

Water Resources Research Center Annual Technical Report FY 2001

Introduction

The Minnesota WRI program is administered by the University of Minnesota Water Resources Center (WRC), which is a collaborative enterprise involving several college-level units: the College of Natural Resources (CNR), College of Agricultural, Food & Environmental Sciences (COAFES), and the Minnesota Extension Service (MES), plus the University of Minnesota Graduate School, which provides funds to administer the Water Resources Science graduate program, which is housed administratively in the WRC. The WRC has co-directors, who divide the overall responsibilities for Center operations between them. Patrick Brezonik reports to the dean of CNR and is responsible for administering the WRI program. He also is Director of Graduate Studies for the WRS Program. James L. Anderson reports to the deans of COAFES and MES and is responsible for extension operations. The co-directors share responsibilities for other outreach and research activities of the Center.

Research Program

In situ measurement of denitrification in agricultural streams

Basic Information

Title:	In situ measurement of denitrification in agricultural streams
Project Number:	2000MN9G
Start Date:	9/1/2000
End Date:	8/31/2001
Funding Source:	104G
Congressional District:	5
Research Category:	Water Quality
Focus Category:	Nitrate Contamination, Non Point Pollution, Methods
Descriptors:	denitrification, agriculture, surface drainage, isotopes
Principal Investigators:	Patrick L Brezonik, Lorin Kent Hatch

Publication

In situ measurement of denitrification in agricultural streams

P. L. Brezonik, Professor and PI, (brezo001@umn.edu), Department of Civil Engineering, University of Minnesota; and **L. K. Hatch**, Assistant Professor and Co-PI, Department of Biology, Macalester College; **B. O'Connor**, Research Assistant, Department of Civil Engineering, University of Minnesota

Funding source: USGS WRRI 104G National Competitive Grants Program

Project duration: September 1, 2000 to August 31, 2002

Summary

Nitrate contamination of ground water and streams is common in landscapes dominated by agricultural activities. Associated impacts of this pollution range from local violations of drinking water standards designed to prevent methemoglobinemia to national concerns (e.g., Gulf of Mexico hypoxia). Significant quantities of nitrate are exported from agricultural lands through drainage ditches and low-order natural streams, but our understanding of nitrogen transport and transformation in these agricultural streams is far from complete. Denitrification may be an important mechanism for nitrate removal in these streams, and this would mitigate water quality and health hazards downstream. Several methods can be used to measure denitrification, but the most common ones involve laboratory experiments with sediment cores, where conditions are not conducive to obtaining *in situ* rates. Our research is comparing several methods used to assess *in situ* denitrification rates in agricultural streams and evaluating their accuracy. We also are evaluating how variations in key environmental factors may affect the importance of this process as a nitrogen sink.

Introduction

Contamination of ground water and streams by nitrate is a problem in many agricultural areas. Impacts associated with this pollution range from local (contamination of wells used for drinking water) to national (e.g., hypoxia in the Gulf of Mexico). Excess nitrogen loading, principally in the form of nitrate from the Mississippi River, is considered to be the cause of a large hypoxic zone in the nearshore Gulf of Mexico (Goolsby et al. 1999, Rabalais et al. 1999), and a large fraction of this nitrogen is thought to be derived from non-point agricultural sources in the Cornbelt region of the Upper Mississippi River Basin (UMRB). The UMRB generates roughly one-third of the nitrate loads reaching the Gulf of Mexico, while the Ohio River basin generates roughly one-fifth of the nitrate reaching the Gulf. The Midwest region thus is responsible for roughly half of the non-point source loads of nitrate entering the Gulf of Mexico. These loads have been attributed to heavy precipitation on intensively row-cropped soils that have extensive networks of surface ditches and subsurface tile drains, are high in organic matter content, and receive high rates of inorganic and organic nitrogen amendments (Randall and Mulla 1998). Nitrogen applied to the soil surface or mineralized from soil organic matter can be delivered in the nitrate form to surface waters by leaching and drainage through subsurface tile drains after heavy precipitation.

