Shake the solution adequately.
7) Measure the pH after the addition of NaOH. The pH of the solution can change readily due to the acid equilibrium of arsenic in solution. Consequently, if the pH is too alkaline >8.3, Nitric acid can be heavily diluted with DI-H_2O, and added to the solution to decrease pH.
8) When appropriate pH is reached, set solution aside for the batch procedure.

Batch Procedure

Transfer the samples of limestone adsorbent to the appropriately labeled round bottom flasks from the plastic cups using the micro-spatula. Ensure that all adsorbent is carefully transferred to the r-b flasks.

Assuming a blank is being run in the batch experiment, pipet 100mL of DI-H_2O into the flask. All other samples and the duplicate sample must be filled with 100mL of the pH pre-adjusted arsenic solution described above. Pipet 100mL of arsenic solution to each of the samples, including the duplicate.

All samples must then be secured to the Burrell wrist action shaker. Ensure that the clamps holding the round bottom flasks are secure, as the motion of the shaker can loosen the clamp. Turn the dial to HOLD, and allow the shaker to continuously agitate the samples for a predetermined period (~48 hours).

Laboratory Preparation of Samples

After the predetermined agitation period, turn the dial on the wrist action shaker to OFF. Allow the samples to settle for a period of approximately 30 minutes. After settling, remove the sample from the wrist action shaker. Decant the solution into a disposable plastic cup.

Place an unused 0.45 μm filter in the small volume filtration apparatus. Withdraw ~10 mL of solution using the 30mL syringe. Affix the filtration apparatus to the syringe. Apply pressure to the syringe to begin filtration. Transfer this solution directly to the appropriately labeled vial. Cap or stopper the vial and set aside for elemental analysis. After use, discard the filter and acid wash the syringe and filtration device.

If necessary, transfer additional solution from the round bottom flask to the disposable plastic cup. Measure and record pH and total conductivity of the solution. After the measurement has been made, dispose of solution and clean glassware accordingly. *In order to avoid cross-contamination of the samples, the sampler should change gloves after each sample has been prepared.* Perform the exact same procedure for all samples as described above.

Additional Comments

For the course of the experimental procedures outlined above, it was noted that a duplicate as well as a blank sample was to be run during the batch process. It is also important to prepare an additional vial for a standard arsenic sample. Using a disposable glass micro-pipet, carefully transfer ~5mL of the arsenic solution described above in "Arsenic solution preparation" into a labeled vial and include it in the elemental analysis as the standard solution.

Factors Affecting Nutrient Availability and Primary Productivity in Black Hills Reservoirs

Basic Information

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Descriptors:	Reservoir Management,Lakes, Phosphorus, Water Quality
Principal Investigators:	Steven R. Chipps, David R. German

Publication

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2. Holcomb, Benjamin. 2002. Nutrient Inputs, Iron Availability and Algal Biomass in Black Hills Watersheds: Implications for Reservoir and Stream Productivity. M.S. Thesis, Wildlife and Fisheries Department, South Dakota State University, Brookings, South Dakota. 98 pp.

EXECUTIVE SUMMARY

Exchange of phosphorus between sediments and water is a major component of the phosphorus cycle in freshwater lakes. Because of the importance of phosphorus as a limiting nutrient in fresh waters, much interest has been devoted to phosphorus availability in lake sediments and mechanisms that regulate it’s movement into the overlying water (Wetzel 2001; Bostrom et al. 1982). In general, sediment phosphorus concentration is only weakly linked to phosphorus concentration in lakes and reservoirs (Scheffer 1998). A variety of factors can regulate phosphorus release from lake sediments and include 1) the ability of sediments to retain phosphorus, 2) conditions of the overlying water and 3) faunal characteristics (e.g., bioturbation) of lake sediments (Wetzel 2001).

In freshwater systems, iron is an important agent that binds phosphorus under aerobic (i.e., oxygenated) conditions. As a result, iron availability and redox condition can have important implications for sediment nutrient concentration in lakes and reservoirs.

Natural bog iron deposits are characteristic features of the upper Rapid Creek watershed in the Black Hills of western South Dakota. To explore relationships among iron availability, nutrient concentrations and algal biomass in Black Hills reservoirs, we quantified limnological characteristics of Pactola, Deerfield, Sheridan, and Stockade reservoirs from October 2000 to October 2001. External phosphorus input (total P) ranged from 0.5 mg P/m^2/d in Deerfield Reservoir to 7.3 mg P/m^2/d in Stockade Reservoir and was poorly related to sediment phosphorus concentration. Although total phosphorus concentration was lowest in Pactola Reservoir ($\bar{x}$=12 µg/L), sediment phosphorus availability was relatively high compared to other reservoirs.

Iron (Fe) inputs varied appreciably across reservoirs, ranging from 5.5 mg Fe/m^2/d in Deerfield Reservoir to 132.4 mg Fe/m^2/d in Pactola Reservoir. Sediment iron availability was significantly higher in Pactola Reservoir ($\bar{x}$=51.5 mg/g) than in other Black Hills reservoirs (overall $\bar{x}$=26.6 mg/g) owing to 1) high Fe loading rates and 2) aerobic conditions in the hypolimnion. Because of high sediment Fe availability, sediment P:Fe ratio in Pactola Reservoir was low ($\bar{x}$=2.5) compared to other reservoirs (overall $\bar{x}$=4.5), implying that under aerobic conditions, Pactola sediments act as a strong buffer to sediment phosphorus release. In reservoirs that experienced summer hypolimnetic anoxia (i.e., Sheridan and Stockade reservoirs), we observed significant increases in water column phosphorus concentration measured near the sediment-water interface, underlying the importance of redox potential on internal phosphorus loading in Black Hills reservoirs.

Phosphorus loading rates provided reasonable estimates of nutrient concentration in Black Hills reservoirs. As a result, mass-balance models should prove useful for addressing effects of external phosphorus inputs on reservoir nutrient levels. Factors known to affect internal nutrient loading, however, varied appreciably across reservoirs. Using multiple regression analysis, we developed an empirical model for predicting reservoir nutrient concentration that incorporated measures of 1) sediment P availability, 2) sediment Fe concentration and 3) redox potential. This model explained about 80% of the variation in hypolimnetic phosphorus concentration and should prove useful for modeling effects of hypolimnetic conditions (e.g., anoxia) on nutrient availability in Black Hills reservoirs.

Total zooplankton density was lowest in Pactola Reservoir ($\bar{x}$=51.4/L) and highest in Stockade Reservoir ($\bar{x}$=187.7/L). Copepods were a dominant component of the zooplankton community in Pactola and Deerfield reservoirs, comprising about 60 percent of total zooplankton biomass. Moreover, the cladoceran community in Pactola and Deerfield reservoirs was dominated by *Daphnia galeata mendotae*, whereas in Sheridan and Stockade reservoirs, *D. pulex* was the dominant grazer. We postulate that differences in *Daphnia* composition likely reflect a combination of reservoir productivity and predation pressure by zooplanktivorous fishes. As a larger cladoceran, *D. pulex* is generally regarded as a more efficient filter feeder than *D. mendotae,* but is also more susceptible to fish predation. In general, abundance of herbivorous zooplankton appeared to have little affect (i.e., grazing pressure) on water transparency in Black Hills reservoirs. Rather, biomass of primary consumers was positively correlated to algal abundance in Black Hills reservoirs.

INTRODUCTION

Trophic status and productivity vary considerably among Black Hills reservoirs in western South Dakota (German 1997). Differences in reservoir productivity can be attributed to several factors that include 1) basin morphology, 2) nutrient availability, 3) flushing rate, 4) sediment redox potential, and 5) food web structure. Summer water transparency, for example, ranges from a low of 0.6 m in Stockade Reservoir to a high of 9 m in Pactola Reservoir, with Sheridan and Deerfield reservoirs exhibiting intermediate water clarity (3 and 5 m respectively). In general, nutrient availability and algal biomass are lowest in Pactola Reservoir (total phosphorus=0.010 mg/L; chlorophyll-a=2.9 µg/L) and highest in Stockade Reservoir (0.080 mg/L; 32.9 µg/L; German 1997).

Pactola and Deerfield reservoirs are U.S. Bureau of Reclamation projects that provide important sources of domestic and agricultural water supplies for the region. Water quality in these reservoirs is considered very good with high transparency and relatively low algal biomass (German 1997). Factors that regulate nutrient availability and primary productivity in Black Hills Reservoirs, however, are not well understood. Natural iron deposits occur throughout the upper Rapid Creek watershed (see Appendix A). While considered a local water quality problem, high iron content in downstream water may be important in limiting phosphorus availability, particularly in Pactola Reservoir. Under aerobic conditions, iron is the most important agent immobilizing dissolved, reactive phosphorus in aquatic environments. When productivity and microbial decomposition increase, the hypolimnion of lakes and reservoirs can become anoxic (e.g., low redox potential). When this occurs, iron Fe^{+++} is reduced to Fe^{++} and both iron and phosphorus are released into solution contributing to increased reservoir nutrient concentrations and increased productivity (i.e., internal nutrient loading). Hence, redox conditions at the sediment-water interface play an important role in regulating phosphorus availability and may have important implications for maintaining water quality in Black Hills reservoirs.

Sheridan and Stockade reservoirs are managed by the State of South Dakota and provide important regional recreation opportunities. Both reservoirs may be particularly susceptible to 'internal' nutrient loading because the hypolimnion in these systems often becomes anoxic in summer months (German 1997). Moreover, these reservoirs are located in different watersheds than Pactola and Deerfield reservoirs and generally exhibit higher nutrient concentrations.

Biological communities of lakes and reservoirs can also have an important influence on algal biomass and resulting water quality (Carpenter et al. 1985). Food web structure, for example, can play an important role in regulating the abundance and composition of phytoplankton. Large, herbivorous zooplankton such as *Daphnia*, often play an important role in regulating algal biomass. Zooplanktivorous fishes can significantly reduce *Daphnia* abundance -- an effect that can lead to increased algal biomass and reduced water quality (Carpenter et al. 1985). As a result, trophic interactions may play an important role in regulating algal biomass in lakes and reservoirs. In Black Hills reservoirs, fish community composition varies considerably -- from predominantly warm water fishes in Sheridan and Stockade reservoirs (e.g., centrarchid and percid assemblages) to coolwater fishes in Pactola and Deerfield (e.g., salmonids). While fish abundance and composition are well documented for Black Hills reservoirs, species composition and size structure of planktonic zooplankton are poorly understood. Information on relative abundance and size structure of zooplankton populations can provide important information regarding the potential impacts from planktivorous fishes that influence algal biomass and resulting water quality.

RESEARCH OBJECTIVES

The goals of this study are to explore relationships among iron concentrations, nutrient availability, algal biomass and zooplankton abundance in four, Black Hills reservoirs (Pactola, Deerfield, Sheridan and Stockade). Specific objectives are to 1) quantify seasonal nutrient availability and phytoplankton biomass, 2) quantify phosphorus and iron availability in reservoir sediments, 3) determine phosphorus and iron loading rates, and 4) measure species composition and size structure of planktonic zooplankton in Black Hills Reservoirs.

STUDY AREA

Four major reservoirs occur within the Black Hills of western South Dakota: Pactola, Deerfield, Sheridan, and Stockade. Pactola is the largest and deepest reservoir at 318 ha (max depth=48 m) whereas Stockade is the smallest reservoir at 49 ha (max depth= 15.2 m). Deerfield and Sheridan reservoirs are comparable in size at about 160 ha and maximum depths of about 21 m. Pactola Reservoir is characterized as a meso-oligotrophic reservoir with water transparency often reaching 9 m and summer total phosphorus concentrations of 0.007 mg/L (German 1997). Deerfield reservoir is primarily mesotrophic (total phosphorus = 0.011 mg/L), whereas Sheridan (total phosphorus=0.032 mg/L) and Stockade reservoirs (total phosphorus=0.124 mg/L) are characterized as eutrophic systems (German 1997).

METHODS

Seasonal Nutrient Availability and Algal Biomass

Black Hills reservoirs were sampled seasonally (i.e., 3-4 month intervals) from October 2000 through October 2001. We sampled five sites in each reservoir, except in February when three sites per reservoir were sampled through the ice (Appendix B). At each site, we collected two water samples for analysis of total phosphorus and chlorophyll *a* concentration. Water samples were collected at the surface and 1 m above the sediments at each site using a 2 L Kemmerer bottle. Water samples for total phosphorus analysis were transferred to clean, 250 ml Nalgene bottles and frozen for later analysis (SDSU Water Resources Laboratory). Chlorophyll *a* samples were collected by filtering 250 ml of water through a GF/F filter, wrapping filters in aluminum foil, then freezing filters for later analysis. Chlorophyll *a* was measured using a Turner Design TD-700 fluorometer after 24 h of extraction in 90% acetone. We measured water quality characteristics at 0.5-1.5 m intervals from the deepest site in each reservoir using a YSI DataSonde Model 650. Parameters measured by the DataSonde included dissolved oxygen, temperature, pH, redox potential, specific conductivity, total dissolved solids, ammonia, nitrate, and turbidity (Appendix C). Secchi disk readings were also recorded at reservoir sites where vertical profiles were taken.

External Phosphorus and Iron Inputs

We measured external P and Fe inputs for each reservoir during June-July, 2001. Data on reservoir inflows and outflows were combined with information on phosphorus and iron concentrations measured at stations above and below each reservoir. Water samples collected for iron measurements were stored in 500 ml bottles and fixed with 5 ml of nitric acid. Samples for phosphorus concentration were collected and analyzed as previously described. Inflow and outflow discharge was calculated from 1) mean depths and water velocities measured at each station or 2) data obtained from USGS and/or U.S. Bureau of Reclamation gauging stations. Sampling occurred weekly from early June through July (8 weeks). Areal loading rates for P and Fe were calculated by dividing mean daily inputs (kg/d) by the area of the reservoir. We modeled reservoir phosphorus concentration using the Dillon-Rigler mass-balance model (1974) because it has been successfully used to predict phosphorus concentrations in western reservoirs (Mueller 1982). The equation used to model reservoir phosphorus concentration was:

$$P = L\, \tau / z\, (1-R)$$

where P is reservoir phosphorous concentration (mg/L), L is areal annual phosphorus loading rate (g $P/m^2/y$), τ = hydraulic residence time (y), z = mean depth (m), and R = fractional phosphorus retention. Phosphorus retention (R) was estimated as:

$$R = 1 - (q_o\, [P]_o / \sum q_i\, [P]_{i.}\ ,$$

where q_o = outflow discharge volume (m^3/y), $[P]_o$ = outflow P concentration (mg/L), q_i = inflow volume (m^3/y), and $[P]_i$ = inflow P concentration (mg/L) (Dillon and Rigler 1974; Mueller 1982).

Sediment Phosphorus and Iron Availability

The ratio of sediment phosphorus-to-iron (P:Fe) can provide important information about phosphorus storage potential in lakes and reservoirs (Jensen et al. 1992; Sondergaard 1993; van der Molen and Boers 1994). Under aerobic conditions, Fe binds about 10% of its own weight in phosphorus (Scheffer 1998). Hence, knowledge of sediment P:Fe ratios can provide important insight regarding nutrient buffering capacity of lake sediments. Under anaerobic conditions (i.e., reducing environment) Fe^{+++} is reduced to Fe^{++}, effectively releasing P from the sediments and contributing to increased nutrient levels (referred to as internal nutrient loading).

Because the upper Rapid Creek drainage contains several natural bog-iron deposits, we postulated that Fe availability in Pactola Reservoir would be relatively high compared to other reservoirs. To quantify sediment P:Fe ratios, we collected core samples from mid-reservoir sites seasonally from October 2000 to October 2001. Three replicate core samples were collected from each reservoir using a 73 cm weighted coring device (Wildco corer, Wildco Corporation). Sediment cores were extruded from the coring device using a stainless steel plunger and the upper 6 cm layer was extracted and frozen for later processing. Composite sediment samples from the upper 6 cm layer were then homogenized, dried to a constant weight at 60°C, and analyzed for iron (mg/g) and total phosphorus (mg/g) content by South Dakota State University Soils Testing Laboratory, Brookings, South Dakota.

Zooplankton Composition and Size Structure

At each reservoir site, three zooplankton samples were obtained from the upper 5 m using a vertically towed 10 cm Wisconsin net with 63-µm mesh. All zooplankton were preserved in 10 % Lugol's solution and transported to the laboratory for identification and enumeration. In the laboratory, zooplankton were sub sampled by quantifying all zooplankton in 10% sub samples. Zooplankton were identified, counted and 30 individuals of each species measured for total length (mm) to determine density, species composition, size structure, and biomass of the population (Pennak 1989). Individual mass -- estimated using length-weight regression equations (Dumont et. al. 1975) – was multiplied by taxa-specific density to obtain biomass estimates. Differences in total crustacean zooplankton abundance, species composition, size structure, and biomass were determined using analysis of variance (SAS Institute Inc. 1999).

RESULTS & DISCUSSION

Seasonal Nutrient Availability and Algal Biomass

Bivariate plots of Secchi depth versus chlorophyll *a* biomass revealed that water transparency was inversely related to algal biomass in Black Hills reservoirs (Figure 1; Table 1). Mean annual Secchi depths ranged from 2 m in Stockade Reservoir to 8 m in Pactola Reservoir and were similar to values reported by German (1997). Similarly, mean annual chlorophyll *a* biomass was lowest in Pactola Reservoir ($\bar{x}$=0.6 µg/L) and highest in Stockade Reservoir ($\bar{x}$=7.0 µg/L; Table 1). Chlorophyll *a* biomass was

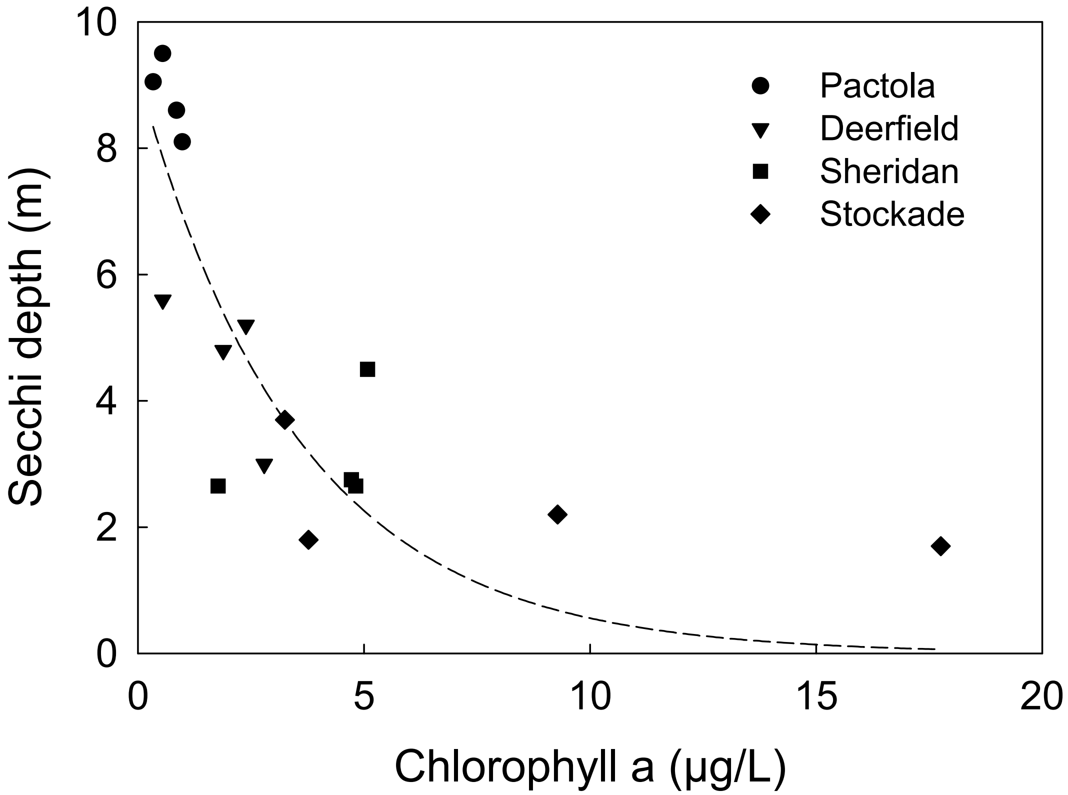


Figure 1. Relationship between Secchi depth and surface algal biomass (chlorophyll a) in Pactola, Deerfield, Sheridan, and Stockade reservoirs, October 2000 to October 2001. Regression line was fitted to the equation, Secchi depth= 9.17e-0.28CHLa (r2= 0.69, P< 0.001).

Table 1. Mean Secchi depth and chlorophyll *a* concentration measured in Black Hills reservoirs from October 2000 to October 2001. Chlorophyll *a* samples were taken 1 m below the surface and 1 m above the bottom. Values in parentheses represent 1 SE.

Reservoir	Sample date	n	Secchi depth (m)	Surface chlorophyll a (µg/L)	Bottom chlorophyll a (µg/L)
Pactola	Oct. 2000	5	9.1	0.34 (0.05)	0.17 (0.02)
	Feb. 2001	3	-	0.40 (0.11)	0.84 (0.06)
	May 2001	5	9.5	0.55 (0.07)	1.73 (0.56)
	Aug. 2001	5	8.6	0.86 (0.14)	1.43 (0.24)
	Oct. 2001	5	8.1	0.98 (0.16)	1.09 (0.19)
	mean	23	8.8	0.64 (0.07)	1.07 (0.17)
Deerfield	Oct. 2000	5	5.6	0.55 (0.09)	0.80 (0.16)
	Feb. 2001	3	-	1.01 (0.51)	2.22 (0.56)
	May 2001	5	3	2.79 (0.20)	4.33 (1.04)
	Aug. 2001	5	5.2	2.39 (0.24)	2.35 (0.56)
	Oct. 2001	5	4.8	1.88 (0.16)	1.38 (0.28)
	mean	23	4.7	1.79 (0.20)	2.22 (0.37)
Sheridan	Oct. 2000	5	2.7	1.78 (0.39)	1.57 (0.42)
	Feb. 2001	3	-	no data	4.40(1.50)
	May 2001	5	2.7	4.82 (0.16)	3.40 (0.69)
	Aug. 2001	5	2.8	4.72 (0.19)	2.9 (0.87)
	Oct. 2001	5	4.5	5.08 (0.24)	2.78 (1.02)
	mean	23	3.1	4.10 (0.33)	2.67 (0.39)
Stockade	Oct. 2000	5	1.8	3.78 (0.23)	3.90 (0.31)
	Feb. 2001	3	-	1.14 (0.10)	0.67 (0.18)
	May 2001	5	3.7	3.25 (0.25)	2.78 (0.39)
	Aug. 2001	5	1.7	17.76(0.71)	13.12 (1.69)
	Oct. 2001	5	2.2	9.28 (0.75)	7.01 (0.69)
	mean	23	2.4	7.55 (1.29)	5.91 (0.98)

strongly correlated with total phosphorus concentration in Black Hills reservoirs (Figure 2), implying that phosphorus is the limiting nutrient to algal productivity.

Phosphorus concentrations varied appreciably among Black Hills reservoirs with mean values ranging from 12 µg/L in Pactola Reservoir to 81 µg/L in Stockade Reservoir (Table 2). Similarly, nitrate (NO_3^-) and ammonia (NH_4^+) concentrations were generally lowest in Pactola Reservoir and highest in Stockade Reservoir (Table 3). Summer hypolimnetic dissolved oxygen concentration was appreciably low in Deerfield, Sheridan and Stockade reservoirs (Figure 3) whereas hypolimnetic oxygen concentration in Pactola reservoir remained above 4 mg/L throughout the year. Reduction of summer hypolimnetic dissolved oxygen was associated with significant increases in total phosphorus concentration measured near the sediments in Deerfield, Sheridan and Stockade reservoirs (Figure 4). In Stockade Reservoir, for example, total phosphorus concentration near the sediments increased from 60 µg/L in May to over 140 µg/L in August 2001.