The Minnesota River Basin (MNRB) is typical of tributary basins of the Upper Mississippi and Ohio River Basins that contribute to hypoxia in the Gulf of Mexico (Randall and Mulla 1998). The MNRB (Mulla and Mallawatantri 1997) has moderate to heavy annual precipitation (56-79 cm/yr), intensive row-cropping (92% of the land), extensive tile drainage (>40% of the land), extensive soils with high organic content (>80% of the land has an organic content exceeding 4%), and high rates of nitrogen application via fertilizer (county-wide averages up to 12.5 t km⁻² yr⁻¹) and manure (county-wide averages up to 4.5 t km⁻² yr⁻¹). As a result, the 4.0 million ha MNRB has a mean annual nitrate yield of 3.1 kg N km⁻² d⁻¹ (11.2 kg ha⁻¹ yr⁻¹), and its Le Sueur watershed has a mean annual nitrate yield of 6.4 kg N km⁻² d⁻¹ (Randall and Mulla 1998). These values are similar to the mean annual nitrate yields for other Midwest rivers; e.g., 5.5, 4.8, and 3.5, kg N km⁻² d⁻¹, respectively, for the Iowa, Illinois, and Wabash Rivers (Goolsby et al. 1999).

Much of the nitrate exported from agricultural lands in the Cornbelt is transported through drainage ditches, but we have only a poor understanding of the nitrogen transformation processes in these waterways. Depending on physical circumstances, denitrification could be a significant pathway for nitrate removal from these systems, enhancing water quality and reducing health hazards downstream. Several methods are available to measure denitrification, but they usually are conducted using sediment core experiments in the laboratory, where handling and incubation conditions are not conducive to obtaining accurate estimates of *in situ* rates. Even when rates are mea-

sured using field incubations, ambient hydrodynamic conditions are not replicated in the incubated samples, and correspondence between measured rates and *in situ* values is questionable.

The principal objectives of this project are to (i) assess *in situ* denitrification rates in agricultural streams and (ii) determine how these rates vary with stream stage, flow, and temperature. We are comparing *in situ* results obtained by ^{15}N tracer, ^{15}N natural abundance ratios, and mass balance methods. Part of our field work uses in-stream mesocosms for assessments. We are making measurements over a range of discharge and stage. Field work is being conducted in the eastern Minnesota River Basin, an agricultural area with high nitrate levels in its streams and rivers.

Methods

We selected two stream sites within the eastern region of the Minnesota River Basin: Waseca Stream in Waseca County and Beauford Stream in Blue Earth County. The Beauford site is ~ 20 miles west of the Waseca site (Figure 1). Beauford Stream has an older, downstream section with vegetation both on the banks and in the channel, as well as a recently ditched upstream section (constructed in 1999) that is devoid of vegetation. Comparison of the sections with respect to mass balance and stable isotope analysis is being done to assess effects of in-stream vegetation on nitrogen dynamics. We installed three piezometers adjacent to each of the three locations (Waseca, Beauford Unvegetated, Beauford Vegetated).

We found it necessary to apply different assessment methods for denitrification based on specific objectives. For example, we are using mass balance and stable isotopes to assess large-scale denitrification rates and N-tracer and sediment core analyses to assess small-scale sediment/stream interactions. Details are given below.

(A) *Assessment of stream size, flow, and temperature effects on denitrification.* We measured denitrification rates for this component using mass balance (Bachmann et al. 1991) and stable isotope methods in the Beauford and Waseca systems. These two approaches allowed us to assess denitrification rates under differing flow and temperature regimes. During late summer (July/August, 2001 and 2002) we collected water samples in the Beauford and Waseca systems (first order, stations 400 m apart). Stream and ground water analyses (APHA 1998) included nitrate, ammonium, and total dissolved and total nitrogen for the mass balance method.

The dual isotope method was employed concurrently to assess denitrification losses using stable isotopes, following the procedures of Revesz et al. (1997).

(B) *Assessment of sediment core-based denitrification measurement methods.* We are evaluating the importance of surface sediment nitrification as a nitrate source by measuring nitrate concentrations in pore water profiles of cores obtained across the stream cross-section at various locations along the Waseca Stream stretch. Cores were extruded into 1-2 cm thick segments in the laboratory, and pore water for chemical analysis was obtained by centrifugation (if the sediments were sufficiently unconsolidated) or dilution/extraction with deionized water (if the sediments were too firm for centrifugation). *In situ* mesocosms (clear plexiglass 14.6 cm diameter cylinders) with battery-powered stirrers were used in $^{15}\text{N}\text{-NO}_3^-$ addition experiments during the mass balance sampling periods (Waseca Stream only).

Results

Mass balance studies

The results of several upstream-downstream (400 m) mass balance studies during July and August of 2001 and 2002 are presented in Table 1. In general, nitrate concentrations were higher in the Waseca system than in the Beauford system, although elevated nitrate concentrations were present at Beauford during the August 28, 2002, sampling event.



Figure 1. The Minnesota River Basin and Waseca Watershed location.

Table 1. Mass balance results for 2001 and 2002

Date	Site	Average Nitrate Conc		Nitrate Loss (mg-N L ⁻¹)	Discharge Velocity (m/s)	Nitrate Loss Rate ^a (mg-N L ⁻¹ hr ⁻¹)
		Upstream (mg-N L ⁻¹)	Downstream (mg-N L ⁻¹)			
7/17/01	Waseca	15.63	15.04	0.59	0.04	0.21
8/2/01	Waseca	13.69	13.52	0.17	0.08	0.12
8/3/01	Waseca	13.67	13.30	0.37	0.08	0.27
8/23/01	Beauford	3.67	2.87	0.80	0.01 ^b	0.07
8/24/01	Beauford	2.73	1.65	1.08	0.01 ^b	0.10
7/2/02	Waseca	16.52	16.56	---	0.40	---
7/30/02	Beauford	3.76	2.12	1.64	0.03 ^b	0.44
7/31/02	Waseca	2.91	3.24	---	0.08	---
8/27/02	Waseca	8.07	8.91	0.16	0.27	0.38
8/28/02	Beauford	11.51	11.2	0.31	0.15 ^b	0.42

a - nitrate loss rate is calculated as a zero order loss rate in the advective-dispersion equation assuming dispersion transport is negligible

b - discharge velocity was estimated from flow measurement and average x-sectional areas.

Note. 8/3/01 Waseca data represents a nighttime sampling event; 8/24/01 Beauford data represents the unvegetated reach

Stable isotopes

During the mass balance studies, we collected composite water samples at the upstream and downstream ends of the 400-m stream reaches. These samples were sent to a laboratory in Canada where both the ¹⁵N and ¹⁸O

Table 2. Stable Isotope results from 2001 samples

Date	Site	location	¹⁸ O NO3	¹⁵ N NO3	Repeat
8/24/01	beauford unveg	down	8.34	14.18	
8/24/01	beauford unveg	up	8.76	15.23	
8/23/01	beauford veg	down	8.06	12.61	12.97
8/23/01	beauford veg	up	8.58	12.32	
7/17/01	waseca	down	8.22	8.35	
8/2/01	waseca	down	8.09	7.82	
8/3/01	waseca	down	8.14	9.47	
7/17/01	waseca	up	7.37	8.22	
8/3/01	waseca	up	8.21	9.23	9.44
8/2/01	waseca	up	8.91	9.55	

isotope ratios were measured on the same nitrate ions (Table 2). Initial results indicate that N had a wide range of $\delta^{15}\text{N}$ values (from 7.82 to 15.23), while $\delta^{18}\text{O}$ values had a much smaller range (from 6.91 to 8.76). Results from the 2002 samples are still pending.

Sediment cores

In 2002 we collected stream bottom sediment cores after completing each mass balance study (Table 3). Initial results for porewater in the cores indicate that nitrate concentrations were relatively low (range: not detectable to 1.71 mg N/L) compared with ammonium concentrations (range: not detectable to 831 mg N/L). Additional porewater quality characteristics included soluble reactive P (range: 7.2 to 223.1 $\mu\text{g/L}$), loss on ignition (range: not