Using seasonal measurements of Secchi depth, chlorophyll *a* biomass and total phosphorus concentration, we calculated trophic state indices (TSI scores) for each reservoir (Table 4). TSI reflects the ‘trophic state’ of lakes and reservoirs where values < 30 are indicative of oligotrophy, 50 to 70 indicate eutrophic conditions and values >70 are often characteristic of hypereutrophic conditions (Carlson 1977). Based on chlorophyll *a* biomass, mean TSI scores were 25, 34, 48 and 46 for Pactola, Deerfield, Sheridan and Stockade reservoirs. Factors such as nutrient availability, zooplankton grazing, and nonalgal sources of turbidity can have an important influence on seasonal variation in TSI scores. To better understand factors affecting TSI scores, deviation of TSI relationships can be represented graphically as proposed by Carlson (1992). In the example plot depicted by Figure 5, values that fall above the x-axis imply increased P limitation. Points to the right of the y-axis indicate that water transparency is higher than that predicted by algal biomass, such as dominance by large cyanobacteria or increased zooplankton grazing and subsequent decreases in small particles (Wetzel 2001). Conversely, points to the left of the y-axis in the lower left diagonal indicate that water transparency is lower than predicted by algal biomass as a result of suspended sediment or small, non-algal

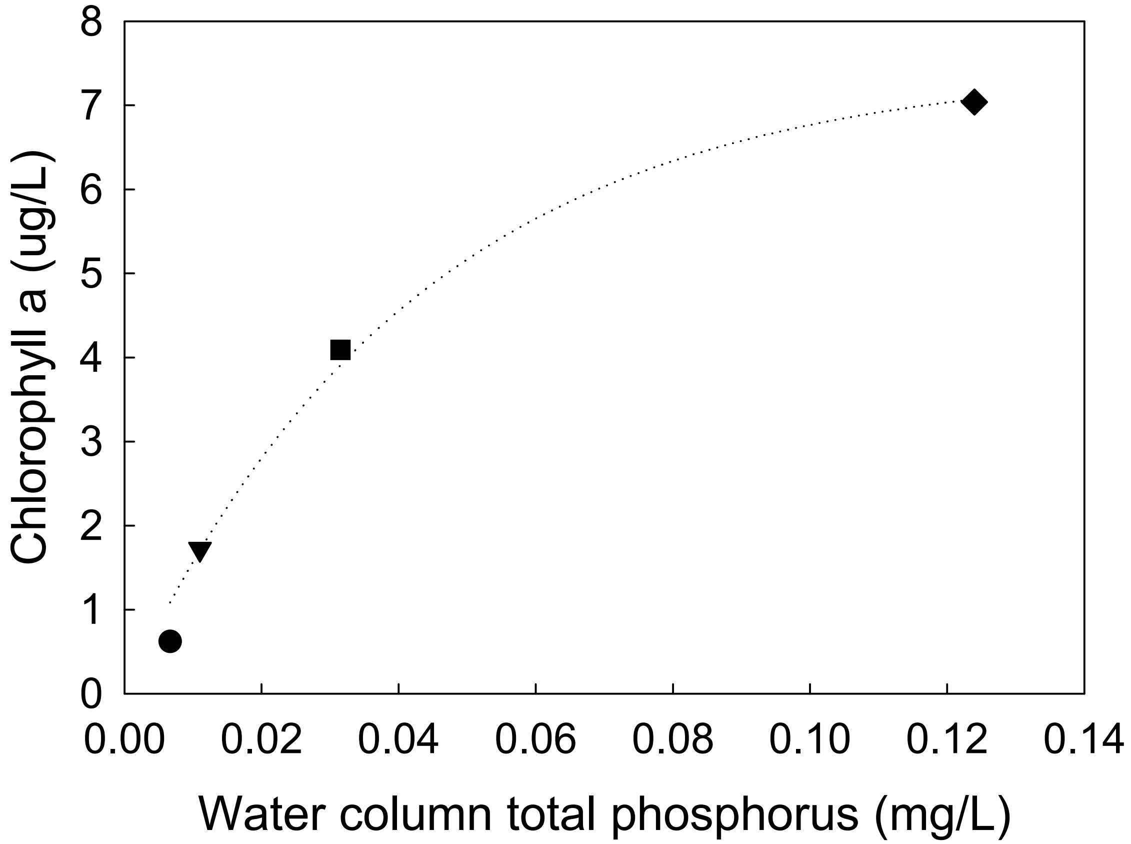


Figure 2. Relationship between mean algal biomass and mean surface phosphorus concentration for Pactola, Deerfield, Sheridan, and Stockade reservoirs from October 2000 to October 2001. Regression line was fitted to the equation CHLa= 7.48(1-e-23.45TP) (r2= 0.99, P= 0.005).

Table 2. Mean total phosphorus (TP) concentration measured in Black Hills reservoirs from October 2000 to October 2001. Samples were taken 1 m below the surface and 1 m above the bottom. Values in parentheses represent 1 SE.

Reservoir	Sample date	n	Surface TP (mg/L)	Bottom TP (mg/L)
Pactola	Oct. 2000	5	0.012 (0.005)	0.024 (0.009)
	Feb. 2001	3	0.011 (0.005)	0.017 (0.002)
	May 2001	5	0.005 (0.002)	0.008 (0.001)
	Aug. 2001	5	0.007 (0.002)	0.011 (0.002)
	Oct. 2001	5	0.028 (0.009)	0.020 (0.003)
	mean	23	0.013 (0.003)	0.016 (0.002)
Deerfield	Oct. 2000	5	0.041 (0.014)	0.047 (0.018)
	Feb. 2001	3	0.025 (0.008)	0.023 (0.008)
	May 2001	5	0.012 (0.003)	0.012 (0.004)
	Aug. 2001	5	0.011 (0.004)	0.022 (0.003)
	Oct. 2001	5	0.033 (0.003)	0.052 (0.015)
	mean	23	0.024 (0.004)	0.032 (0.006)
Sheridan	Oct. 2000	5	0.035 (0.005)	0.010 (0.032)
	Feb. 2001	3	0.044(0.007)	0.026 (0.007)
	May 2001	5	0.022 (0.003)	0.025 (0.003)
	Aug. 2001	5	0.032 (0.002)	0.084 (0.019)
	Oct. 2001	5	0.032 (0.003)	0.140 (0.046)
	mean	23	0.0318 (0.002)	0.078 (0.015)
Stockade	Oct. 2000	5	0.094 (0.009)	0.105 (0.010)
	Feb. 2001	3	0.026 (0.006)	0.068 (0.033)
	May 2001	5	0.048 (0.004)	0.057 (0.006)
	Aug. 2001	5	0.124 (0.004)	0.144 (0.032)
	Oct. 2001	5	0.111 (0.004)	0.109 (0.003)
	mean	23	0.085 (0.008)	0.099 (0.010)

Table 3. Mean water quality values averaged from vertical profiles taken in Black Hills reservoirs from October 2000 to October 2001. Data were collected using a YSI DataSonde. See Appendix C for raw data summary.

Parameter	Unit	Pactola	Deerfield	Sheridan	Stockade
Temperature	°C	10.95	11.14	10.53	13.68
Dissolved oxygen	mg/L	8.96	6.24	4.63	5.56
pH	--	8.28	8.24	8.01	8.34
Specific conductance	µS/cm	363.3	385.4	304.5	312.3
Total dissolved solids	mg/L	0.236	0.251	0.198	0.203
Turbidity	NTU	1.05	2.30	2.68	2.52
ORP	mV	178.1	157.2	181.3	167.5
NO_3	mg/L	16.3	30.0	46.6	44.1
NH_3	mg/L	0.006	0.005	0.010	0.029
NH_4	mg/L	0.138	0.120	0.397	0.439

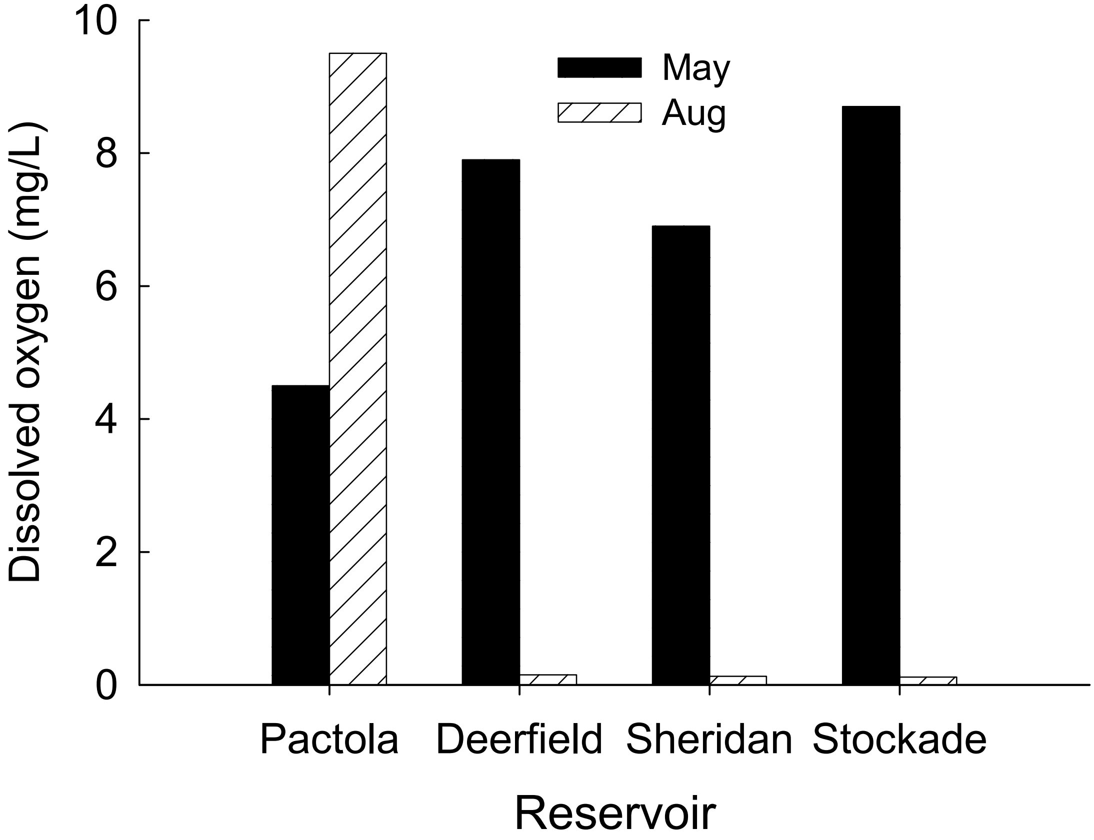


Figure 3. Dissolved oxygen concentration measured near the sediment-water interface in May and August 2001 in Pactola, Deerfield, Sheridan, and Stockade reservoirs.

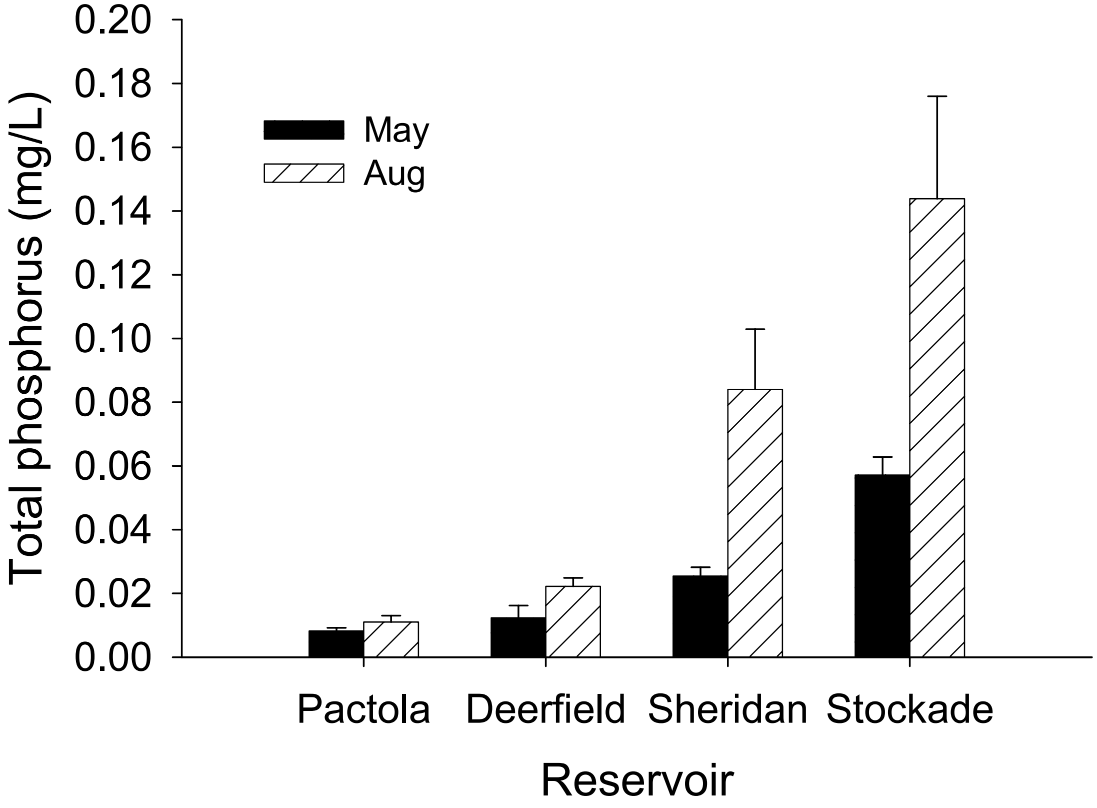


Figure 4. Total phosphorus concentration measured near the sediment-water interface in May and August 2001 in Pactola, Deerfield, Sheridan, and Stockade reservoirs. P values are given for each reservoir comparing total phosphorus concentration in May vs. August (Student's T-Test). Vertical bars represent 1 S.E.

Table 4. Seasonal Trophic State Index (TSI) values calculated from total phosphorus (TSI_{TP}), Secchi depth (TSI_{SD}), and chlorophyll a (TSI_{CHL}) in Pactola, Deerfield, Sheridan, and Stockade reservoirs.

Reservoir	Sample date	TSI_{TP}	TSI_{SD}	TSI_{CHL}
Pactola	Oct. 2000	40.50	28.26	19.98
	Feb. 2001	38.55	*	21.58
	May 2001	27.92	27.56	24.66
	Aug. 2001	31.54	28.99	29.07
	Oct. 2001	51.96	29.86	30.42
	mean	38.09	28.67	25.14
Deerfield	Oct. 2000	57.84	35.17	24.74
	Feb. 2001	50.57	*	30.74
	May 2001	40.50	44.17	40.68
	Aug. 2001	38.75	36.24	39.16
	Oct. 2001	54.38	37.40	36.82
	mean	48.41	38.25	34.43
Sheridan	Oct. 2000	55.51	45.96	36.23
	Feb. 2001	58.61	*	67.91
	May 2001	48.55	45.96	46.03
	Aug. 2001	53.90	45.42	45.82
	Oct. 2001	54.04	38.33	46.54
	mean	54.12	43.92	48.51
Stockade	Oct. 2000	69.62	51.53	43.63
	Feb. 2001	51.11	*	31.85
	May 2001	60.09	41.15	42.16
	Aug. 2001	73.65	52.35	58.82
	Oct. 2001	72.05	48.64	52.46
	mean	65.31	48.42	45.78

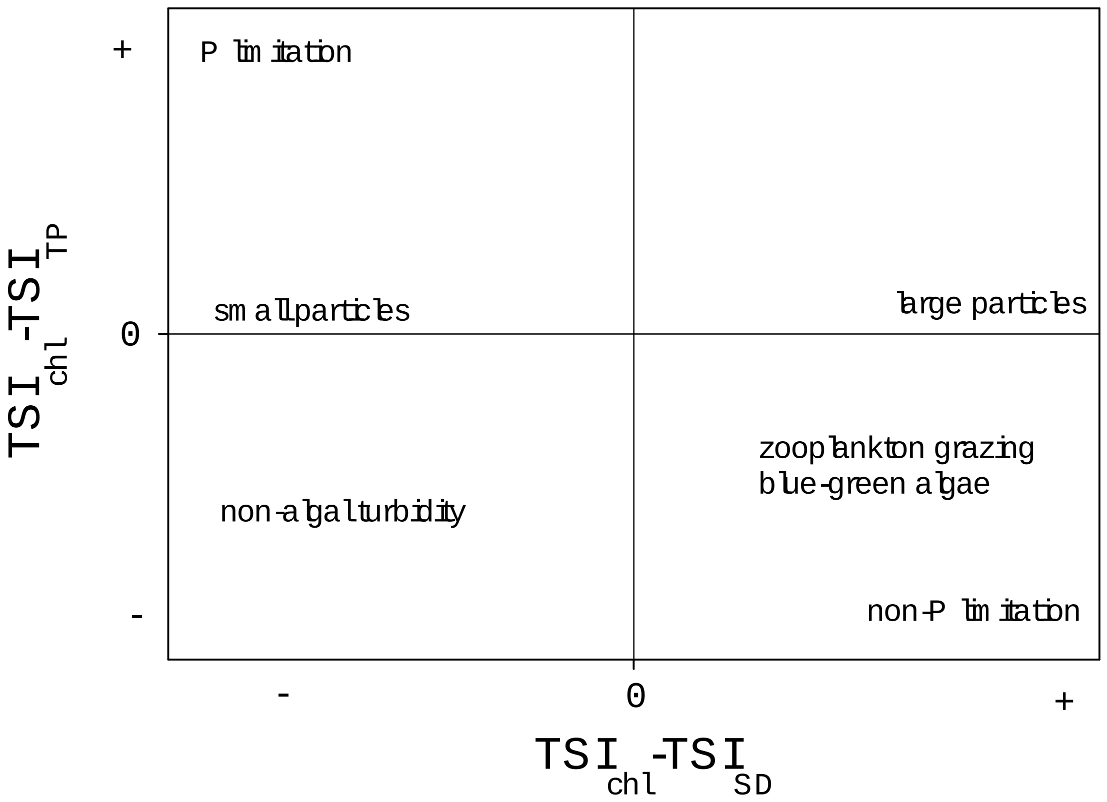


Figure 5. Potential factors that affect deviations in TSI relationships. Adopted from Carlson (1992).

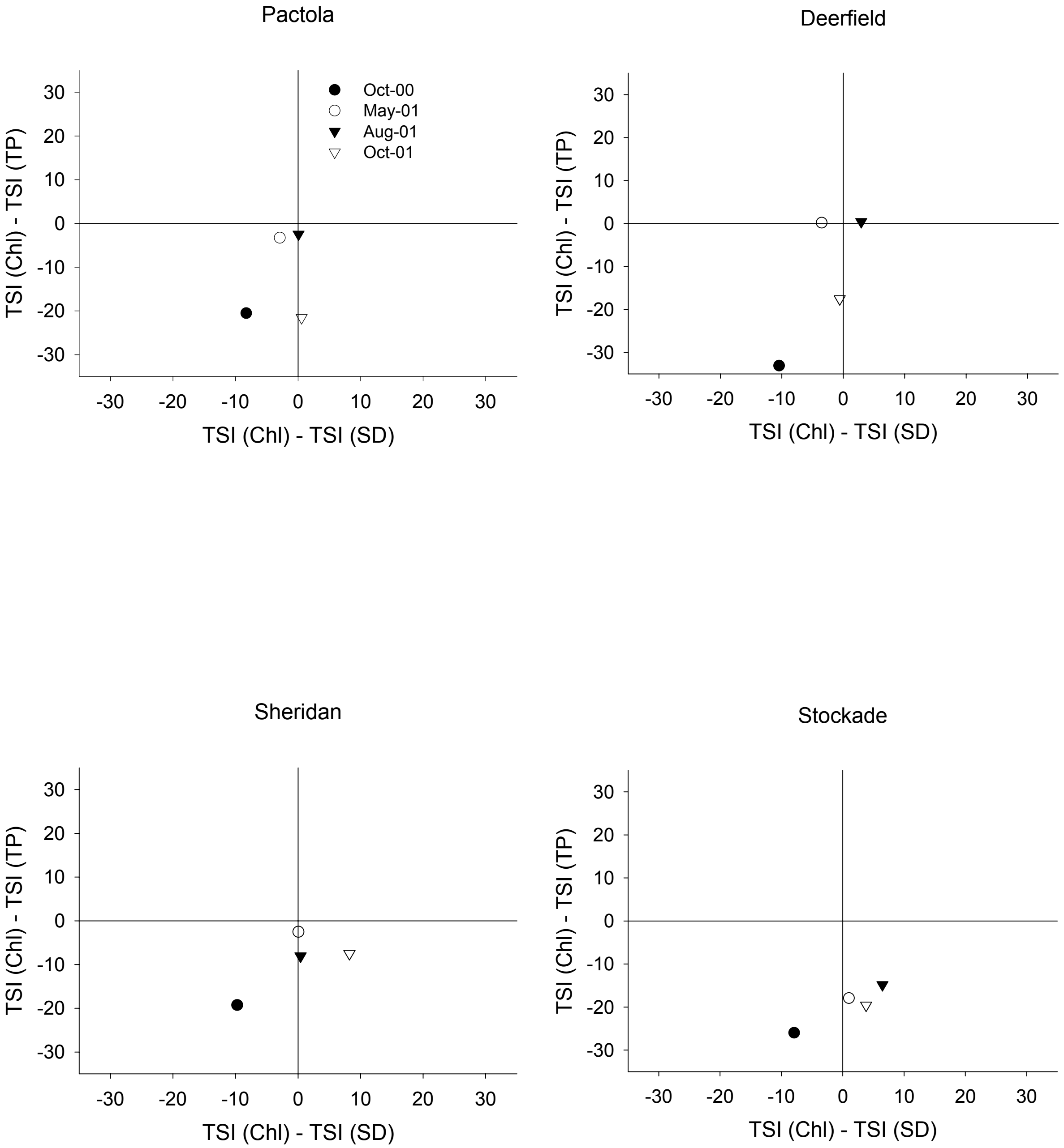
particles. Patterns in seasonal TSI relationships were generally similar among Pactola, Deerfield and Sheridan reservoirs (Figure 6); in spring and summer months, water transparency in these reservoirs was reasonably well-predicted by algal biomass. However, in autumn months (October), factors other than phosphorus-limited algal biomass appear to influence water transparency in Black Hills reservoirs. In autumn 2000, for example, water transparency was generally lower than that predicted by algal biomass indicating that non-algal turbidity can affect water transparency in Black Hills reservoirs. In Stockade Reservoir, seasonal patterns in TSI scores reveal that factors other than phosphorus limitation may influence algal abundance and water transparency (Figure 6). In general, algal biomass was lower than predicted by total phosphorus concentration, indicating that zooplankton grazing, blue-green algae or, to a lesser extent, turbidity may influence seasonal TSI score.
In other reservoirs, we found little evidence that zooplankton grazing affected water transparency based on deviations in TSI scores.

External Phosphorus and Iron Inputs

Mean areal phosphorus inputs ranged from 0.53 mg P/m^2/d in Deerfield to 7.3 mg P/m^2/d in Stockade Reservoir (Table 5). Sheridan and Stockade reservoirs had appreciably higher external P loading rates than Pactola and Deerfield reservoirs (Table 5). The upper watersheds of Sheridan and Stockade reservoirs are characterized as some of the most developed in the Black Hills region (Black Hills Conservancy 1974), and may contribute to increased nutrient inputs from agricultural runoff, urbanization, etc.

Mean areal iron inputs varied appreciably among Black Hills reservoirs and ranged from 5.6 mg Fe/m^2/d in Deerfield to 132.4 mg Fe/m^2/d in Pactola Reservoir (Table 5). Areal iron inputs in Sheridan and Stockade reservoir averaged 67.9 and 120.5 mg Fe/m^2/d.