Table 3. Sediment core data 2002

Date	Sample	Depth	NO ₃ ⁻ (mg-N L ⁻¹)	NH ₄ ⁺ (mg-N L ⁻¹)	SRP (ug L ⁻¹)	LOI %	Cl (mg L ⁻¹)	SO ₄ ²⁻ (mg L ⁻¹)
7/2/02	Upstream	0-1 cm	1.47	4.0	52.7	3.56	4.39	10.05
Waseca	Upstream	1-2 cm	1.45	nd	67.1	3.09	5.65	10.29
	Upstream	2-3 cm	nd	74.2	76.7	4.24	3.80	10.84
	Downstream	0-1 cm	1.35	5.6	183.1	1.42	2.90	
	Downstream	1-2 cm	1.71	30.5	171.9	1.16		
	Downstream	2-3 cm	1.53	94.2	223.1	1.82	5.81	11.09
7/30/02	Upstream	0-1 cm	nd	72.8	15.4	3.30	7.37	nd
Beauford	Upstream	1-2 cm	nd	32.0	13.1	3.44	2.59	nd
	Upstream	2-3 cm	1.46	27.1	7.2	nd	2.79	nd
	Downstream	0-1 cm	nd	43.8	24.9	4.18	nd	nd
	Downstream	1-2 cm	nd	43.8	39.0	2.31	nd	nd
	Downstream	2-3 cm		Sample was lost in transit				
8/27/02	Upstream	0-1 cm	1.38	56.3	111.4	3.72	2.84	10.09
Waseca	Upstream	1-2 cm	nd	39.3	94.8	3.54	2.92	nd
	Upstream	2-3 cm	nd	44.0	83.9	3.55	2.89	nd
	Downstream	0-1 cm	nd	288.9	58.1	4.09	3.77	12.85
	Downstream	1-2 cm	nd	429.1	108.9	4.76	5.95	12.55
	Downstream	2-3 cm	0.77	630.8	50.6	4.22		11.18
8/28/02	Upstream	0-1 cm	1.50	23.5	60.6	4.66	3.14	
Beauford	Upstream	1-2 cm	1.52	35.4	44.8	5.52	3.03	10.93
	Upstream	2-3 cm	1.45	28.6	37.3	5.66	3.82	10.96
	Downstream	0-1 cm	nd	25.2	98.8	3.24	3.36	11.14
	Downstream	1-2 cm	1.46	50.3	78.9	4.67	3.13	11.35
	Downstream	2-3 cm	nd	28.6	73.6	3.93	9.40	nd

SRP - soluble reactive phosphorus

LOI - loss of ignition percent organic matter

nd - no detect

detectable to 5.66 %), chloride (range: not detectable to 9.4 mg/L), and sulfate (range: not detectable to 12.9 mg/L).

15N nitrate mesocosm additions

We added the equivalent of 1 mg/L ¹⁵N-NO₃⁻ to three mesocosms and 2 mg/L to three other mesocosms. Although we have not completed analysis of the data, loss rates of total nitrate over time during the August 27, 2002, sampling period in Waseca Stream are summarized in Table 4. Initial results indicate loss rates of 0.06 and 0.04 mg NO₃⁻-N/h over the 20-h period for the 1 and 2 mg/L additions, respectively.

Table 4. August 2002 mesocosm results

Time (hr)	1 mg/L addition NO ₃	2 mg/L addition NO ₃
0	10.179 (0.112)	11.289 (0.204)
3	9.809 (0.086)	10.772 (0.242)
17	9.052 (0.401)	10.595 (0.246)
20	8.886 (0.565)	10.416 (0.265)

Note: units in mg/L (95% CI)

Ongoing work and initial conclusions

We are analyzing our current data and waiting for results of stable isotope and mesocosm samples from a contract laboratory. We expect to receive this information in early 2003. Initial findings of the project will be presented at the American Society of Limnology and Oceanography meeting in February 2003 in Salt Lake City.

Publications will be prepared after data analysis is completed.

Measurable differences in nutrient concentrations occur along the courses of our streams, and these differences are most noticeable during daylight. The loss of up to 1.64 mg/L TN along a 400-m stretch of stream (Table 1) indicates that in-stream loss processes are important at the stream-reach scale. The natural abundance of ^{15}N stable isotope in nitrate varied measurably in the stream samples suggesting this variable may be useful in estimating nitrate dynamics in the streams, but abundance of ^{18}O isotope showed only small variations suggesting that the dual isotope approach of Revesz et al. may not work in all streams.

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Basic Water Resources Center Grant

Basic Information

Title:	Basic Water Resources Center Grant
Project Number:	2001MN3361B
Start Date:	3/1/2001
End Date:	2/28/2002
Funding Source:	
Congressional District:	4, 5
Research Category:	
Focus Category:	Education, None, None
Descriptors:	conferences, newsletter, outreach, education
Principal Investigators:	Patrick L Brezonik, James L Anderson

Publication

**Water Resources Center
Annual Technical Report
FY 2001**

The Minnesota WRI program is administered by the University of Minnesota Water Resources Center (WRC), which is a collaborative enterprise involving several college_level units: the College of Natural Resources (CNR), College of Agricultural, Food & Environmental Sciences (COAFES), and the Minnesota Extension Service (MES), plus the University of Minnesota Graduate School, which provides funds to administer the Water Resources Science graduate program, which is housed administratively in the WRC. The WRC has co_directors, who divide the overall responsibilities for Center operations between them. Patrick Brezonik reports to the dean of CNR and is responsible for administering the WRI program. He also is Director of Graduate Studies for the WRS Program. James L. Anderson reports to the deans of COAFES and MES and is responsible for extension operations. The co_directors share responsibilities for other outreach and research activities of the Center.

The WRC has an administrative staff consisting of an associate administrator, accountant, senior secretary/editor, grant coordinator, and two part_time graduate students who are responsible for newsletter and report editing and Web site maintenance. The Center also has two Ph.D._level senior fellows (one in resource economics and one in water quality/environmental engineering), an education coordinator, three extension program coordinators, and six extension educators located in off_campus offices.

The WRC has an administrative oversight council that includes the deans of the three colleges to which it reports, an associate vice_president of research and associate dean of the Graduate School, and the heads or directors of key departments/programs on the Twin Cities and Duluth campuses of the University. The Center's external advisory committee consists of senior faculty, directors of other University water_related centers, and representatives of major state and federal water agencies.

The Center ran its WRI grant proposal competition for FY 2001 in a manner similar to previous years. An announcement of the competition and guidelines for proposal preparation were distributed to faculty on the various university campuses in early October, and a deadline for proposal submission was set for early November. Proposals received by the deadline were sent to peer reviewers, and care was taken to select reviewers who did not have an obvious conflict of interest. At least one reviewer was a faculty member from the University of Minnesota (usually from a department different than that of the PI submitting the proposal); one was from a federal, state or regional agency located in Minnesota; and one was from a university or federal laboratory outside Minnesota. Three or more reviews (usually four) were received for all proposals. A separate proposal selection committee then met in early January 2001 to review all proposals and their associated peer reviews. The panel ranked the proposals based on merit and fit to the Center's research program, but it also considered long_standing principles of the Center to support young faculty and to leverage its funds whenever possible. Three new projects were selected for funding in the FY 2001 program:

(1) "Paleohydrologic response of the Mississippi River Headwaters watershed to Holocene climate change," Howard Mooers, Department of Geology, University of Minnesota-Duluth;

(2) "Eutrophication and remediation in context: high-resolution study of the past 200

years in the sedimentary record of Lake McCarrons (Roseville, Minnesota),” Amy Myrbo and Emi Ito, Department of Geology and Geophysics, University of Minnesota, Minneapolis; and

(3) “Fluorochemicals in Minnesota waters: an emerging environmental issue,” Matt Simcik, Environmental and Occupational Health, School of Public Health, University of Minnesota, Minneapolis.

One additional project in our FY 2001 program (“A novel in-situ technology for the treatment of groundwater contaminated with agriculturally-derived nitrate,” Paige Novak and Michael Semmens, Department of Civil Engineering, University of Minnesota, Minneapolis) was a continuation from FY 2000. Partial funding for the Center's FY 2001 grant program was provided by the University of Minnesota's Agricultural Experiment Station through a grant to the Center for Agricultural Impacts on Water Quality, a component of the WRC.

Three projects from the WRCI 104G program were active at the University of Minnesota during FY 2001:

“Role of denitrification as a nitrate sink in agricultural streams,” Lorin Hatch and Patrick Brezonik, Water Resources Center, funded in FY 2000;

“Photochemical fate of pharmaceutical compounds discharged and detected in natural waters,” William Arnold (Department of Civil Engineering) and Kris McNeill (Department of Chemistry), University of Minnesota, Minneapolis, funded in FY 2001; and

“Antibiotic losses in runoff and drainage from manure-applied fields,” Satish Gupta (Department of Soil, Water, and Climate) and Ashok Singh (Veterinary Diagnostic Laboratory), University of Minnesota, St. Paul, funded in FY 2001.

The Center published two completion reports from research projects conducted by WRC staff in FY 2001:

Integrating Modeling and Management of Agriculturally-Impacted Watersheds: Issues of Spatial and Temporal Scale, P.L. Brezonik, W.K. Easter, L. Gerlach, L. Hatch, D. Mulla, and J.A. Perry, Tech. Report 141, December 2001.