Reservoir phosphorus concentration was reasonably predicted from phosphorus loading rate (Figure 7). Comparison of observed and predicted values (i.e., percent difference) revealed that, on the average, the Dillon-Rigler model predicted reservoir nutrient levels within about 5%, although for individual reservoirs the percent



Pactola

Deerfield

Sheridan

Stockade

Figure 6. Seasonal deviations among TSI values for Pactola, Deerfield, Sheridan, and Stockade reservoirs.

Table 5. Mean tributary phosphorus (P) and iron (Fe) inputs measured from June 2001 through July 2001 for Pactola, Deerfield, Sheridan, and Stockade reservoirs. Values in parentheses represent 1 SE.

Reservoir	n	P Loading (mg P/m^2/d)	Fe Loading (mg Fe/m^2/d)
Pactola	8	1.31 (0.66)	132.40 (58.75)
Deerfield	8	0.53 (0.15)	5.55 (1.28)
Sheridan	8	4.78 (1.89)	67.89 (27.78)
Stockade	8	7.30 (4.56)	120.45 (85.03)

Table 6. Parameter values used to model phosphorus availability in Black Hills reservoirs. See text for details on the Dillon-Rigler model.

Reservoir	Areal annual P loading (mg P/m^2/y)[a]	Hydraulic residence time (y)	Mean depth (m)	Phosphorus retention (R)
Pactola	476.81	1.24	17.0	0.74
Deerfield	193.12	0.99	9.3	0.33
Sheridan	1745.90	0.56	9.0	0.73
Stockade	2664.51	0.22	4.8	0.41

[a] Note: Mass balance equation uses g P/m^2/y.

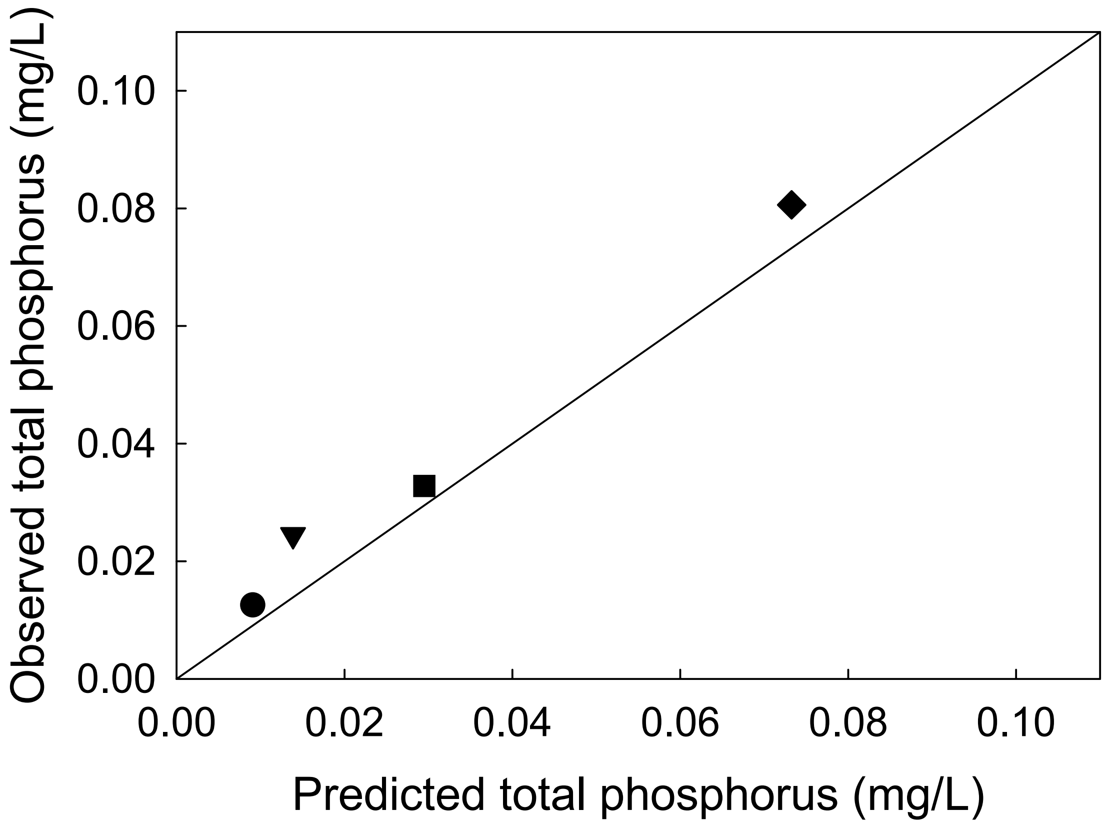


Figure 7. Comparison between observed and predicted total phosphorus concentration in Pactola, Deerfield, Sheridan, and Stockade reservoirs. Predicted phosphorus concentration was modeled using the Dillon-Rigler mass-balance model (see text for details). The diagonal line represents 1:1 correspondence between observed and predicted values.

difference between observed and predicted values was somewhat variable ranging from +6% in Sheridan to +50% in Deerfield Reservoir. Nonetheless, by combining information on P inputs, P retention and water residence time (Table 6), the Dillon-Rigler model should prove useful for modeling responses of reservoir nutrient levels to changes in external nutrient inputs.

Sediment Phosphorus and Iron Availability

Mean sediment phosphorus concentration differed significantly among reservoirs (ANOVA, df=3, F=7.79; P=0.003) and ranged from 0.7 mg P/g in Deerfield Reservoir to 1.8 mg P/g in Stockade Reservoir (Figure 8). Sediment P was significantly higher in Stockade Reservoir than in other Black Hills reservoirs. Pactola, the most oligotrophic reservoir in the Black Hills, had relatively high sediment phosphorus concentrations, second only to Stockade Reservoir. Bivariate plots of mean sediment P versus mean water column P, however, revealed that sediment phosphorus, by itself, was a poor predictor of reservoir nutrient concentration (correlation analysis, r=0.60, P=0.22; Figure 9).
Mean sediment iron concentration also varied among reservoirs (ANOVA, df=3, F=16.18, P<0.0001) and was significantly higher in Pactola reservoir than in other reservoirs (Figure 10). In general, sediment Fe concentrations in Black Hills reservoirs corresponded to areal Fe inputs (see Table 5). Because Pactola Reservoir had relatively high sediment Fe concentrations (Figure 10), the ratio of sediment P-to-Fe was appreciably lower in Pactola than in other Black Hills reservoirs (Figure 11). Moreover, mean phosphorus concentration in Black Hills reservoirs was positively related to sediment P:Fe ratio (Figure 12).

Using stepwise multiple regression analysis, we evaluated effects of 1) P:Fe ratio,2) sediment P, 3) sediment Fe, 4) dissolved oxygen concentration and 5) redox potential on phosphorus concentration near the sediment-water interface (i.e., bottom water samples). Although redox potential varied little with dissolved oxygen level (as expected) we used this as a potential explanatory variable because at very low oxygen levels (i.e., near anoxia), redox potential declines precipitously in Black Hills reservoirs (Figure 13). Based on a multiple regression model, sediment P, sediment Fe and redox potential explained about 80%

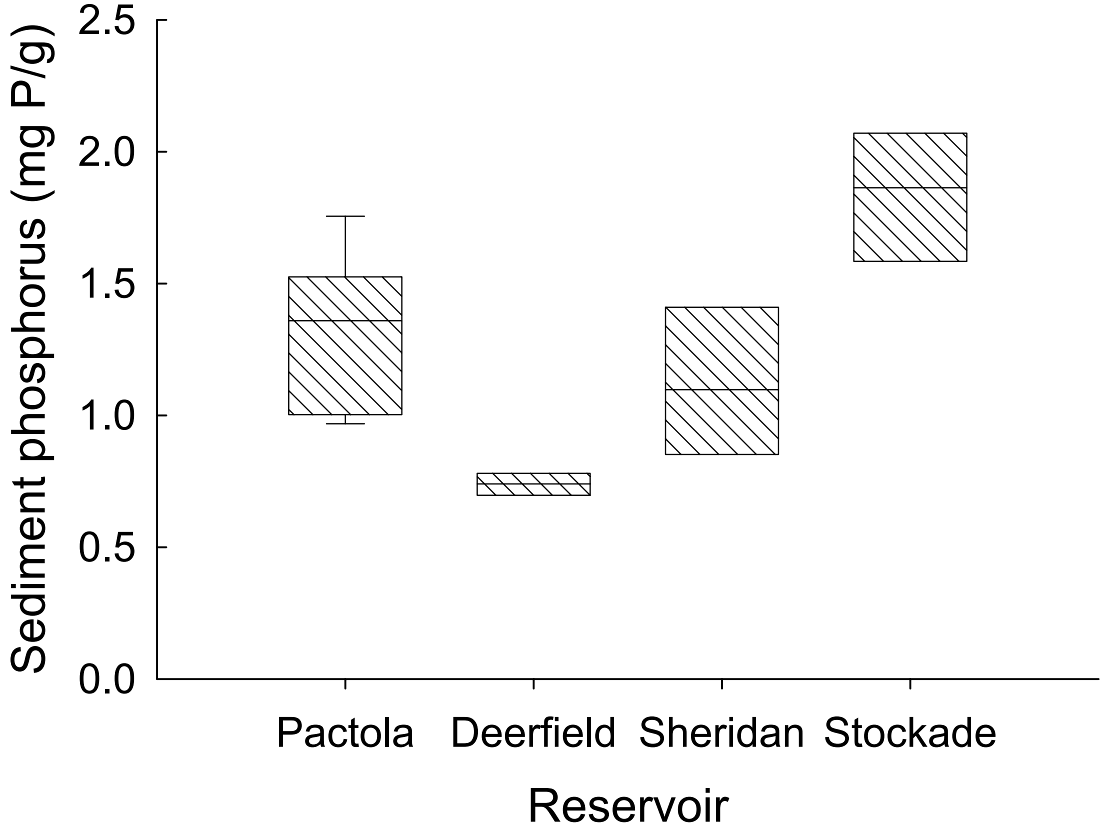


Figure 8. Sediment phosphorus values measured in Pactola, Deerfield, Sheridan, and Stockade reservoirs from October 2000 to October 2001. Horizontal bars in box plots represent medians; shaded area represents 25th and 75th percentiles and vertical bars represent 10th and 90th percentiles. Mean values with the same letter are not significantly different (Fisher's LSD, $P > 0.05$).

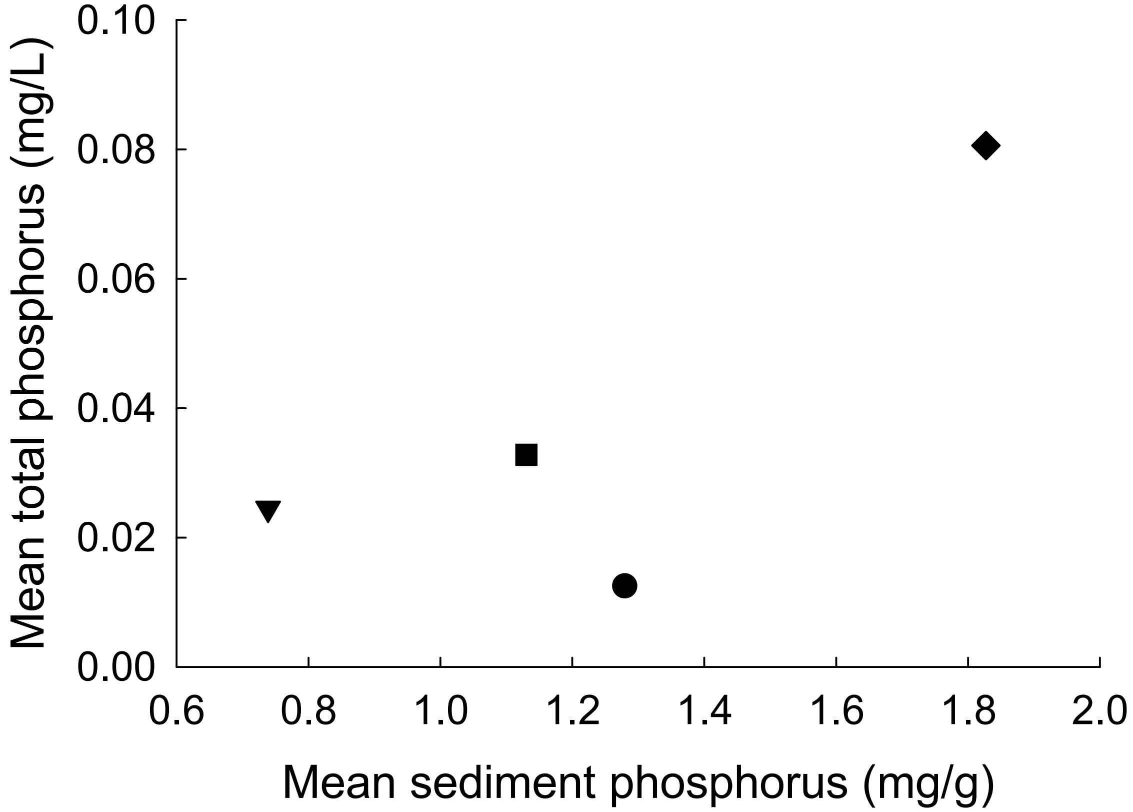


Figure 9. Mean water column phosphorus versus mean sediment phosphorus measured in Pactola, Deerfield, Sheridan, and Stockade reservoirs from October 2000 to October 2001. Relationship was not significant (correlation analysis, r=0.60, P= 0.22).

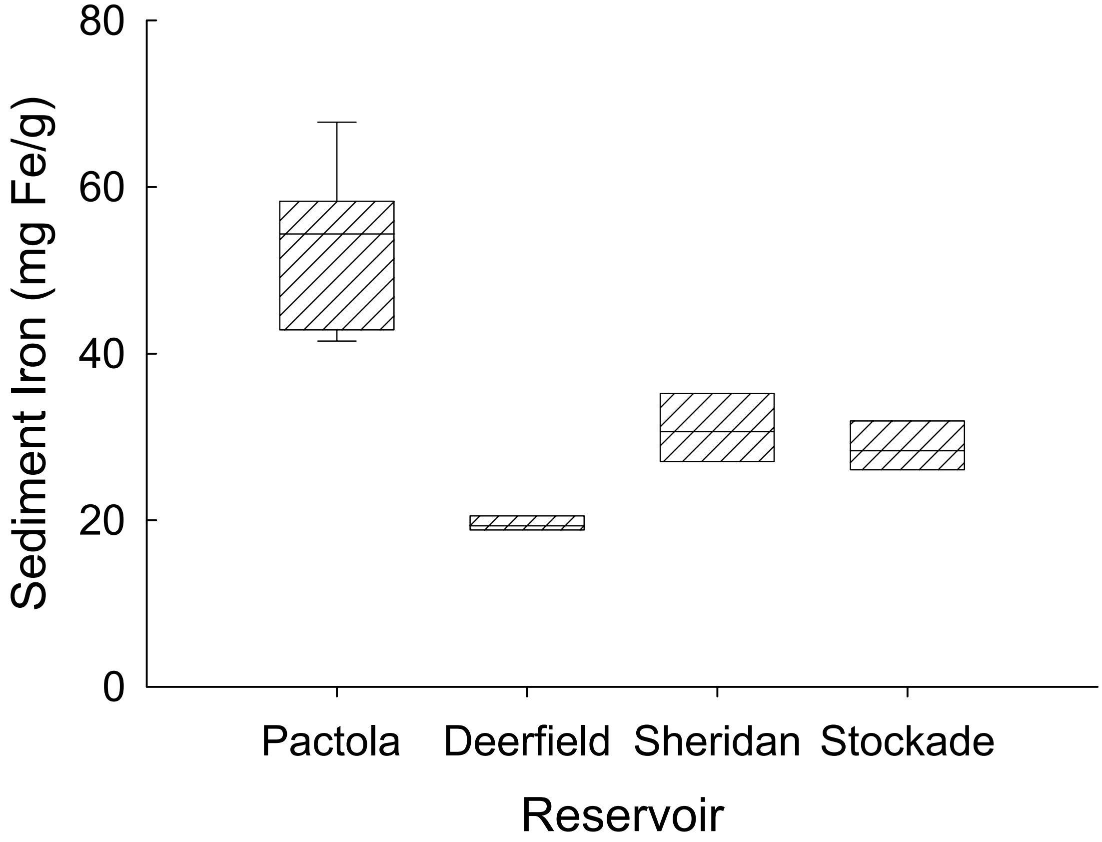


Figure 10. Sediment iron measurements in Pactola, Deerfield, Sheridan, and Stockade reservoirs from October 2000 to October 2001. Horizontal bars in box plots represent medians; shaded area represents 25th and 75th percentiles and vertical bars represent 10th and 90th percentiles. Mean values with the same letter are not significantly different (Fisher's LSD, P > 0.05).

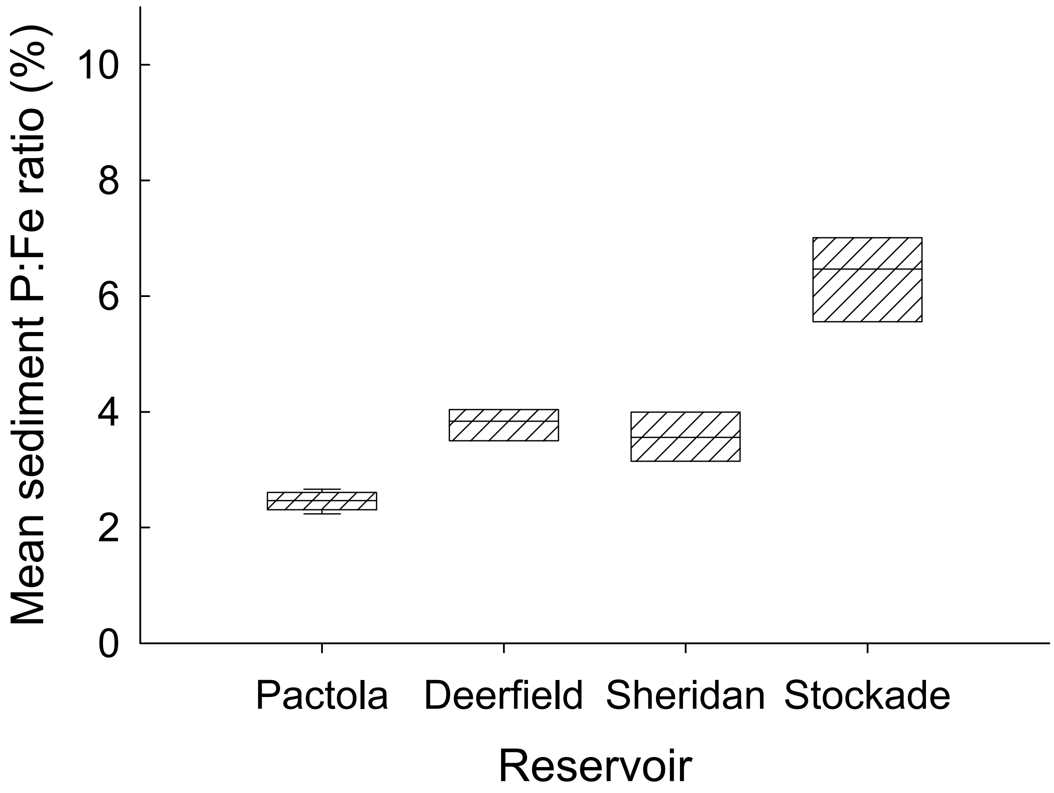


Figure 11. Sediment P:Fe ratios measured in Pactola, Deerfield, Sheridan, and Stockade reservoirs October 2000 to October 2001. Horizontal bars in box plots represent medians; shaded area represents 25th and 75th percentiles and vertical bars represent 10th and 90th percentiles. Mean values with the same letter are not significantly different (Fisher's LSD, P > 0.05).

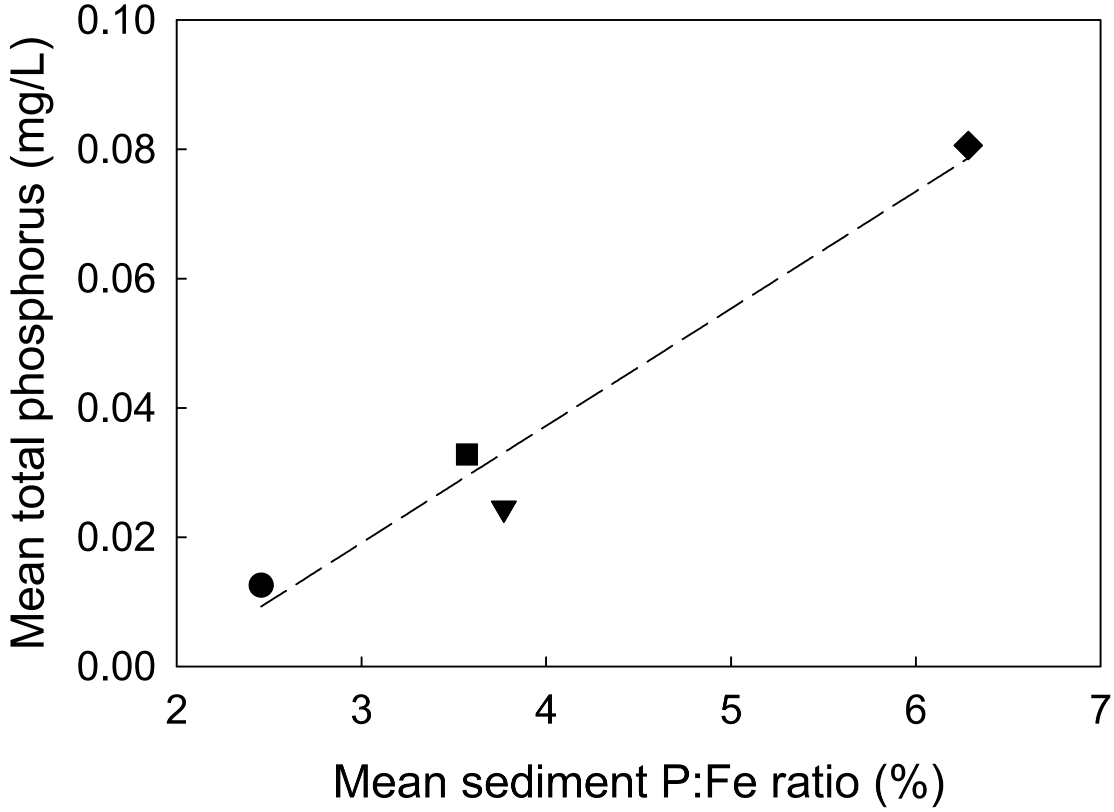


Figure 12. Relationship between mean water column phosphorus and mean sediment P:Fe ratio measured in Pactola, Deerfield, Sheridan, and Stockade reservoirs from October 2000 to October 2001. Total phosphorus (TP) can be predicted from P:Fe ratio as, TP= 0.181*(P:Fe) – 0.0353 (linear regression analysis; r2= 0.96, P= 0.02).