Methods for Classifying Lakes Based on Measures of Development Impacts, R.A. Osgood, P.L. Brezonik, and L. Hatch, Tech. Report 143, January 2002

In addition, Center published the first in an expected continuing series of annual reports summarizing its research program:

Advances in Water Resources Research: Project Summaries for 2001 Tech. Report 142, January 2002.

The WRC continued to publish its quarterly newsletter, Minnegram, during FY 2001 and did the planning and organization for its biennial water conference, *Minnesota Water 2002*, which was held at the convention center in St. Cloud, Minnesota, in April 2002. A major

overhaul and updating of the WRC and WRS Web sites was initiated in FY 2001, and the revised sites went on_line in early spring of 2002.

Eutrophication and Remediation in Context: High-Resolution Study

Basic Information

Title:	Eutrophication and Remediation in Context: High-Resolution Study
Project Number:	2001MN3381B
Start Date:	3/1/2001
End Date:	2/28/2002
Funding Source:	
Congressional District:	5
Research Category:	
Focus Category:	Sediments, Water Quality, None
Descriptors:	Anoxia, Geochemistry, varved lake sediments, human impact, Eutrophication
Principal Investigators:	emi.ito.1

Publication

Eutrophication and remediation in context: High-resolution study of the past 200 years in the sedimentary record of Lake McCarrons (Roseville, Minnesota)

Amy E. Myrbo, Research Assistant, and Emi Ito, Professor and PI, (eito@umn.edu), Limnological Research Center, Department of Geology and Geophysics, University of Minnesota, Minneapolis

Funding source: USGS-WRRI 104B National Grants Competition and the Center for Agricultural Impacts on Water Quality

Project duration: September 2001 to February 2003

Summary

Lakes in urban settings receive major inputs of nutrients and salt from the lawns and roads that surround them. Increased biological productivity and salinization of lake bottom waters cause degradation of water quality in these valuable municipal resources. Monitoring efforts provide water quality information with high temporal resolution; however, due to logistical and budgetary constraints, monitoring rarely captures more than a few years' data; hence, these snapshots may not accurately represent the high interannual variability of physical and chemical parameters in lakes.

This study uses sediment cores and certain water chemistry analyses to generate a high-resolution record of historic and pre-European changes in the chemistry and productivity of Lake McCarrons, Roseville, Minnesota, with the goal of placing recent (1985-2001) monitoring data in a long-term context. Geochemical and isotopic parameters recorded in lake sedimentary components over time are used as proxies for processes and changes in the water column; a minimal number of water analyses are used to calibrate the system with respect to the isotopic proxies and to answer specific questions germane to the sediment study.

Results to date indicate that Lake McCarrons has undergone cycles of increased biological productivity in this century, and that productivity is as high now as it has been at any time during this period. Sediment data also suggest that the degree of bottom-water anoxia has increased over the past 40 years; this observation is further supported by water chemistry data indicating that the lake does not fully mix at fall and spring overturn, behavior which would feed back and support the development of greater anoxia. Data currently in hand will be supplemented with high-temporal-resolution analyses covering the past 2-3 centuries, as well as for selected intervals representing periods thousands of years ago. We hope that this information is useful to lake managers making decisions on remedial measures with reference to the "natural" state of the lake.

Introduction

Cultural eutrophication of urban lakes is a significant problem worldwide. The tension between shoreline development and the preservation of natural systems leads to expensive and sometimes divisive remediation efforts, the degree of success of which may not be known for years. Monitoring is a time- and labor-intensive effort, which can provide a high-resolution view of lake dynamics, but only on a short time scale. The historical record of lake level, productivity, anoxia, and chemistry, where it exists, is short and incomplete; water quality modelers then have only a few years of data with which models can be compared or validated. Long-term trends are easily masked by year-to-year variability in water quality; natural cycles are extremely hard to detect over the course of a few years, the typical duration of most monitoring projects. However, broad trends exert a significant influence on water quality assessments and remediation efforts.

The study of lakes through their sedimentary records provides a lower-resolution but much longer-term picture of lake evolution: geochemical and biological sediment components provide an array of information about past changes in chemistry, flora and fauna, and water level. In lakes that are annually laminated (varved), a history of the lake year by year may be constructed from this information. Where sediments are not laminated, deposition rates are estimated, and a quasi-annual record is produced.

This study is in the process of generating a high-resolution record in a number of geochemical proxies (stable isotopes, nutrients, minerals, etc.) for the past 200 years in Lake McCarrons, a eutrophic Minnesota urban lake, based on a high-quality sediment core from 16 m water depth. This analysis will be supplemented by approximately

50 additional analyses performed on a 4.1-meter core taken in 1999 that is now curated at the Limnological Research Center (LRC) Core Repository. Combined, these studies will provide the context for long-term (thousands of years) and medium-term (hundreds of years, including >50 years before European settlement) natural variability and rates of change in lake water quality, as well as illuminating trends that had their inception long before any human impact on the lake system.

Analytical work

Water column analyses

During the summers of 2001 and 2002, water samples and basic limnological data were collected every 2-4 weeks. Water samples were taken at three depths in the lake (2 m below the water surface; 1 m above the sediment surface, and ~1 m below the thermocline) for major ions and carbon stable isotopic composition ($\delta^{13}\text{C}$) of dissolved inorganic carbon. At the same time measurements of dissolved oxygen, temperature, and pH were made at selected depths, and Secchi depth was measured.

Sediment analyses

A sediment core from 16 m water depth was used for the study. Before sampling, digital images of the core were taken, and the boundaries between putative annual layers (cyclic packages of one dark [winter] and one light [summer] layer) were marked on these images using Photoshop (see Figure 1). For each layer, at least two smear slides (consisting of a small amount of sediment spread on a microscope slide and embedded in optical cement) were taken: one each from the dark and light layers, and one from any additional visible discrete layers. These slides are used to estimate abundance of sediment components such as algal organic matter, diatoms, and minerals such as calcite (precipitated in the water column) and quartz sand (washed in from the shoreline).

Based on the above determinations of how layers represent individual years' deposition, the laminated portion of the core (the top ~50 cm) was sectioned into 89 pieces, following the contacts between the dark (below) and light (above) layers. Numbered as "v" samples (for "varved," e.g., v01, v02, ..., v89), these are taken to represent the 89 years of sedimentation preceding the year 2000, as the core was taken in the winter of 2000-2001. All of the "v" samples are included in the analyses described below. Below the top ~50 cm, the sediments are massive (i.e., not laminated or poorly laminated). Eighty-four cm of this portion of the core were cut into 0.5 cm sections, and every other sample was analyzed (e.g., 1.0-1.5 cm and 2.0-2.5 cm but not 1.5-2.0 cm). Only data for the "v" samples are included in this report.

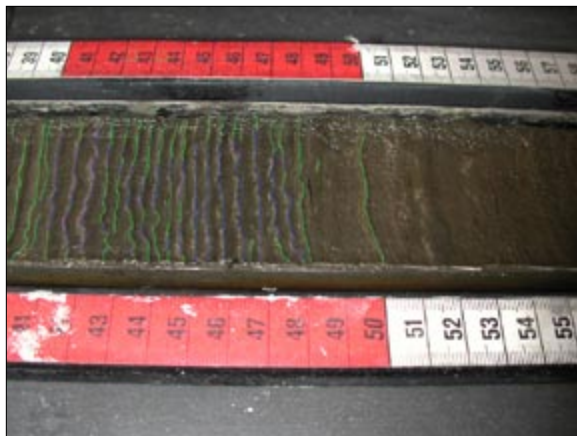


Figure 1. Portion of Lake McCarrons core at McC-01-MP showing demarcations of annual layers. Blue lines indicate clear boundaries; green lines indicate contacts in which we feel less confidence. Note the transition at ~48 cm from laminated to massive sediment.

Sediment analyses conducted thus far include (1) carbon coulometry to determine weight percentage of carbonate, (2) elemental analysis to determine weight percent organic carbon, nitrogen, and sulfur, and (3) stable isotopic analysis to determine $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of carbonate. In progress are (4) biogenic silica measurements to determine weight percent diatom frustules, (5) stable isotopic analysis to determine $\delta^{13}\text{C}$ of organic matter, and (6) scanning electron microscopy (SEM) to investigate size, preservation, and crystallinity of calcite grains over time. The sedimentary phosphorus analysis budgeted in the original proposal has been put on hold because of the consideration that, due to its redox-sensitive mobility and biological importance, it is likely not a true measure of surface-water P concentrations (e.g., Engstrom and Wright 1984). The remaining work, along with an evaluation of the site for an additional study (using fossil diatoms to infer P, Cl, and pH values; discussed later in this report), is slated to be completed during the remainder of the grant period.