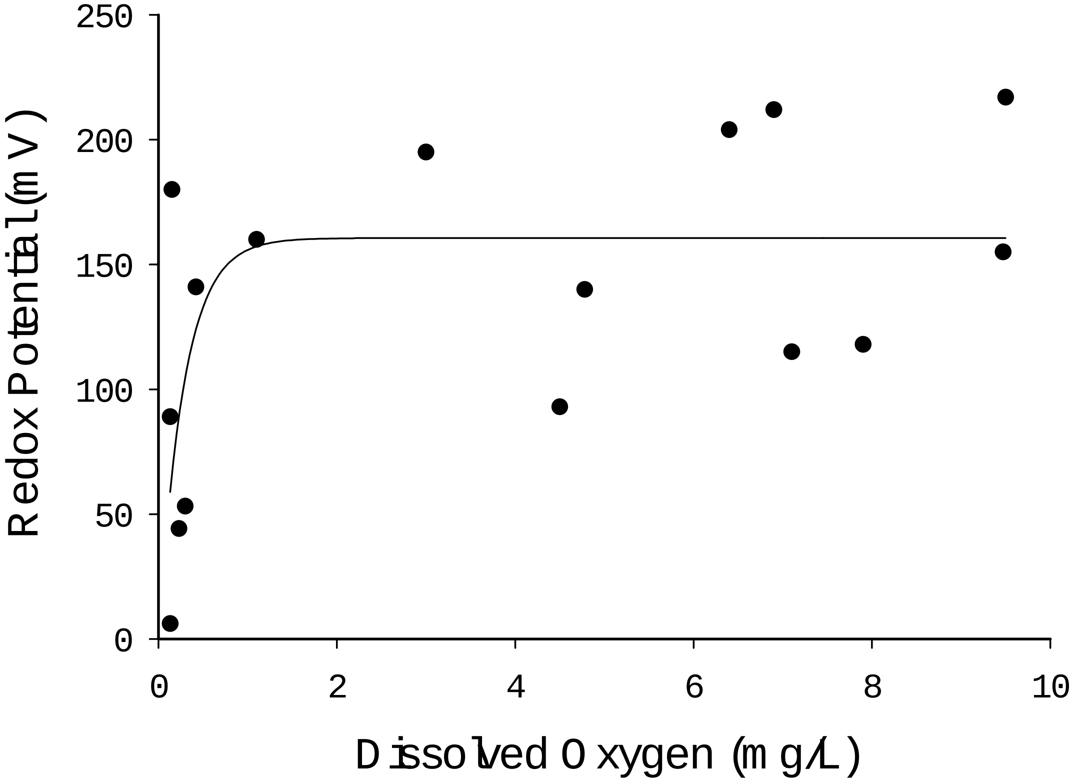


Figure 13. Relationship between redox potential and dissolved oxygen concentration in Black Hills reservoirs. The line was fitted using the equation, redox potential = 160.5(1-e-3.51*DO), r2=0.35, P=0.01.

of the variation in hypolimnetic phosphorus concentration (R^2=78%, P=0.0002). Because hypolimnetic phosphorus concentration was strongly correlated with phosphorus concentration in surface waters, this model may be useful for evaluating changes in reservoir nutrient levels resulting from changes in sediment P, sediment Fe or redox condition (Figure 14). Questions regarding changes in hypolimnetic dissolved oxygen concentration (see Figure 13), for example, could be incorporated into the model to evaluate potential impacts on reservoir nutrient concentration (Figure 15).

Zooplankton Composition and Size Structure

Mean total zooplankton density was lowest in Pactola Reservoir (51.4/L) and highest in Stockade Reservoir (187.7/L; Figure 16). Total zooplankton abundance in Sheridan and Deerfield reservoirs was similar at 103.8/L and 112.0/L (ANOVA, Tukey's HSD, P = 0.97). Zooplankton biomass was a good indicator of reservoir productivity, as mean summer algal biomass was positively correlated with mean summer zooplankton biomass in Black Hills reservoirs (Figure 17).

Zooplankton abundance differed appreciably across reservoirs (Figures 18 and 19); copepods were a dominant component of the zooplankton community in Pactola and Deerfield reservoirs, comprising about 60 percent of total zooplankton biomass (Figure 20). Although species richness was similar across reservoirs (number of taxa=9), species composition varied (Table 7); the cladoceran community in Pactola and Deerfield reservoirs was dominated by *Daphnia galeata mendotae*, whereas in Sheridan and Stockade, *Daphnia pulex* was the dominant grazer (Figure 21). *Daphnia pulex* is typically larger and often out competes *Daphnia galeata mendotae* for abundant food resources (Prazakova 1991). However, planktivorous fishes generally prefer *Daphnia pulex* because of their larger body size (Brooks and Dodson 1965; Cerny and Bytel 1991). Lower food availability (algal biomass) combined with increased abundance of pelagic, planktivorous fishes (e.g., salmonids) in Pactola and Deerfield reservoirs, may favor *D. galeata* over *D. pulex*, although this hypothesis is not definitive given a lack of information on zooplankton selectivity and consumption rates by reservoir fishes.

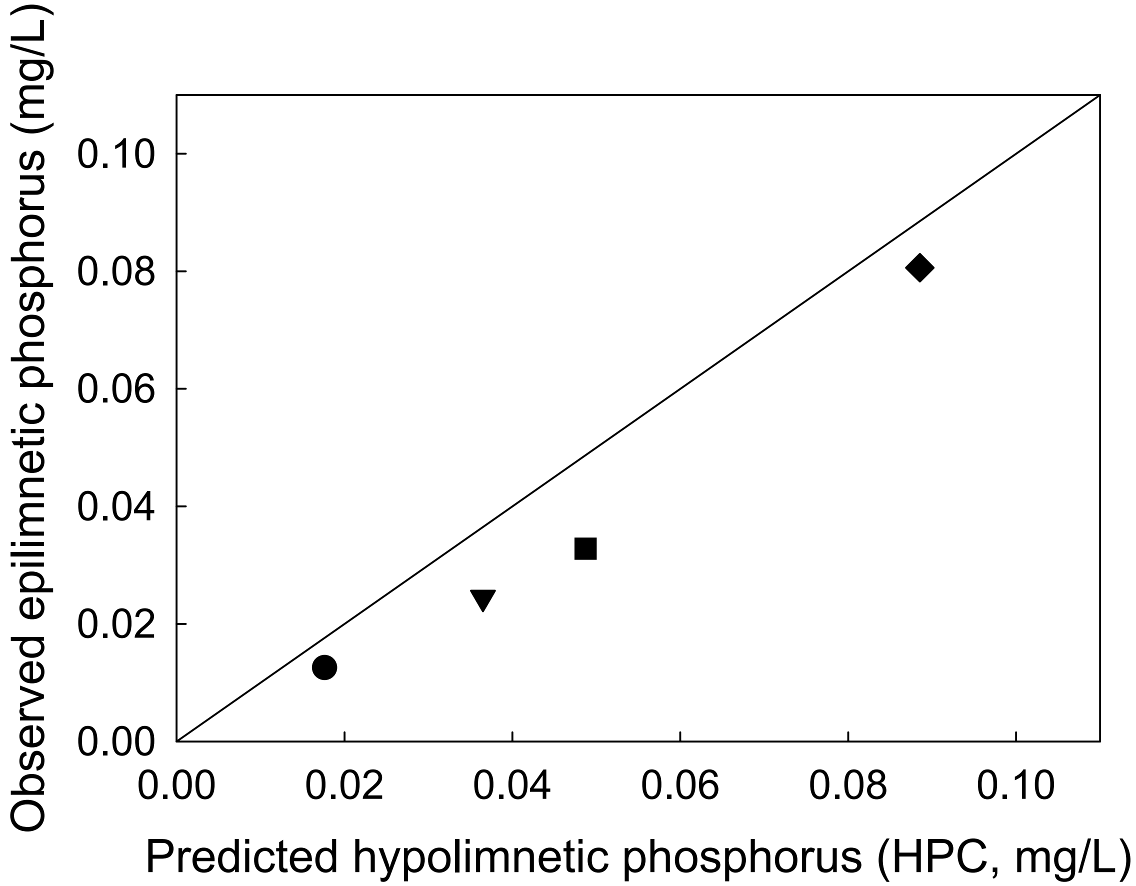


Figure 14. Relationship between epilimnetic phosphorus concentration and predicted hypolimnetic phosphorus concentration in Pactola, Deerfield, Sheridan, and Stockade reservoirs. Hypolimnetic phosphorus concentration (HPC) was predicted as, HPC = 0.0584 + 0.0633(sediment P) – 0.0013(sediment Fe) – 0.00034(ORP); multiple regression analysis, R2=0.78, P=0.0002. The diagonal line represents 1:1 correspondence.

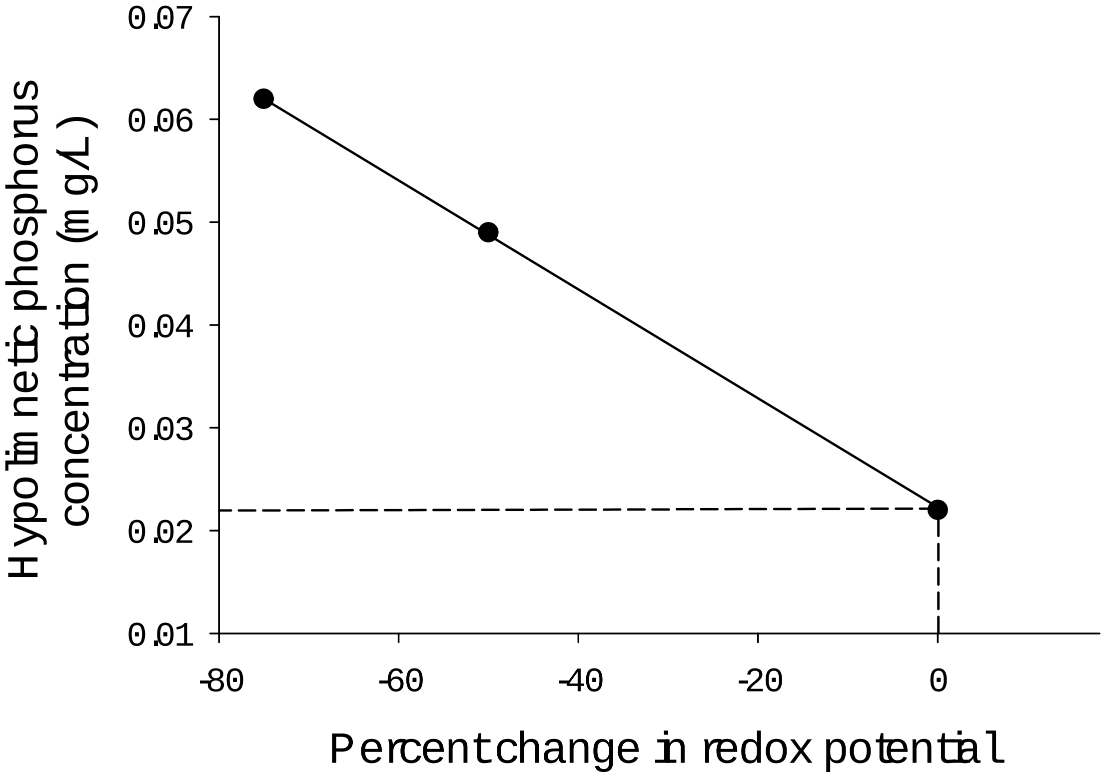


Figure 15. Model simulations showing effects of reduced redox potential on hypolimnetic phosphorus concentration for Pactola Reservoir. Dotted line represents observed condition (i.e., no change). Hypolimnetic phosphorus concentration was predicted from the equation given in Figure 14. Sediment phosphorus (1.4 mg/g) and sediment iron (55 mg/g) were held constant, and redox potential (155 mV) was reduced by 50 and 75%.

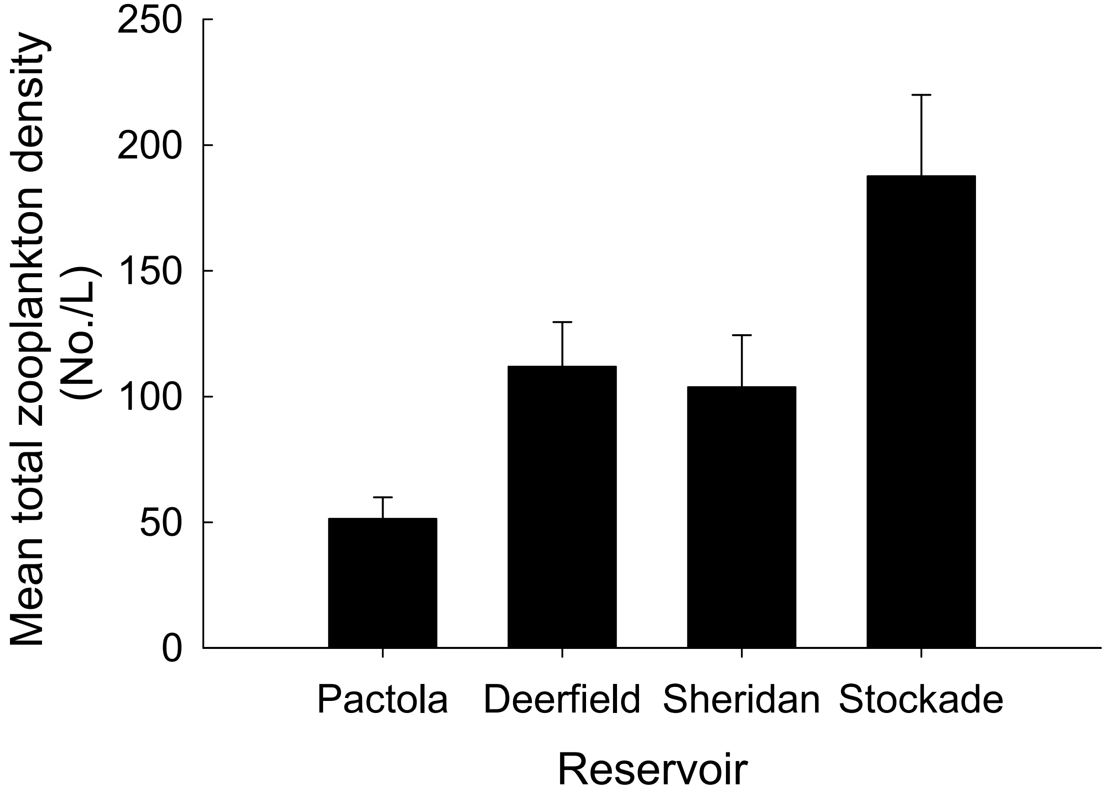


Figure 16. Mean total zooplankton abundance for Pactola, Deerfield, Sheridan, and Stockade reservoirs from October 2000 to October 2001. Means with the same letter are not significantly different (Tukey's multiple comparison test, P > 0.05). Vertical bars represent 1 S.E.

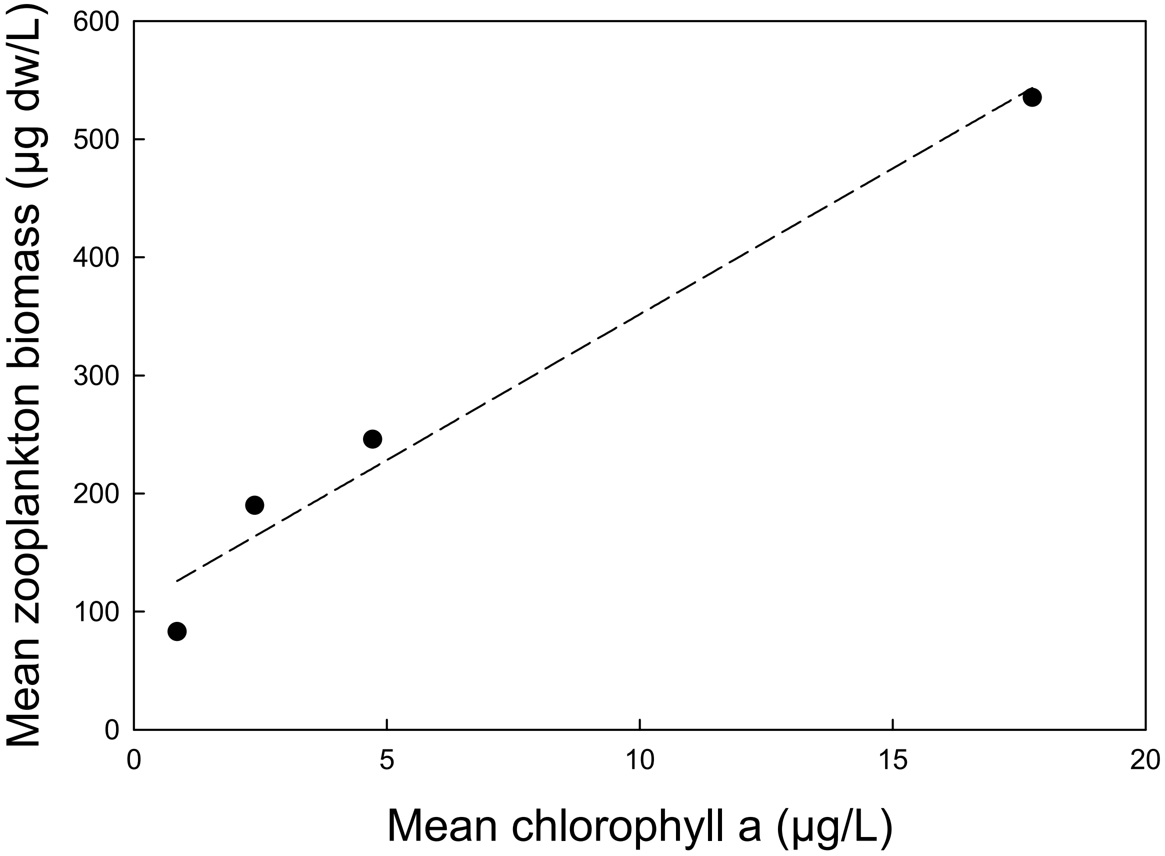


Figure 17. Relationship between mean total zooplankton biomass and mean algal biomass in Black Hills reservoirs. Values represent data collected in August 2001. Pearson's correlation coefficient and corresponding P-value are given.

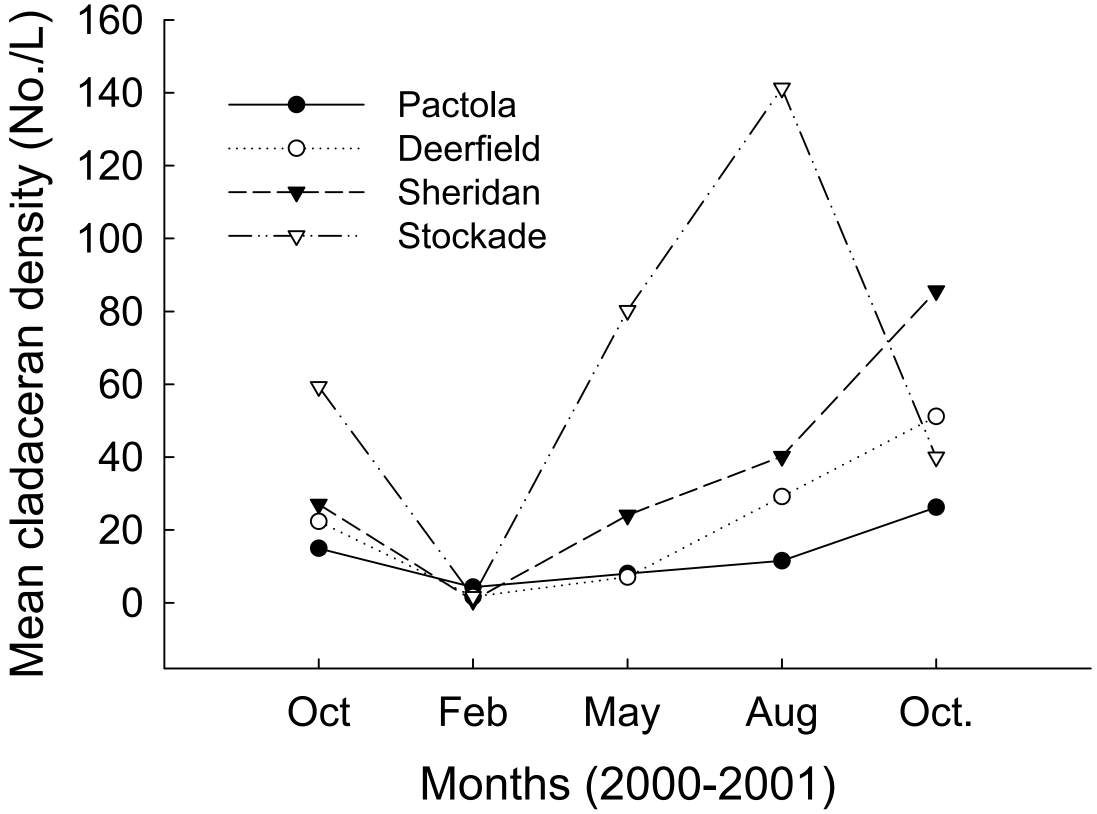


Figure 18. Seasonal cladoceran density in Pactola, Deerfield, Sheridan, and Stockade reservoirs from October 2000 to October 2001.

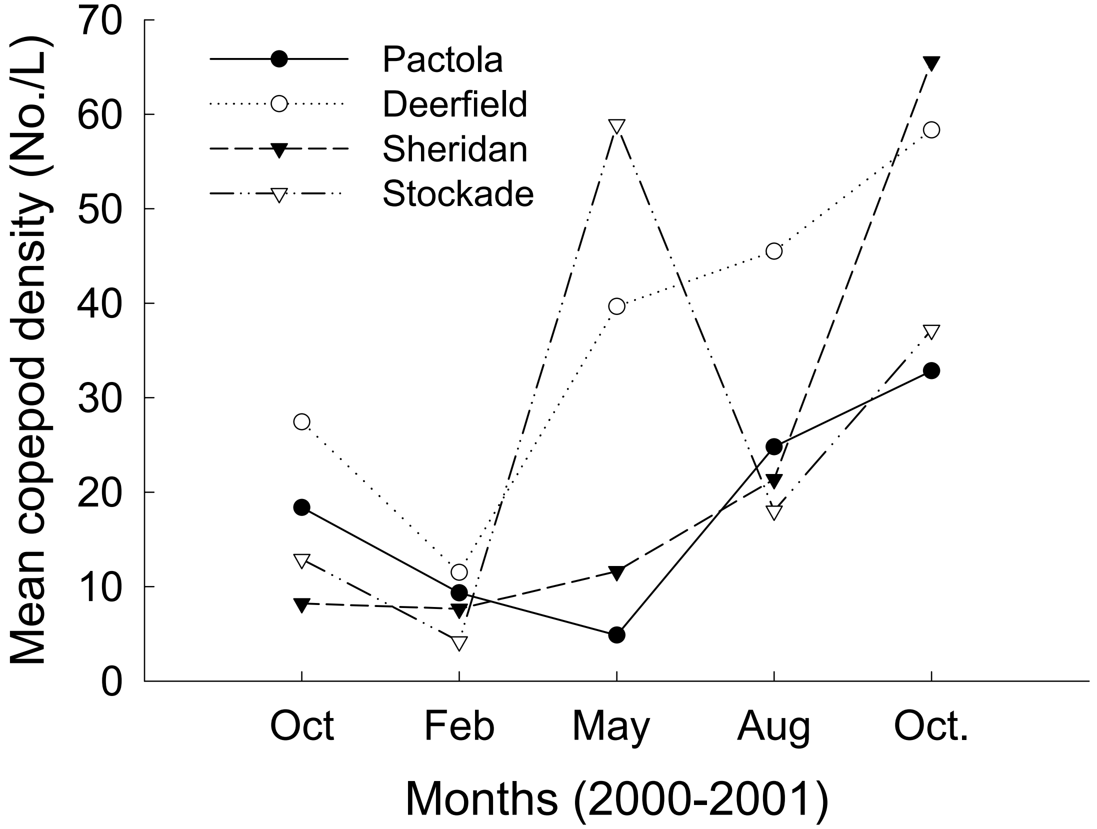


Figure 19. Seasonal copepod density in Pactola, Deerfield, Sheridan, and Stockade reservoirs from October 2000 to October 2001.

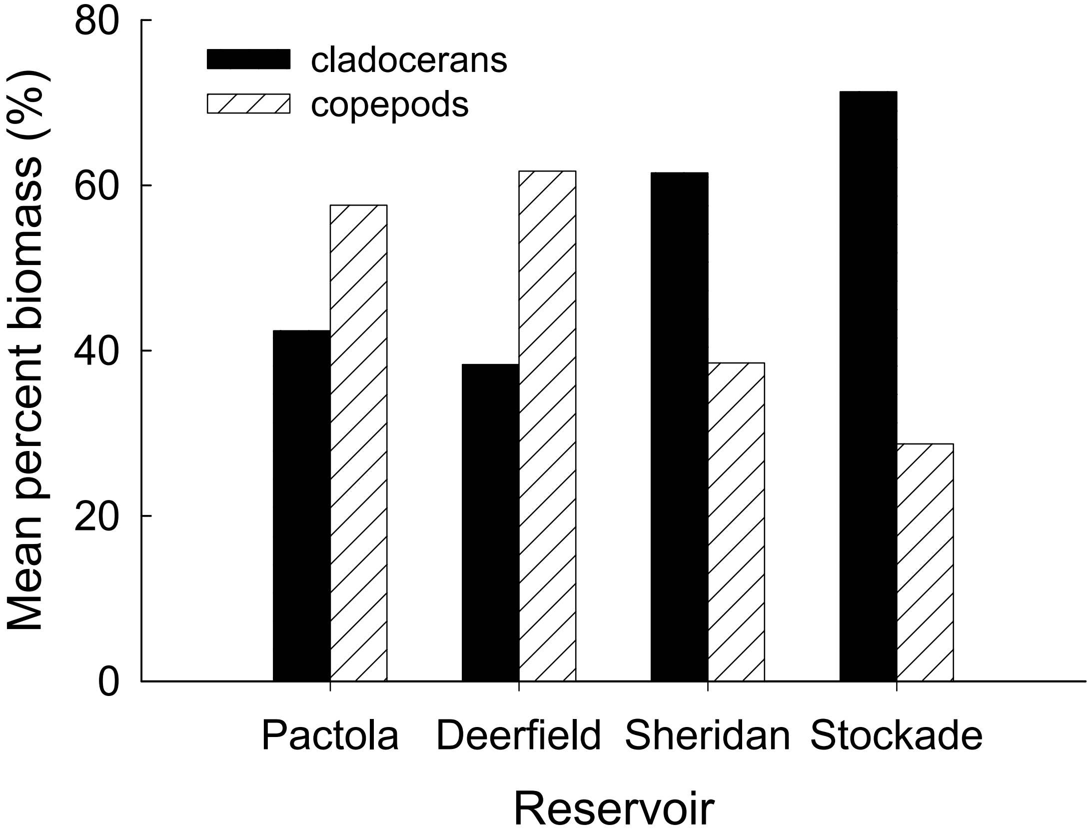


Figure 20. Mean percent cladoceran and copepod biomass in Pactola, Deerfield, Sheridan, and Stockade reservoirs from October 2000 to October 2001. For each taxa (i.e., cladaceran or copepods), values with the same letter are not significantly different (Tukey's multiple comparison test, $P > 0.05$).

Table 7. Summary of zooplankton species composition in Pactola, Deerfield, Sheridan, and Stockade reservoirs (October 2000 to October 2001). 'X'= present, '---' = absent.

Species	Pactola	Deerfield	Sheridan	Stockade
Daphnia g. mendotae	X	X	X	X
Daphnia pulex	X	---	X	X
Ceriodaphnia lacustris	X	X	X	X
Alona costata	X	X	X	X
Camtocercus macrurus	---	X	---	---
Bosmina longirostris	X	X	X	X
Chydorus sphaericus	X	X	X	X
Diaptomus siciloides	X	X	X	X
Cyclops bicuspidatus	X	X	X	X

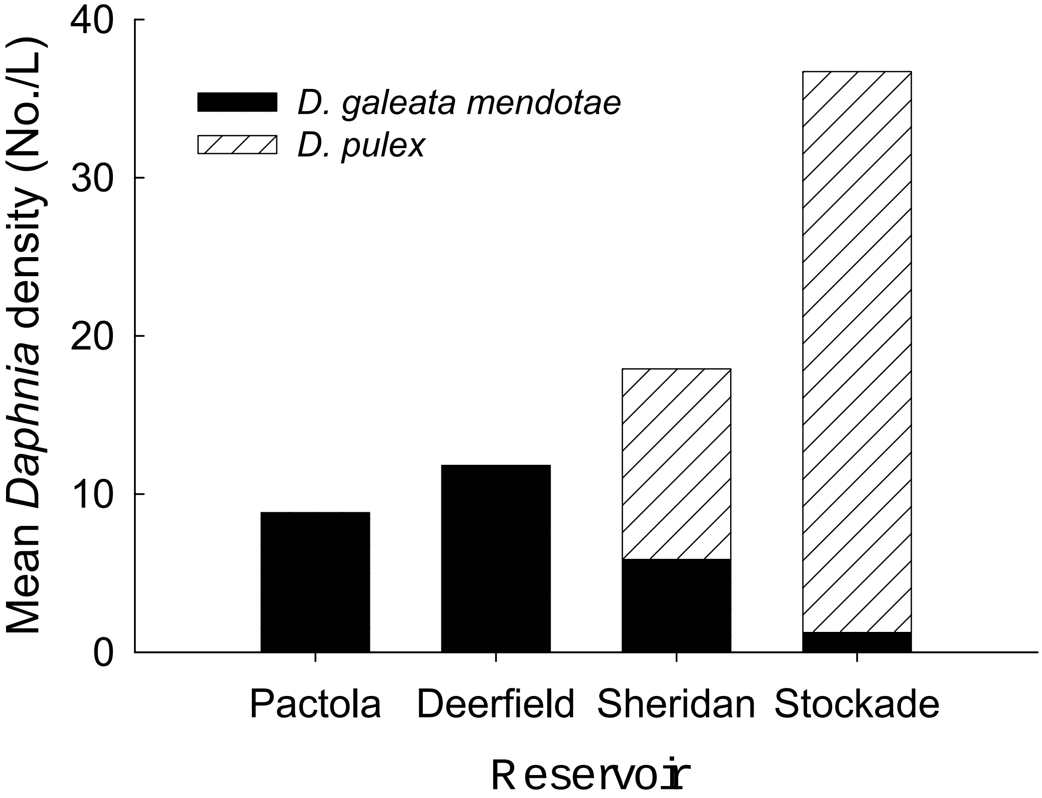


Figure 21. Mean annual abundance of D. galeata mendotae and D. pulex for Pactola, Deerfield, Sheridan, and Stockade reservoirs from October 2000 to October 2001.

CONCLUSION & RECOMMENDATIONS

Mechanisms regulating sediment phosphorus release have important implications for reservoir productivity. The potential for anoxic conditions was most pronounced following summer thermal stratification (i.e., August) in Deerfield, Sheridan, and Stockade reservoirs. By altering redox potential near the sediment-water interface, hypolimnetic anoxia can contribute to increased sediment P release. In contrast, the hypolimnion of Pactola Reservoir remains well oxygenated throughout the year providing an effective ‘barrier’ to sediment phosphorus release. The observation that sediment phosphorus levels were relatively high in Pactola Reservoir illustrates the importance of aerobic conditions as a buffer to sediment phosphorus release. Sediment phosphorus storage, however, could have important implications for future reservoir productivity. If the hypolimnion of Pactola Reservoir was to become anoxic in summer months, it is likely that internal phosphorus loading would contribute to increased phosphorus availability in the reservoir (see Figure 15).

The models evaluated here should prove useful for future water quality monitoring in Black Hills reservoirs. Dissolved oxygen concentration, redox potential, and phosphorus concentration are routinely collected by State and/or Federal agencies and can be used to assess (i.e., predict) potential changes in reservoir nutrient concentrations affecting productivity of Black Hills reservoirs.

REFERENCES

Black Hills Conservancy Sub-District, 1974. Water quality management plan for the Black Hills region. Publication #7, Appendix A Lake Management Data.

Bostrom, B., M. Jansson, and C. Forsberg. 1982. Phosphorus release from lake sediments. Arch. Hydrobiol. Beih. Ergebn. Limnol. 18: 5-59.

Brooks, J.L. and S.I. Dodson. 1965. Predation, body size, and composition of zooplankton. Science. 150: 28-35.

Carlson, R. E. 1977. A trophic state index for lakes. Limnol. Oceanogr. 22: 361-369.

Carlson, R. E. 1992. Expanding the trophic state concept to identify non-nutrient limited lakes and reservoirs. In Proceedings of a National Conference on Enhancing the States' Lake Management Programs. Monitoring and Lake Impact Assessment. Chicago. Pp. 59-71.

Carpenter, S.R., J.F. Kitchell, and J.R. Hodgson. 1985. Cascading trophic interactions and lake productivity. Bioscience 35: 634-639.

Cerny, M. and J. Bytel. 1991. Density and size distribution of *Daphnia* populations at different fish predation levels. Hydrobiologia. 225: 199-208.

Dillon, P.J. and F. H. Rigler. 1974. A test of a simple nutrient budget model predicting the phosphorus concentration in lake water. Journal Fish. Res. Board of Canada. 31: 1771-1778.

Dumont, H.J., I. Van de Velde, S. Dumont. 1975. The dry weight estimate of biomass in a selection of Cladocera, Copepoda and Rotifera from the plankton, periphyton and benthos of continental waters. Oecologia 19: 75-97.

German, D. R. 1997. South Dakota Lake Protection Water Quality Report. Water Resources Institute, South Dakota State University. 30 pp.

Jensen, J. P., Kristensen, P., Jeppesen, E. and Skytthe, A. 1992. Iron phosphorus ratio in surface sediment as an indicator of phosphate release from aerobic sediments in shallow lakes. Hydrobiologia 235-236:731-743.

Mueller, D. 1982. Mass balance model estimation of phosphorus concentrations in reservoirs. Water Resources Bulletin 18: 377-382.

Pennak, R.W. 1989. Freshwater invertebrates of the United States, 3rd Edition. John Wiley and Sons, New York, NY.

Prazakova, M. 1991. Impact of fishery management on Cladoceran populations. Hydrobiologia 225: 209-216.

SAS Institute Inc., SAS® Procedures Guide, Version 8, Cary, NC; SAS Institute Inc., 1999.

Scheffer, M. 1998. Ecology of Shallow Lakes. Chapman & Hall. New York. 357 pp.

Sondergaard, M., P. Kristensen, and E. Jeppesen. 1993. Eight years of internal phosphorus loading and changes in the sediment phosphorus profile of Lake Sobygaard, Denmark. Hydrobiologia 253: 345-356.

Van der Molen, D. and P. C. M. Boers. 1994. The influence of internal loading on phosphorus concentration in shallow lakes before and after reduction of the external loading. Hydrobiologia 275/276: 379-389.

Wetzel, R. G. 2001. Limnology, 3rd Edition. Acad

Alternative Conservation Practices to Improve Soil and Water Quality

Basic Information

Title:	Alternative Conservation Practices to Improve Soil and Water Quality
Project Number:	2001SD1941B
Start Date:	3/1/2001
End Date:	2/28/2003
Funding Source:	104B
Congressional District:	First
Research Category:	Not Applicable
Focus Category:	Conservation, Water Quality, Agriculture
Descriptors:	Agricultural Waterways, Subsurfae Drainage, Water Quality, Conservation
Principal Investigators:	Hal D. Werner, Alan R. Bender, Todd T. Trooien

Publication

1. Kathol, John. 2002. Using a Precipitation-Runoff Model to Predict Runoff for Frequency Based Storms. South Dakota State University Agricultural and Biosystems Engineering Special Topics Course #795, Brookings, South Dakota.

Abstract

The overall goal of the project was to monitor water quantity and quality discharges from small agricultural watersheds and compare results to the practices used on the watershed. Section 104 funds provided for operation, labor, and some equipment. Matching funds were obtained from the SD Corn Utilization Council (SDCUC). Monitoring equipment was installed on three waterways – one with a grassed waterway together with drain tile, one with drain tile but without grass, and one without tile or grass. Water quality samples were collected from tile discharge in 2001 and 2002. No runoff events were recorded in 2001. Runoff was measured on two of the watersheds in 2002. Results indicate that practices such as grassed waterways and subsurface tile drainage can reduce surface runoff from small agricultural watersheds in Eastern South Dakota.

Field installation and data collection

Waterways were selected to provide a range of practices but still be somewhat similar. Three cooperators were selected in cooperation with the SDCUC and the Farm Bureau. All watershed sites were in Moody County in Eastern South Dakota. Topographic maps were completed at all three sites using GPS survey equipment. All watersheds were planted to row crops. A 31-acre watershed with a grassed waterway and subsurface drainage was selected northwest of Flandreau, SD. The other two watersheds were southeast of Flandreau and were about 3000 feet apart. The second watershed was 33 acres and had subsurface drainage but no grassed waterway. The final watershed was 46 acres with neither grass nor subsurface drainage. Some small linear wetlands were embedded in the waterway.

Four automatic water samplers were purchased with three having bubbler options to provide water flow rate in addition to collecting water quality samples. H-flumes were constructed complete with approach sections and bubbler wells. These were installed at the outlet of each waterway during late June and early July, 2001, along with a continuous recording rain gage. A sampler collected tile outflow from the grassed waterway in 2001. In 2002 another sampler was loaned to the project so that tile outflow could be sampled at both sites that had tile.

The watershed with the tile and grass waterway had been recently reshaped, reseeded, and tile installed in 2000. Figure 1 is a photo of the flume and sampler being installed at the outlet of the waterway. A second sampler was installed at this site to collect water quality samples from the tile outflow. Figures A1 and A4 are aerial pictures and topographic maps, respectively, of the watershed area. General soil types were Moody silty clay loam and Houdek clay loam with Davison-Crossplain silt loams in the waterway areas.

The site having the waterway with tile drainage but no grass had been cropped for many years without any visible erosion in the waterway. The waterway had very flat side slopes with no clearly defined channel. Figure 2 is a picture of the waterway outlet and sampling equipment. Figures A2 and A5 are aerial pictures and topographic maps, respectively, of the watershed area. An established tile line was underneath the waterway. Soils in this watershed were predominantly Moody silty clay loam with some Wakonda-Chancellor silty clay loams.

Figure 2 - Installation of sampling equipment on tile/grass waterway.

Figure 1 - Installation of sampling equipment on tile-only wterway.

The third watershed included a waterway with neither grass nor tile drainage. Figures A3 and A6 are aerial pictures and topographic maps, respectively, of the watershed area. Embedded wetlands existed in the waterway. Soils were Moody-Trent and Moody silty clay loams with Wakonda-Chancellor silty clay loams through the waterway areas.

Water quality samples were collected during runoff events and were analyzed at the Water Quality Lab at SDSU. Samples were tested for conductivity, nitrogen, and phosphorus. Table 2 is a summary of the water quality analysis from the tile outlet samples. Table 3 is a summary of the water quality analysis from the surface runoff samples.

In general, precipitation during the 2001 and 2002 summers was below normal. Table 1 gives the monthly precipitation for the two growing seasons recorded by the NWS observer at Flandreau, SD. In 2001 April and June precipitation was above normal. A significant rainfall/runoff event the middle of June came before the equipment was installed. After the samplers were installed in 2001, no significant runoff event occurred before the samplers were removed in October. A November rain/snow event created runoff but was not recorded. Three water samples were analyzed from the tile outlet at the grassed waterway site.

2002 precipitation was below normal except for August and October. Nine runoff events were recorded at the untreated waterway in April, May, June, August and October. Only two runoff events occurred at the grassed waterway, one in June and one in August. No runoff events occurred at the tile-only waterway. Water quality samples were analyzed from the tile outlets at each of the tiled waterways (Table 2).

Table 1 – Monthly growing season precipitation in inches at Flandreau, SD.

MONTH	**NORMAL**	**2001**	**2002**
April	2.22	7.84	1.52
May	3.00	2.57	1.91
June	3.84	5.07	3.67
July	3.37	1.65	0.74
August	3.06	0.36	7.93
September	2.55	2.33	0.76
October	2.05	1.00*	3.11
TOTAL	**20.09**	**18.72**	**19.64**

* Estimated from nearby station

Results

The three waterways in this project were similar in size and had similar soils, but were different in slope and runoff characteristics. No direct comparison was possible between the waterways. In fact, it would be very difficult to find waterways that would permit statistical comparisons. No runoff was measured from the tile-only waterway and only two significant runoff events occurred on the tile and grass waterway. The untreated waterway had numerous runoff events, some even with small rainfall totals. Tile drainage appeared to reduce the runoff potential with similar rainfall events.

Water quality samples were collected from the tile outflow beneath the grassed waterway on three dates in 2001 (Table 2). Tile flow was intermittent after the first week in July. Nitrate concentrations were consistent between 14 and 15 parts per million (ppm). Even though the concentration was above the drinking water standard of 10 ppm, it was near the concentration that is favorable for plant uptake of nitrogen. Total phosphorus was measured at 0.01 and 0.02 ppm where the detection limit was 0.01. Electrical conductivity of the effluent water was about 1000 micromhos/cm for the three samples.

In 2002 samples of the tile flow were collected at the tile outlets of the two waterways with tile drainage (Table 2). At the tile and grass waterway, nitrate concentrations were below 10 ppm except for the last sample which followed a 2.56 inch rainfall. Electrical conductivity decreased during the course of the season. At the tile-only waterway, nitrate levels were from 13 to 17 ppm except for the last sample in July which was about 12 ppm. Conductivity varied from about 850 to 1370 micromhos/cm. Phosphorus in tile effluent was not tested in 2002 because the levels were near the lower detection level in 2001. Phosphorus levels in surface runoff averaged more than 100 times the tile concentration. Tile flow was intermittent after the first week in July in 2002.

Table 2 – Water quality analysis of tile outflow samples.

	NITRATE	**TOTAL PHOSPHORUS**	**ELECTRICAL CONDUCTIVITY**
GRASS/TILE WATERWAY	ppm	ppm*	micromhos/cm
2001 YEAR			
6/23	14.73	0.01	990
6/29	14.90	0.01	1008
7/5	14.04	0.02	1023
2002 YEAR			
4/16	1.55		1774
5/4	5.26		1417
5/21	8.62		1098
6/28	19.95		869
TILE ONLY WATERWAY			
2002 YEAR			
5/27	15.67		1122
6/12	16.59		1166
6/23	16.13		1292
7/12	11.99		849
8.28	13.61		1339
10/7	13.00		1368

* Detection limit = 0.01 ppm

In 2001 no runoff occurred during the time that the samplers were installed. In 2002 surface runoff samples were collected during two rainfall/runoff events on the tile and grass waterway and seven events on the untreated waterway (Table 3). The a, b, and c samples were at different time intervals during the same event. At the tile/grass waterway, nitrate levels were below one ppm and conductivity was low. Total phosphorus was about 1.6 ppm and total Kjeldahl nitrogen was about four ppm. At the untreated waterway, nitrate concentrations of the samples did not exceed the drinking water standard and were highest during the June 8 event at about 8 ppm. Total Kjeldahl nitrogen ranged from about one ppm to over 35 ppm. Total phosphorus varied from less than one ppm to over 12 ppm. Both varied several fold within one runoff event.

Table 4 lists the runoff events when measurable runoff occurred on the two waterways in 2002. Only two runoff events occurred on the tile/grass watershed. No surface runoff occurred from the tile-only watershed even though rainfall events were similar on this watershed compared to the untreated watershed that was only 3000 ft away. Surface runoff from the untreated watershed occurred nine times with many other small flows not being measurable. At times a small continuous flow discharged from the watershed. Not all flow from the waterway was recorded because the diversion berms overtopped during some events and some flow bypassed the flume. The untreated waterway was prone to runoff even with small rainfall events as evidenced by the May 11 rainfall of 0.16 inches with about 5% running off.

Table 3 – Water quality analysis of surface water runoff in 2002.

	NITRATE	TKN*	TOTAL PHOSPHORUS	ELECTRICAL CONDUCTIVITY
GRASS/TILE WATERWAY	ppm	ppm	ppm	micromhos/cm
6/21a**	0.79	3.83	1.66	99
6/21b	0.90	4.26	1.61	66
8/21a	0.06	1.13	0.34	179
8/21b	0.02	1.16	0.27	69
UNTREATED WATERWAY				
4/16a	1.70	35.56	12.66	1032
4/16b	4.05	6.18	1.89	1084
4/21	3.17	9.19	2.81	1245
5/8	0.98	13.91	3.68	896
5/11	0.91	1.57	0.43	1412
6/3	2.50	2.52	0.46	1913
6/8a	1.81	10.41	3.80	867
6/8b	8.70	5.30	1.20	1472
6/8c	7.50	3.45	0.65	1577
8/6	2.14	7.28	2.40	383
8/21	1.52	6.25	1.88	343
10/4a	7.08	3.49	0.79	599
10/4b	4.19	2.39	0.65	715

* Total Kjeldahl Nitrogen

** letters indicate multiple samples during same event

Appendix B contains precipitation and runoff hydrographs for events at the watersheds. Additional data is included in the addendum report. Further study would be beneficial to evaluate more watersheds and more runoff-producing events. The impact of waterway practices and watershed management needs to be tested on different watersheds with different soils, topography, and management.

A detailed analysis of the watershed runoff characteristics is contained in the addendum report to this report. The addendum report outlines a procedure for calibration of the watershed using the HEC-HMS model and actual runoff data from the two watersheds that had runoff. Calibration of the model then allowed prediction of runoff resulting from standard design storms. Results of the modeling indicated that field practices and management change the runoff characteristics of watersheds. It is important to note that the calibration of the parameters for the watersheds returned values that did not necessarily match with values routinely used to predict runoff from small agricultural watersheds. For example, NRCS curve numbers typically used to predict runoff are much higher than those returned from the calibration. Calibration of specific watershed runoff characteristics may be necessary to accurately predict runoff from small agricultural watersheds in Eastern South Dakota.

Table 4 – Summary of runoff events in 2002.

DATE	PEAK RAINFALL INTENSITY	TOTAL RAINFALL	PEAK DISCHARGE	TOTAL RUNOFF VOLUME	PERCENT RUNOFF
	GRASS/TILE				
6/21	8 in/hr	2.56 in	1.41 cfs	7165 cfs	2.3 %
8/21	5.1 in/hr	2.26 in	0.97 cfs	2975 cfs	1.2 %
	UNTREATED				
4/16	4.0 in/hr	0.60 in	0.53 cfs	3201 cfs	3.2 %
4/21	0.2 in/hr	0.23 in	0.06 cfs	199 cfs	0.5 %
5/8	6.0 in/hr	0.63 in	0.45 cfs	1441 cfs	1.4 %
5/11	0.1 in/hr	0.16 in	0.04 cfs	1335 cfs	5.0 %
6/3	1.9 in/hr	0.97 in	0.44 cfs	3430 cfs	2.1 %
6/8	3.4 in/hr	0.97 in	0.47 cfs	9334 cfs	5.7 %
8/6	2.5 in/hr	2.41 in	2.18 cfs	17962 cfs	4.4 %
8/21	2.9 in/hr	3.25 in	1.35 cfs	29324 cfs	5.4 %
10/4	1.8 in/hr	2.31 in	0.85 cfs	27354 cfs	7.0 %

Results shown in Tables 3 and 4 indicate that water quality from runoff was better than had been anticipated and runoff totals were less than predicted, especially where good practices and management were used. Both subsurface tile and grassed waterways appear to reduce runoff and reduce nutrient levels in runoff.

The watershed sites have been used to train students, farmers and professionals. One masters level graduate student was trained on installation and data collection. He managed those activities during the second season. He also conducted much of the data analysis covered in this report and prepared the addendum report on the hydrologic modeling. Three undergraduate students also participated in the project through fabrication and installation of equipment, data collection, and analysis of data. Project field sites were visited and discussed as part of field trips for the senior level Natural Resource Engineering class at SDSU. Results will be used in class presentations and lab assignments. Several groups of farmers and resource professionals have toured the field sites. Information on the project was also presented at the SD Water and Soil Conference in March 2002.

Summary and Conclusions

Nitrate levels averaged lower in surface runoff samples than in tile outflow. Water quality samples from tile outflow collected over two summers ranged from less than two ppm to nearly 20 ppm. Nitrates in runoff water ranged up to 8.7 ppm. Average nitrate concentrations in tile outflow were not excessive. Good nitrogen management should be able to maintain average nitrogen concentrations at acceptable levels. Phosphorus levels in tile outflow were low at about the minimum detection level. Phosphorus concentrations in tile outflow should not pose any water quality risks.

Total phosphorus levels in the surface runoff were lower than expected ranging from less than one ppm to about 13 ppm. Only one sample was over 3.8 ppm. Average phosphorus levels were lower in the runoff water from the grassed waterway that had subsurface tile than in the untreated waterway.

TKN in the surface runoff was considerably higher than the nitrate nitrogen. Levels seemed to correlate with phosphorus levels. TKN levels were likely associated with organic material and sediment in the runoff water.

No runoff occurred in 2001 during the time that the samplers were installed in the waterways. Runoff was not measurable on the tile-only watershed even though rainfall events were essentially identical as the untreated watershed. In 2002 only two runoff events occurred on the watershed that had the grassed waterway accompanied by tile. Runoff was common in the untreated watershed and nine events were recorded when flow could be quantified. Runoff events on the untreated watershed were triggered with less than 0.2 inches of rainfall.

Observations of the untreated watershed in 2002 indicated crop productivity loss and restriction of field operations even with small rainfalls. This occurred during periods with less than normal rainfall. Runoff events produced erosion and sediment transport. The other two watersheds did not show similar problems. The subsurface tile drainage reduced the amount and severity of runoff from those watersheds. The watershed with the grassed waterway had steeper slopes and a higher risk of runoff (see the addendum report), but still had fewer runoff events, and the runoff had lower levels of contaminants than the waterway without tile.

Recommendations

The study should be continued on the watersheds, especially the two that had runoff in 2002, to document surface and tile runoff with different environmental conditions. Additional study should be done to document runoff conditions from a broader range of small agricultural watersheds. Finally, research is needed to be able to model the hydrology of small waterways that are common in Eastern South Dakota.

Appendix A

Aerial Maps and Topographic Maps of Watersheds

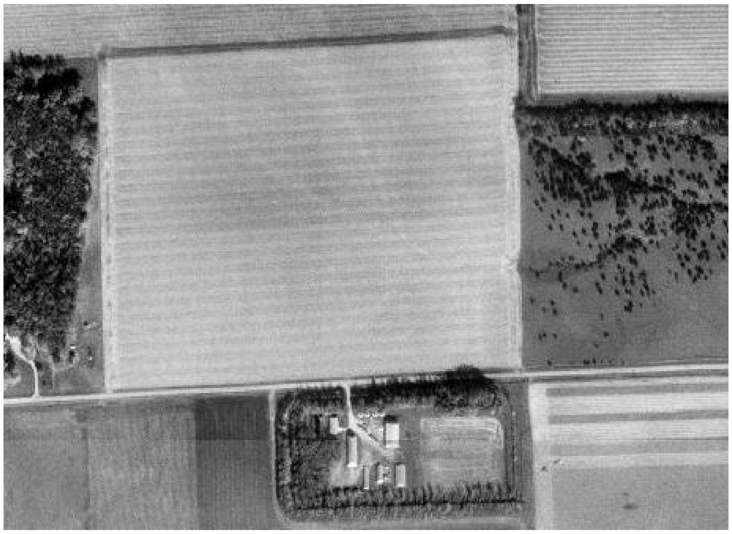


Figure A1 – Watershed with Grass and Tile Waterway.

Figure A2 – Watershed with Tile-Only Waterway.

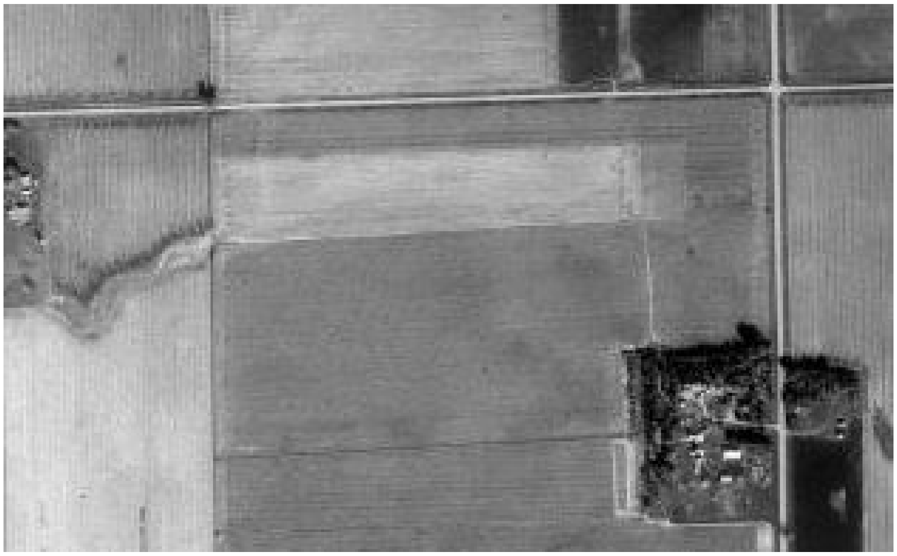


Figure A3 – Untreated Watershed.

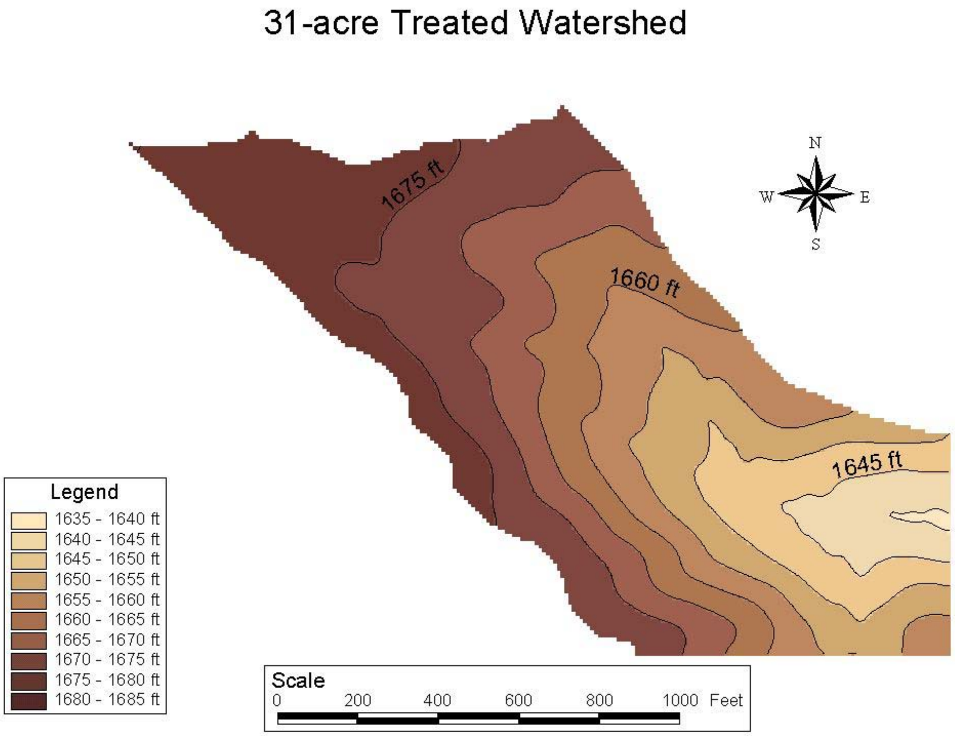


Figure A4 – Topographic Map of Grass/Tile Watershed.

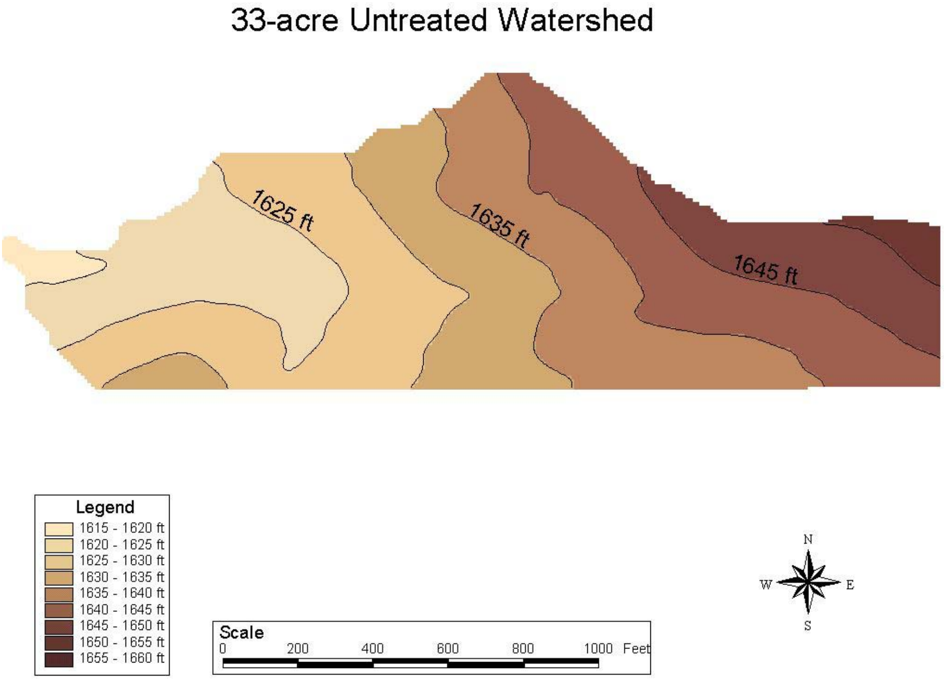


Figure A5 – Topographic Map of Watershed with Tile-Only Waterway.

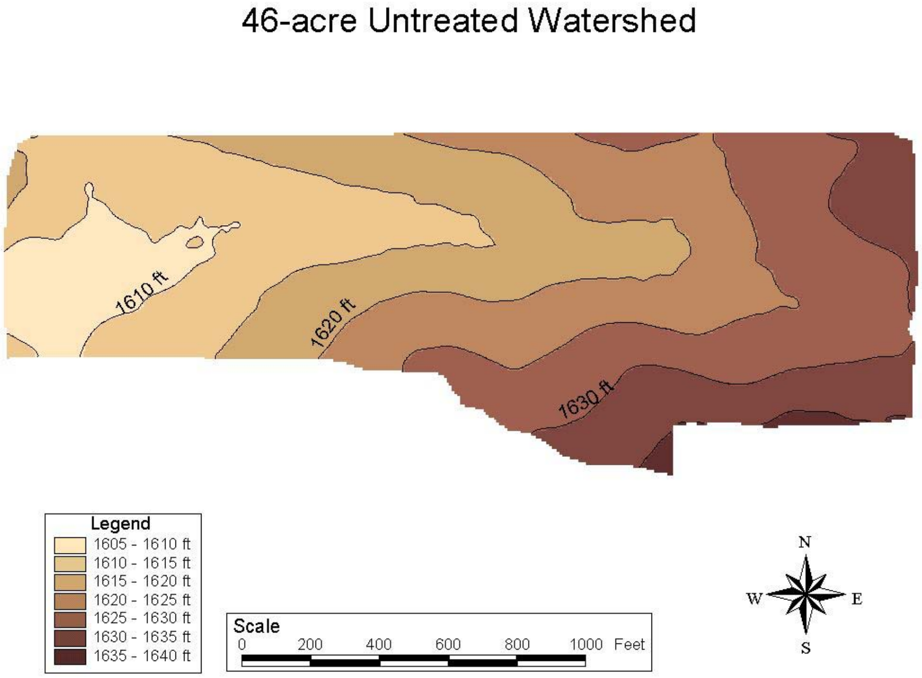
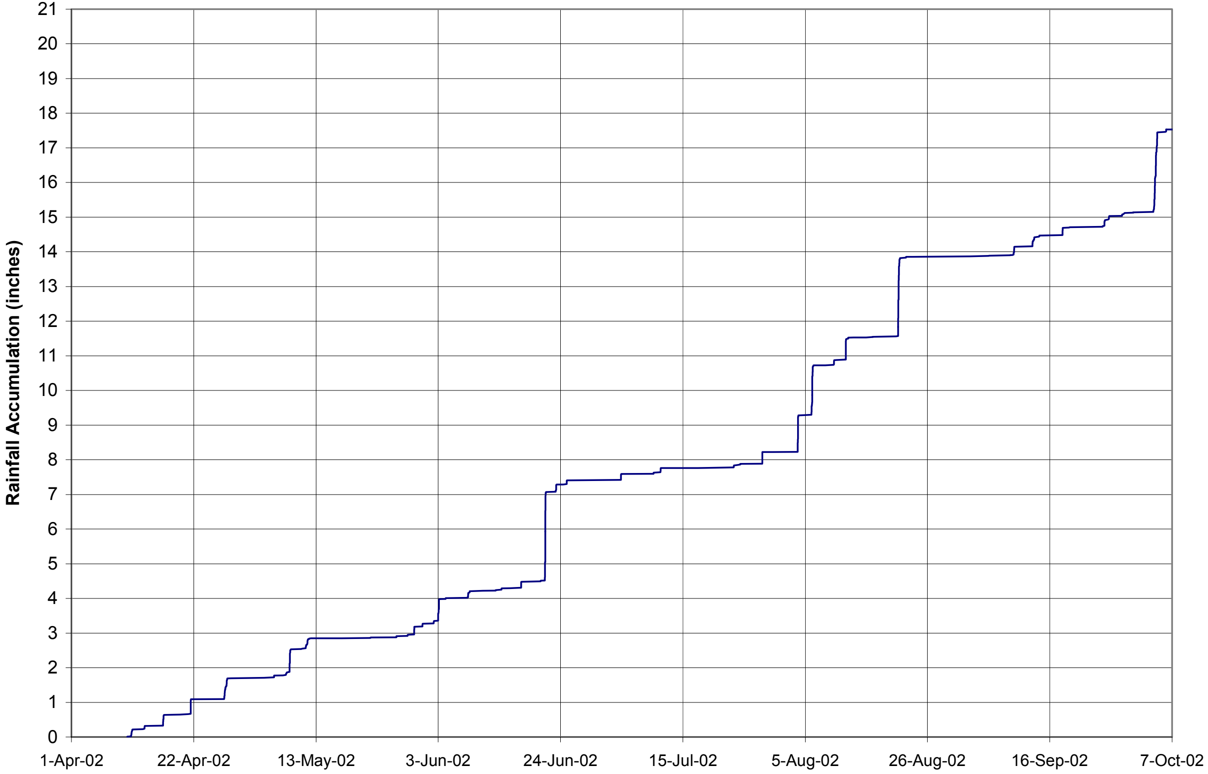


Figure A6 – Topographic Map of Untreated Watershed.

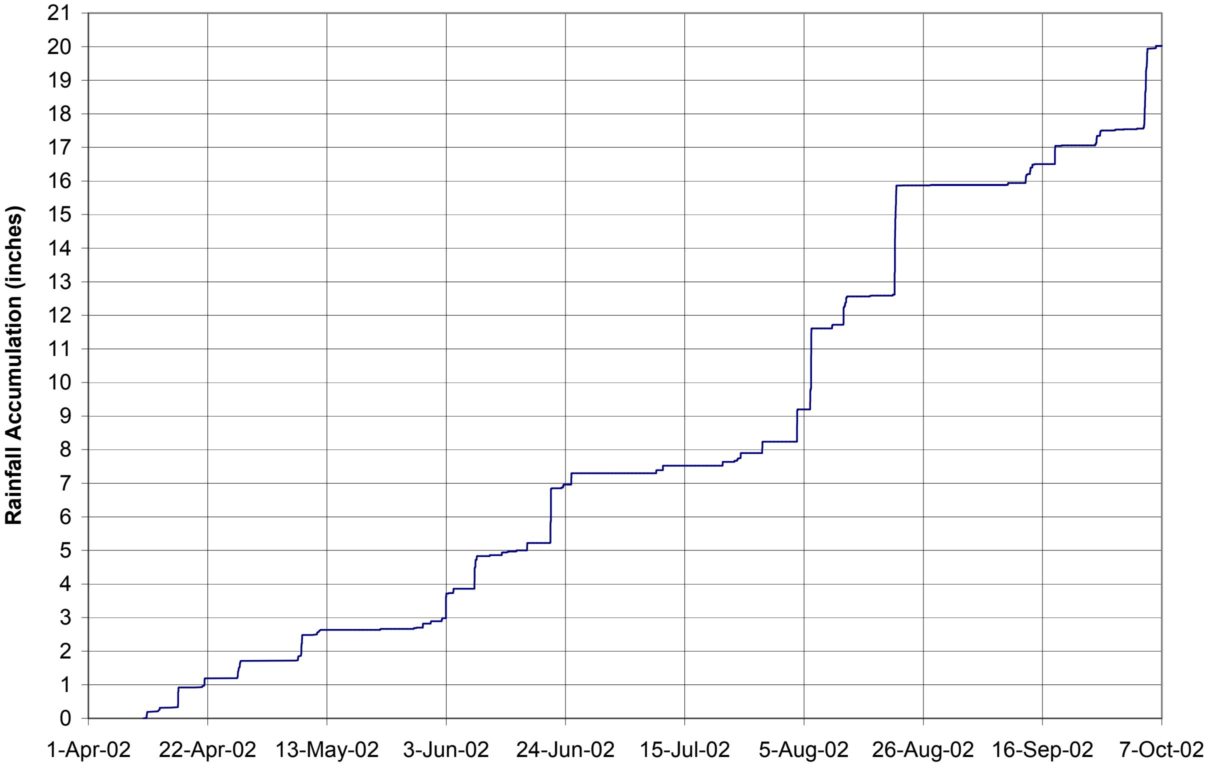
Appendix B

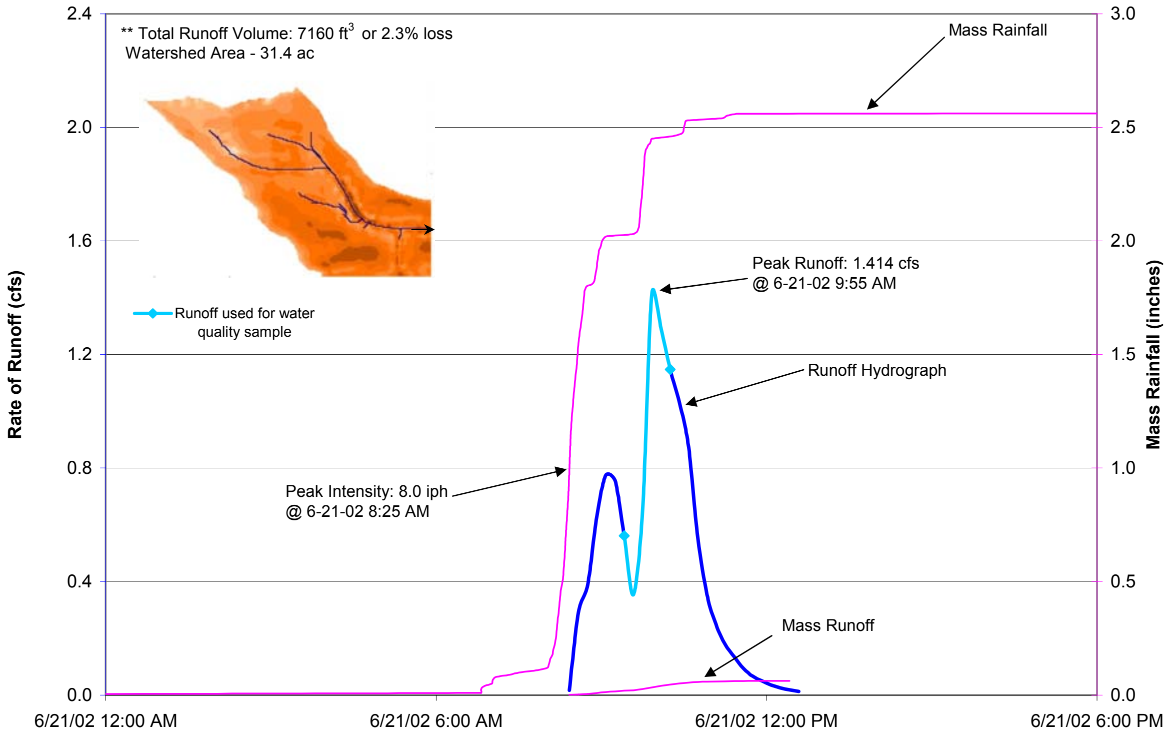
Precipitation and Runoff Hydrographs

Cumulative Rainfall Hyetograph - Grass and Tile Waterway

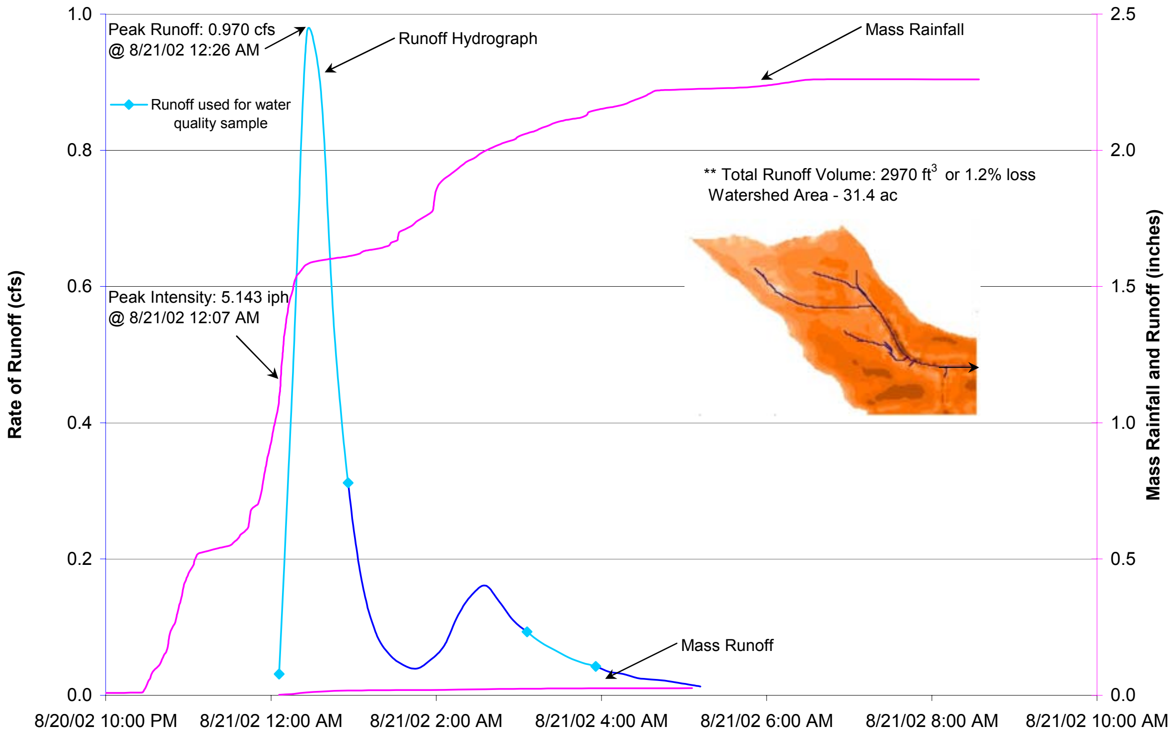


Cumulative Rainfall Hyetograph - Untreated Waterway

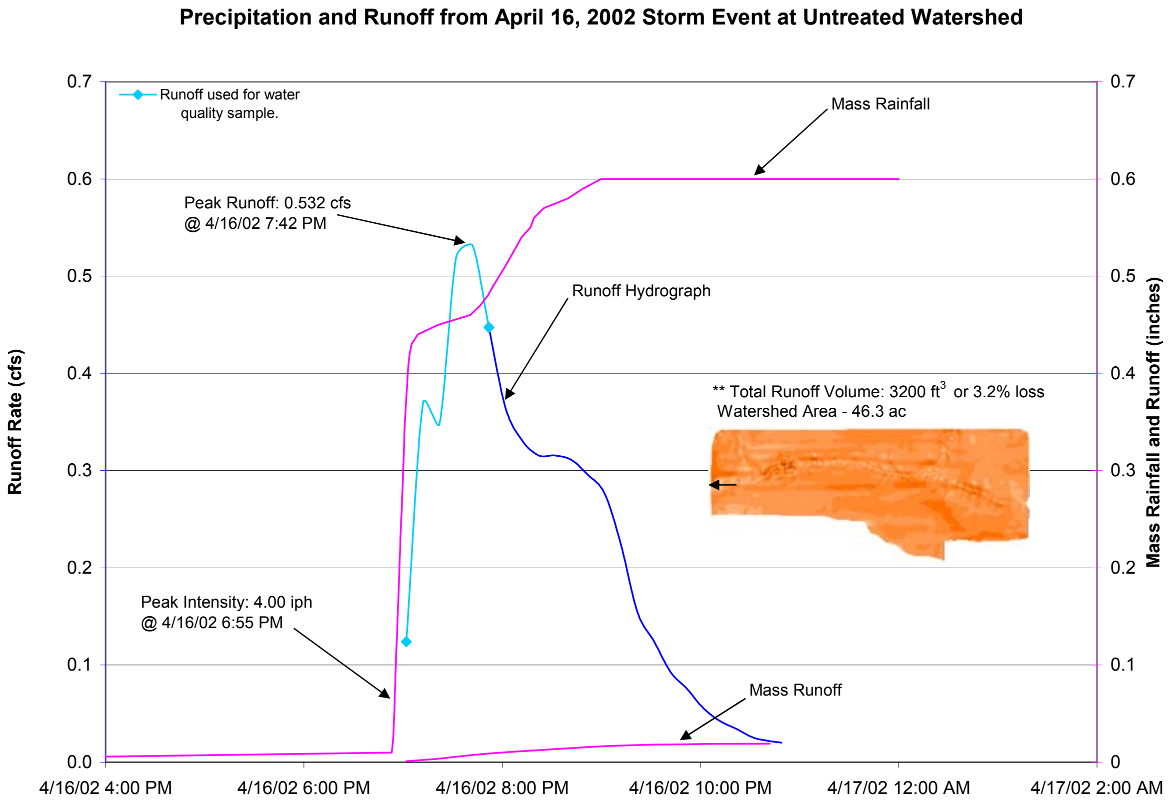




Precipitation and Runoff from June 21, 2002 Storm Event at Grass/Tile Watershed



Precipitation and Runoff from August 21, 2002 Storm Event at Grass/Tile Watershed

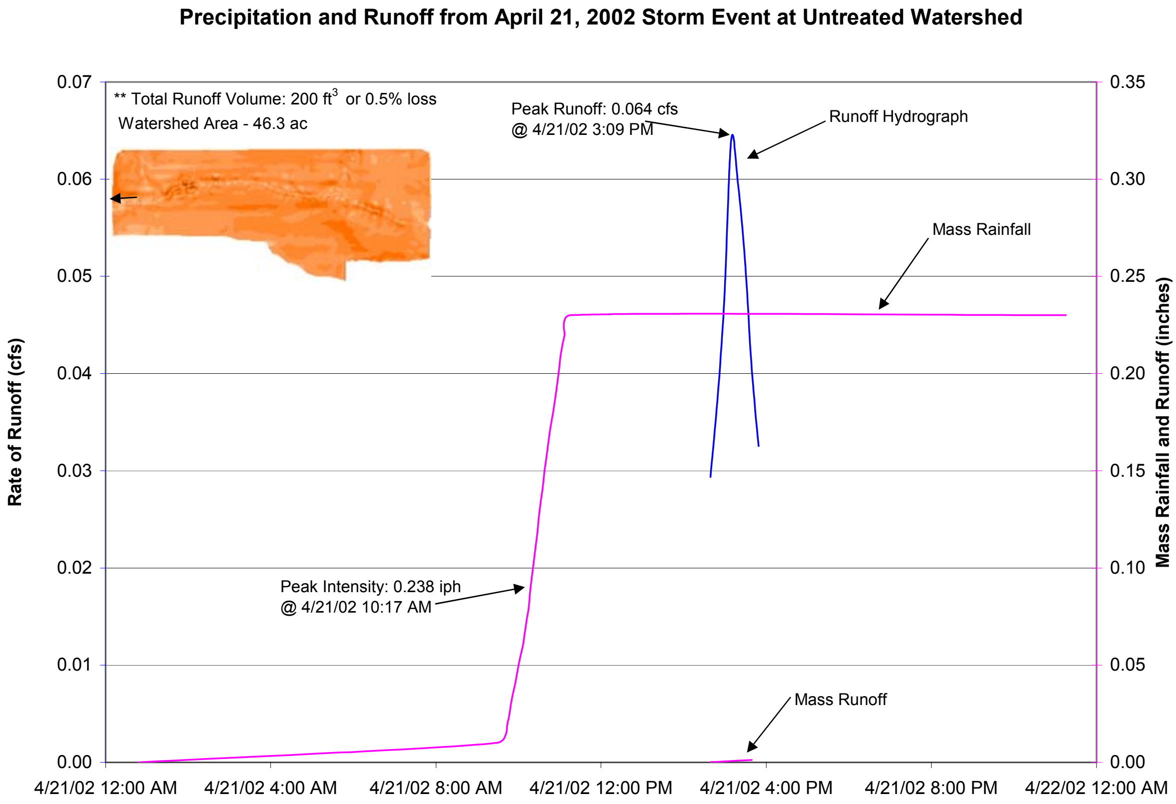


Precipitation and Runoff from April 16, 2002 Storm Event at Untreated Watershed

Peak Runoff: 0.532 cfs @ 4/16/02 7:42 PM

Peak Intensity: 4.00 iph @ 4/16/02 6:55 PM

** Total Runoff Volume: 3200 ft^3 or 3.2% loss
Watershed Area - 46.3 ac



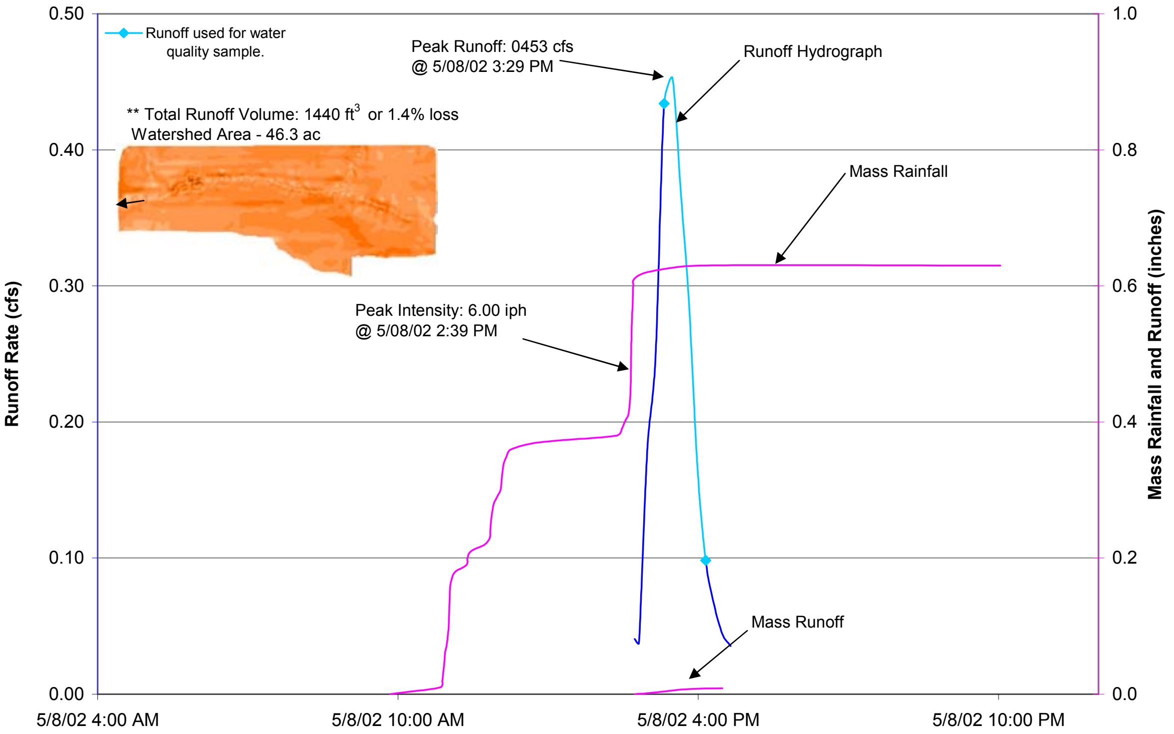
Precipitation and Runoff from April 21, 2002 Storm Event at Untreated Watershed

** Total Runoff Volume: 200 ft^3 or 0.5% loss
Watershed Area - 46.3 ac

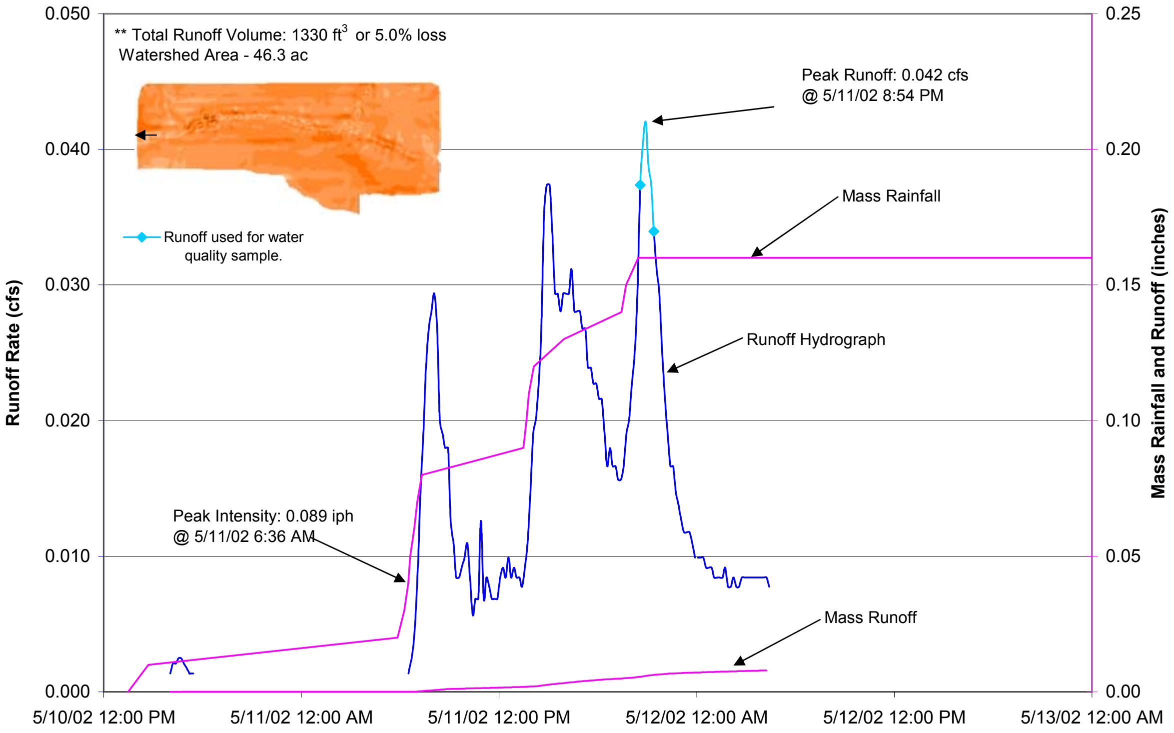
Peak Runoff: 0.064 cfs @ 4/21/02 3:09 PM

Peak Intensity: 0.238 iph @ 4/21/02 10:17 AM

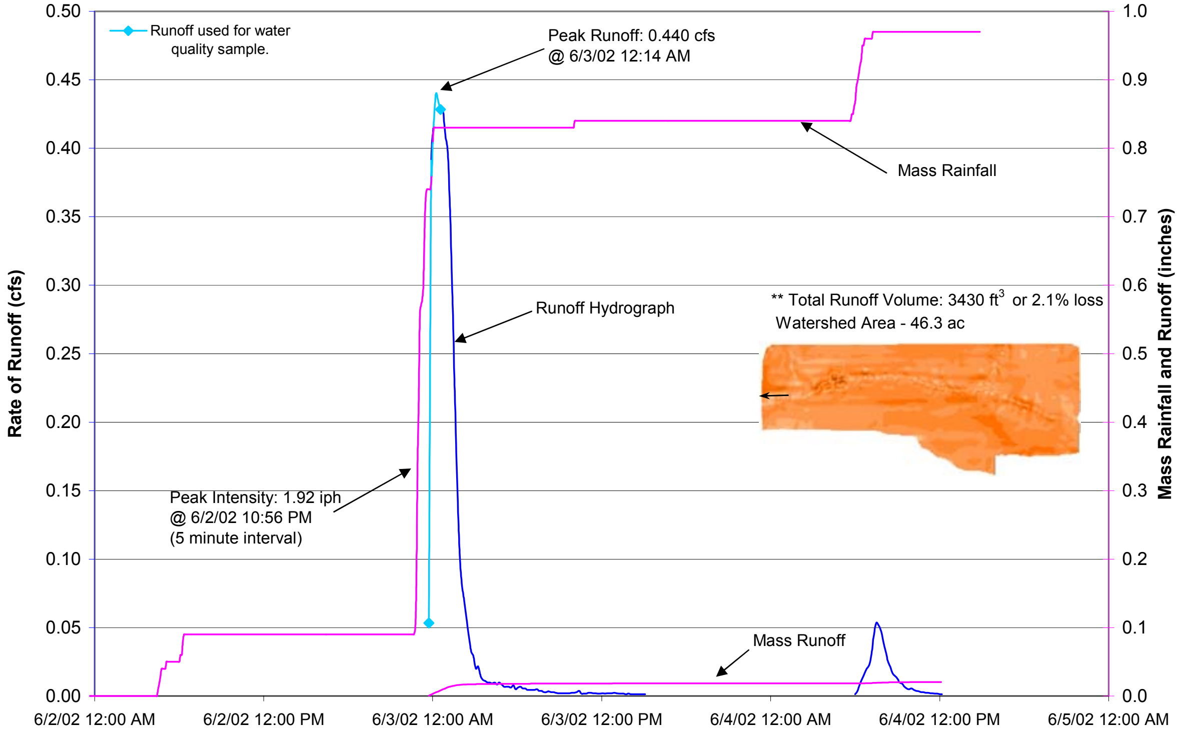
Precipitation and Runoff from May 8, 2002 Storm Event at Untreated Watershed



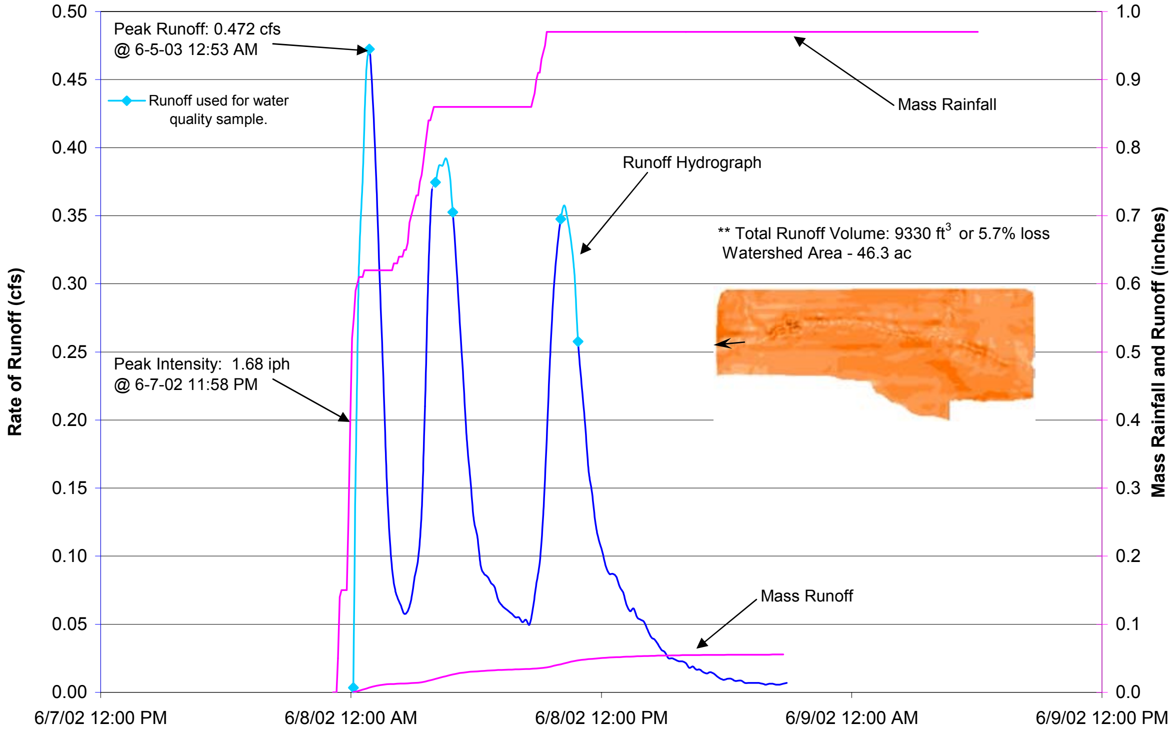
Precipitation and Runoff from May 11, 2002 Storm Event at Untreated Watershed



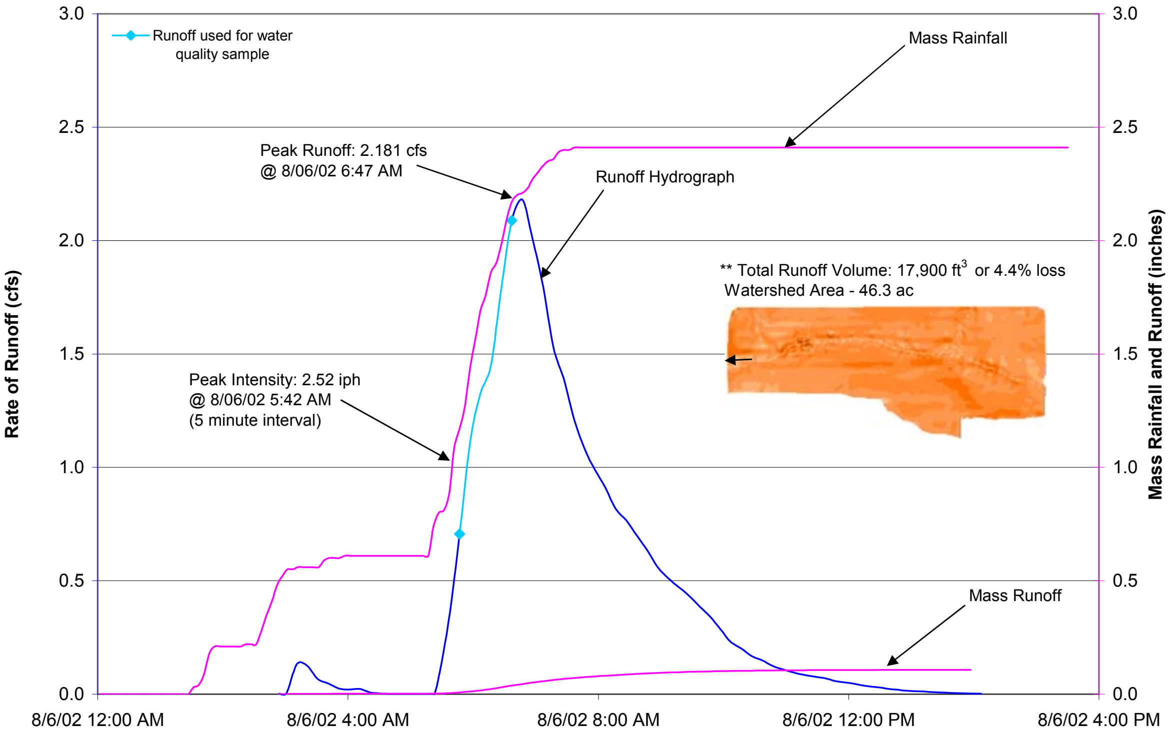
Precipitation and Runoff from June 3, 2002 Storm Event at Untreated Watershed



Precipitation and Runoff from June 8, 2002 Storm Event at Untreated Watershed



Precipitation and Runoff from August 6, 2002 Storm Event at Untreated Watershed

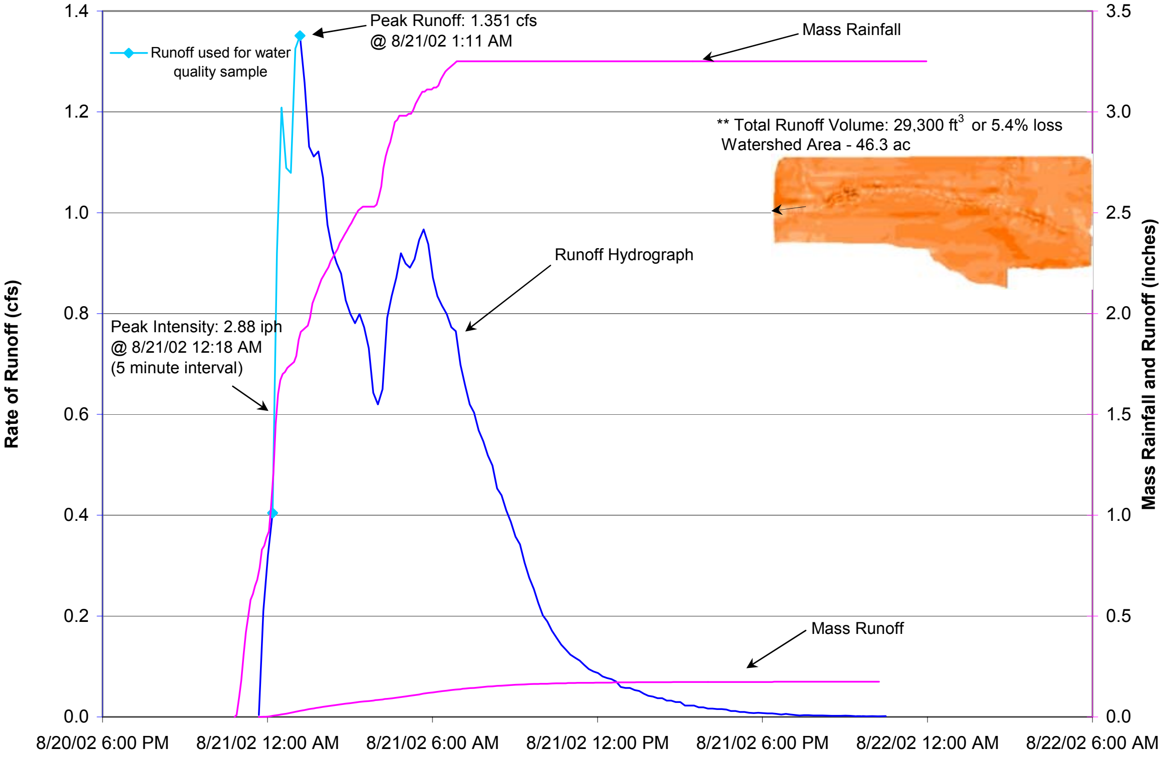


Peak Runoff: 2.181 cfs @ 8/06/02 6:47 AM

Peak Intensity: 2.52 iph @ 8/06/02 5:42 AM (5 minute interval)

** Total Runoff Volume: 17,900 ft^3 or 4.4% loss
Watershed Area - 46.3 ac

Precipitation and Runoff from August 21, 2002 Storm Event at Untreated Watershed

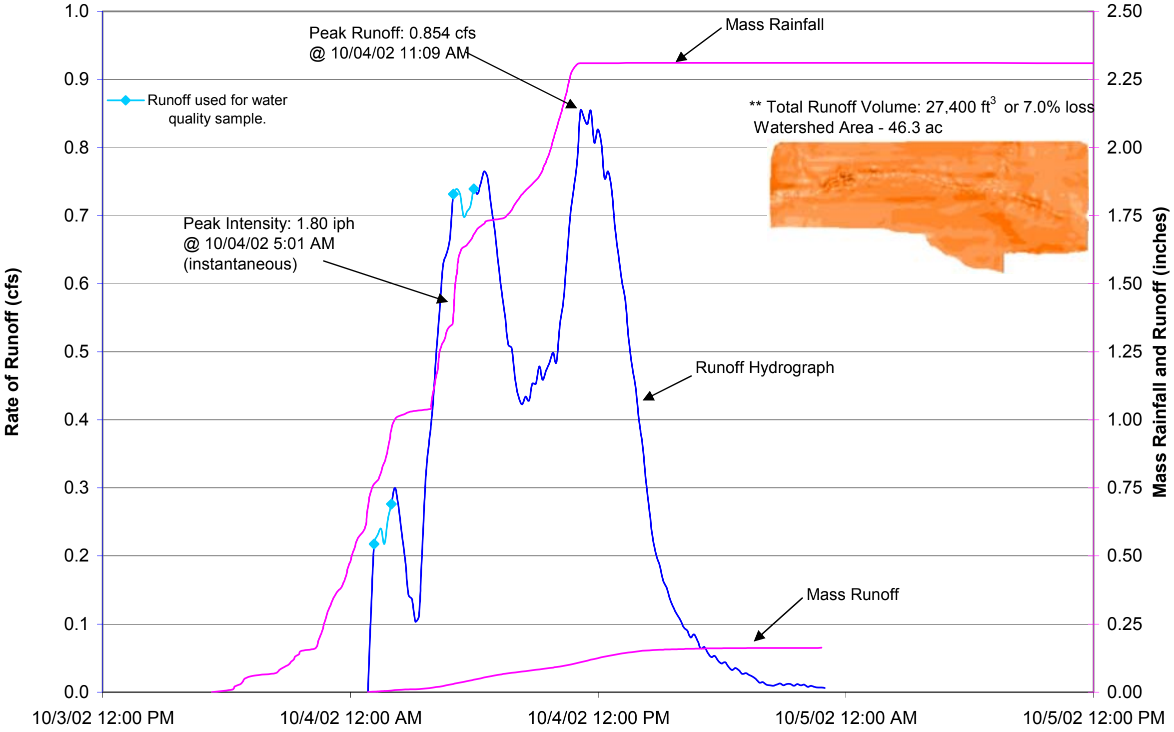


Peak Runoff: 1.351 cfs @ 8/21/02 1:11 AM

Peak Intensity: 2.88 iph @ 8/21/02 12:18 AM (5 minute interval)

** Total Runoff Volume: 29,300 ft^3 or 5.4% loss
Watershed Area - 46.3 ac

Precipitation and Runoff from October 4, 2002 Storm Event at Untreated Watershed



Peak Runoff: 0.854 cfs @ 10/04/02 11:09 AM

Peak Intensity: 1.80 iph @ 10/04/02 5:01 AM (instantaneous)

** Total Runoff Volume: 27,400 ft^3 or 7.0% loss
Watershed Area - 46.3 ac

Hydraulic Calibration of the Upper Soil Layers in a Glacial Till System

Basic Information

Title:	Hydraulic Calibration of the Upper Soil Layers in a Glacial Till System
Project Number:	2001SD1981B
Start Date:	3/1/2001
End Date:	2/28/2004
Funding Source:	104B
Congressional District:	First
Research Category:	Not Applicable
Focus Category:	Agriculture, Hydrology, Non Point Pollution
Descriptors:	Soil Physics, Soil Water Movement,Agriculture
Principal Investigators:	Todd T. Trooien

Publication

1. Kathol, John. (In prep.) MS Dissertation. Hydrology of Drained Grassed Waterways in Glacial Till-Derived Soils. Agricultural and Biological Systems Engineering Department, College of Engineering, South Dakota State University, Brookings, South Dakota.

Problem and Research Objectives:

Soils derived from glacial till are common in the northern Corn Belt and northern Great Plains. In the Dakotas, there are nearly 19 million ha of farm land east of the Missouri River with till-derived soils. Many of these soils derived from till are among the most productive agricultural soils for crops such as corn and soybean.

The mechanism of water redistribution is poorly understood for loess-capped soils with lower layers derived from glacial till. There are three potential mechanisms for water movement to areas lower in the landscape: overland flow as runoff/runon, downward flux then lateral movement at the top of the unsaturated weathered till, and downward then lateral movement within the saturated weathered till. Subsurface water movement remains the most poorly defined. This project focused on the movement of water downward through the upper soil layers.

The results of the field research proposed in this project will be used to validate and improve water flow models currently used for assisting in the definition of yield goals. The growth and yield portions of these models generally perform adequately but the water flow submodels are not yet sufficient to simulate water flow with enough accuracy and precision to estimate the correct amount of water stress experienced by the crop.

Methodology:

The two field sites were located near the top of a hill but not at the crest, in a nearly level area. The soil surface was modified slightly so that the flooded surface was nearly level. The 2001 site was located in the NE ¼ of the SE ¼ of Section 19, R48W, T109N on a Kranzburg soil The 2002 site was in SE ¼ of the SW ¼, Section 18, R48W, T107N on a Houdek clay loam soil. The hydraulic properties at each site were measured using the instantaneous profile method, as described below.

A frame of 50 mm by 300 mm lumber was placed around the flooded area to prevent overland flow (runoff). The frame was inserted (trenched) into the soil about 100 mm to prevent near-surface lateral water movement.

Water was introduced by flooding the soil surface within the frame. An additional area surrounding the framed area was also flooded. This additional flooded area served as a buffer so that measured flow from the interior framed area was vertical. After flooding was complete, the plot area was covered with plastic to prevent evaporation from the soil surface.

During and after flooding, soil matric potentials were measured with tensiometers. The matric potentials and instrument elevations were used to calculate hydraulic gradients. Within the flooded framed area, matric potentials were measured at three depths: 450, 750, and 1050 mm below the soil surface. Matric potential measurements at each depth were replicated four times. Soil water content was measured with the neutron probe in 150 mm intervals to a depth of 1.05 m. The neutron probe measurements were replicated four times.

The plots were flooded on 24 October 2001 and 21 October 2002. Monitoring took place until 21 November 2001 and 26 November 2002. In 2002, an early freeze rendered the tensiometers useless nearly immediately after the flooding took place. In 2001, the tensiometers were operated for the entire monitoring period. In each year, the access tubes and the remainder of the equipment in the plots were removed and monitoring ceased one or two days before the first major (>20 mm) snow fall of the season.

Principal Findings and Significance:

Drainage rates from the plots were small for the relatively short monitoring periods at both sites (Figs. 1 and 2). The 2002 matric potential data are not shown because of the cold weather immediately after water application that caused immediate failure of the tensiometers. The measured water contents and matric potentials show steady but slow drainage of water from each plot after the initial flooding. The lower depths in 2002 show little change of water content but the upper layers were decreasing in water content (Fig. 2). Because the drainage rate at the site in 2001 was small and relatively constant, a single value of hydraulic conductivity was calculated at that site. That value was 2.0 mm per day. The average volumetric water content at the 1.05 m depth corresponding to that value of K was 0.330 m/m (or 33.0%).

The soils at the __ site measured in 2001 apparently increase in clay content with depth. The water content increases with depth (Fig. 1), indicating a greater clay content with a greater water holding capacity. The change of soil clay content (and stored water) with depth is very small at the Houdek (2002) site.

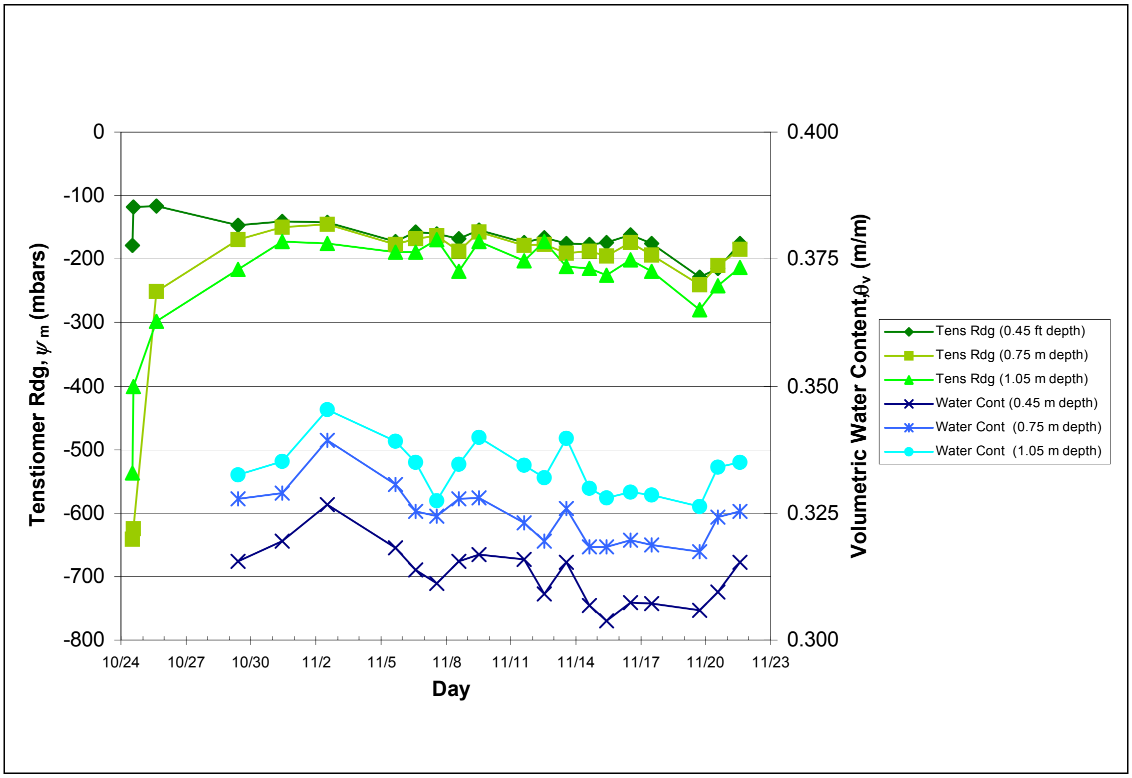


Figure 1. Matric potential and water content during the test in 2001.

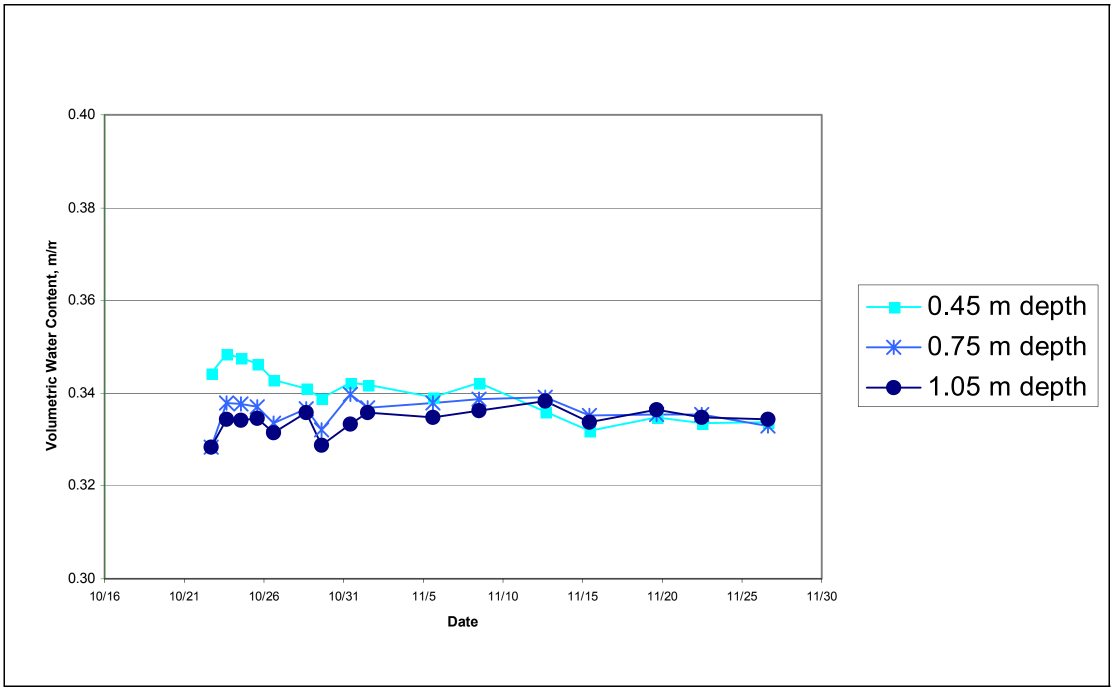


Figure 2. Water content during the test in 2002.

The vertical drainage rates at the two sites were calculated as the change of water content in the top 1.05 m of the soil profile over the entire monitoring period. The average drainage rate in 2001 was 0.48 mm per day and the average in 2002 was 0.27 mm per day. The drainage rate for various depths was also calculated using the 2002 data. The slope of the regression line (stored water regressed by date) is the drainage rate. The drainage rates varied from 0.15 mm per day (for the top 0.45 m of the soil profile) to 0.27 mm per day (0.75 and 1.05 m depths). The R^2 values for all regressions were high (between 0.66 and 0.85).

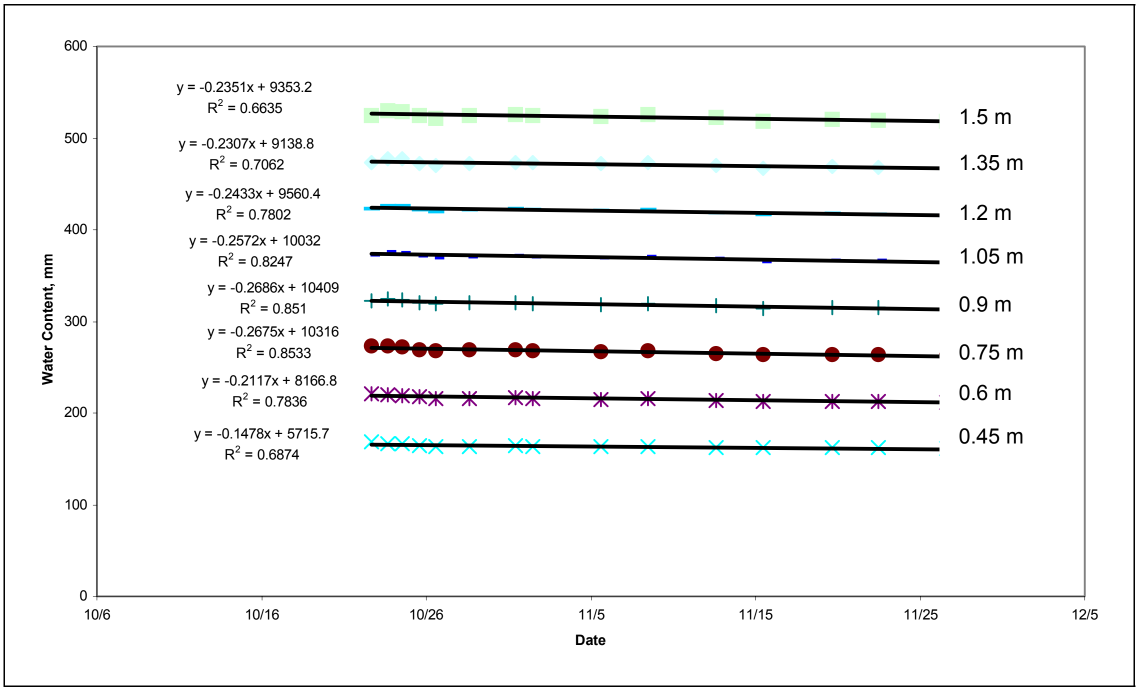


Figure 3. Drainage rate by depth at the Houdek (2002) site.

The instantaneous profile method is accurate and valuable but labor- and land-intensive. Therefore, testing of a single plot for a short time period would have value if the small data set could be extended in some manner. The instantaneous profile method was used to measure soil hydraulic properties of 36 plots during a 4-month period (Trooien and Reichman, 1990). That 4-month study took place in North Dakota at a site with till-derived soils similar to those used in this study. The single measurement of K from each site in this study can be compared to the K-water content function measured in the North Dakota study to compare the hydraulic properties of the three sites. The flooding took place during a period of nearly two months in North Dakota and resulted in water contents much greater than those measured in the current study (Fig. 3). Plotting the K value from 2001 in the current study shows that it fits reasonably well with the curve measured in the North Dakota study (Fig. 3).

The final drainage rate measured in the North Dakota study was 0.6 mm per day, which is similar to the drainage rate measured in 2001. While the drainage rate in 2001 was 0.48

mm per day, which is slightly less than the North Dakota clue of 0.6 mm per day, the water content in 2001 was also less than the water content in the ND study (Fig. 3), so you would expect to measure a lesser drainage rate.

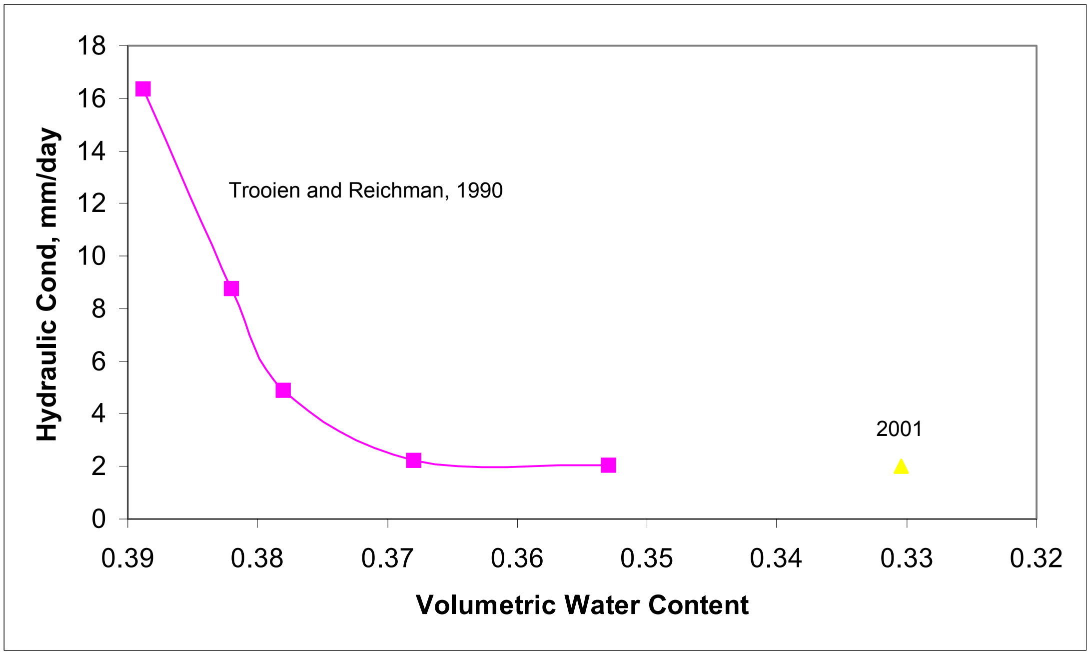


Figure 4. K(theta) function from Trooien and Reichman (1990) and from the __ (2001) site in this study.

References

Trooien, T. P. and G. A. Reichman. 1990. Hydraulic conductivity of till subsoil in North Dakota. Transactions of the ASAE 33(5):1492-1496.

Part Two:

Information Transfer Program: Awaiting completion of MS thesis (see below).

Student Support: No direct student support was provided by this project. One graduate student in Agricultural and Biosystems Engineering is currently completing his MS thesis that includes results from this project. This project provided support for the graduate student in the form of research supplies and travel funds for the graduate student's project and training. Additionally, three undergraduate students participated in various phases of this project although their funding came from other sources.

Information Transfer

Basic Information

Title:	Information Transfer
Project Number:	2001SD2442B
Start Date:	3/1/2001
End Date:	2/28/2002
Funding Source:	104B
Congressional District:	First
Research Category:	Not Applicable
Focus Category:	Education, None, None
Descriptors:	information transfer,Education
Principal Investigators:	Van C Kelley, David R. German

Publication

Public Outreach

The severe drought in western South Dakota the past three years has demonstrated the importance of the services offered by the Water Resources Institute's Water Quality Laboratory. The inherent quality of surface waters in western South Dakota is commonly low, leading to chronic livestock production problems. However, drought has intensified this problem for livestock producers in these semi-arid rangelands. Many dugouts and ponds degraded to the point of causing cases of livestock illness and, in some instances, livestock deaths. Although water quality problems in western South Dakota are common, some isolated cases of livestock illness and deaths due to poor surface water quality occurred in eastern South Dakota in 2001 and continued in 2002. The SD WRI made this issue a priority in its outreach/information transfer efforts by posting information for farmers and ranchers on this subject on the Institute=s web page (http://wri.sdstate.edu/drought.htm). The SDSU Agricultural Communications Department also developed a press release and special web page dealing specifically with the drought. This web page referred producers who had questions about their water quality to the SD WRI web page. Numerous requests were received by SD WRI staff for assistance with identification of potentially toxic algae from surface waters due to dry conditions.

Public outreach takes many forms. One of the most recent at SD WRI is providing information over the Internet. A Web site for the SD WRI and Water Quality Lab has been established. The "Research Projects" section of the SD WRI Web site (http://wri.sdstate.edu) is continuing to be updated. 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. An extensive library of information will eventually be developed on-line. Information regarding analytical services available at the SD WRI's Water Quality Laboratory and information that may be used to address drinking water problems has been redeveloped on-line.

The Water Resources Institute's Water Quality Laboratory provides important testing services to water users across the state. Water Resources Institute staff continues to provide interpretation of analysis and recommendations for use of water samples submitted for analysis. Information transfer to individuals with assistance to identify and solve water quality problems is an important component of the Institute's Information Transfer activities. Interpretation of analysis and recommendations for suitability of use is produced for water samples submitted for livestock suitability, irrigation, lawn and garden, household, farmstead, heat pump, rural runoff, and land application of waste.

SD WRI staff routinely respond to questions unrelated to laboratory analysis 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. WRI continues to provide soil and water compatibility recommendations for irrigation permits to the SD Division of Water Rights.

Agency Interaction

The SD WRI Information Transfer program includes interaction with local, state and federal agencies/entities in the discussion of water-related problems in South Dakota, and the development of the processes necessary to solve these problems. One example of this interaction to solve water quality problems is a program started by the Cooperative Extension Service 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. 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.

In 2001 the Institute co-sponsored the "Phosphorus, Manure & Water Quality Conference". Participating agencies included the South Dakota Department of Environment and Natural Resources, NRCS, South Dakota Lakes and Streams Association, South Dakota Agricultural Experiment Station, South Dakota Cooperative Extension Service, South Dakota Department of Agriculture, South Dakota Cattlemen's Association, SDSU Plant Science Department and Soil Testing Laboratory, and the South Dakota Farm Bureau. In 2002 these groups supported research efforts need to fill gaps in our knowledge of the relationships between soil test P and runoff P. Similar coordination and information sharing is expected as South Dakota moves toward the development of a P-index to address the issue of P buildup in the soil and its impact on water quality. A PhD student in the Atmospheric, Environmental and Water Resources Program at SDSU was hired in the fall of 2002 and is housed in the SD WRI office. This is the first time SD WRI has been able to support a PhD student in more than 20 years. The student's research project, titled "Establishing a Relationship between Soil Test Phosphorus and Runoff Phosphorus for South Dakota Soils Using Simulated Rainfall" will be the subject of the student's PhD dissertation upon completion of her degree program.

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

Youth Education

Water Festivals were included in the NPS Task Force's Information and Education plan in 1992 with one Water Festival held in Spearfish, South Dakota. Water Festivals have since been held in seven sites including Spearfish, Rapid City, Pierre, Huron, Vermillion, Brookings and Sioux Falls. Since their inception, Water Festivals in South Dakota have impacted approximately 58,000 fourth grade students state wide, 12,500 of which have attended our own local festival, the Big Sioux Water Festival (BSWF). SD WRI staff members will continue to support and participate in Water Festivals throughout the state in coming years. SD WRI will continue other activities to support water quality education in local schools including classroom presentations and assisting local educators with field trips.

Information Transfer Program

Student Support

None

Notable Awards and Achievements

Publications from Prior Projects

None