Results to date

Because the study is still in the process of generating data, discussion of results and interpretation is limited in scope. The preliminary water and sediment data are nonetheless promising.

Water chemistry

Major ions

The proposal for this study hypothesized that Lake McCarrons is meromictic or oligomictic (completely mixing never or only infrequently). It is well known from Metropolitan Council studies (Met Council 1988, 1997; West-Mack and Stefan 2000a, 2000b) that the lake is strongly thermally stratified during the summer; a thermister chain recording temperatures at 12 depths was deployed for several ice-free seasons. The Met Council reports do not demonstrate conclusively whether or not the lake does completely mix, in part because thermister measurements were sparse in the hypolimnion (on the order of 2-3.5 m spacing rather than the 1 m spacing of sensors in the epilimnion). Concentrations of conservative elements (i.e., those that do not participate in precipitation-dissolution reactions at concentrations found in the lake) such as Cl^- and Na^+ were used in this study as a measure of the degree of mixing of surface and deep waters. If the lake is mixed, and no great quantity of dilute water enters preferentially into any given layer, the concentration of a conservative ion should be the same throughout the water column. As shown in Figure 2, however, Cl^- concentrations are significantly higher in the hypolimnion than in the epilimnion throughout summer 2001 (data for 2002, and for Na^+ in 2001 and 2002, are similar). This suggests that lake bottom waters are not being entrained when the lake overturns in spring and fall. Concentrations of Cl^- throughout the lake are elevated to 20-50 times typical natural values, presumably due to road salt inputs; it is possible that cold overland or wetland runoff high in dissolved road salt plunges into the hypolimnion in the spring, causing these higher hypolimnetic values. High levels of salt in the hypolimnion

may also contribute to the density difference that retards mixing.

$\delta^{13}\text{C}$ of dissolved inorganic carbon (DIC)

In general, $\delta^{13}\text{C}$ values become more positive (“heavier”) under algal productivity (due to preferential uptake of ^{12}C) and more negative (“lighter”) under degradation of organic matter (due to the release of the same light carbon); the $\delta^{13}\text{C}$ value of DIC is also imparted to carbonate minerals and organic matter that become part of the sedimentary record. Figure 3 shows a profile of $\delta^{13}\text{C}_{\text{DIC}}$ values in Lake McCarrons taken on August 9, 2002, and Figure 4 shows the evolution of surface, intermediate, and deep water values for the growing seasons of 2001 and 2002 (end of summer 2002 data are pending). Note the increase of deep water values above intermediate (upper hypolimnion) values: this trend implies microbial methane production in the bottom waters, an indication of severe anoxia.

Sediment analysis

Figure 5 shows results to date of analysis of the laminated portion of the sediment core. These data, when fully compiled, will be compared with historical and climatological data for the area to investigate

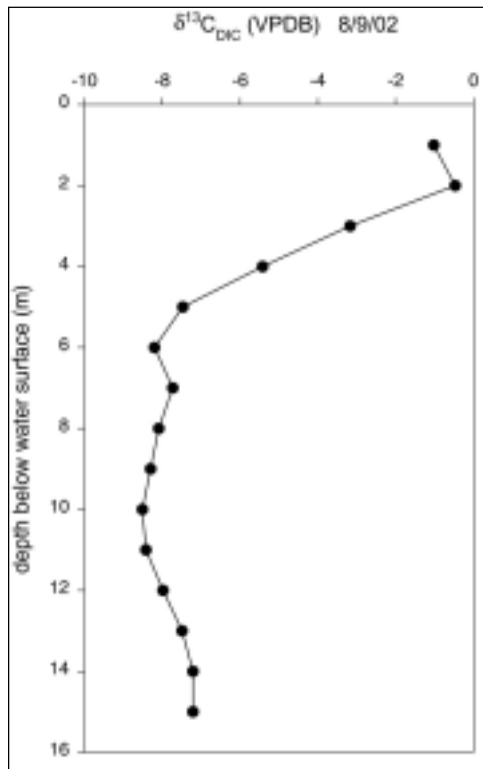


Figure 3. Profile of carbon stable isotopic value of dissolved inorganic carbon in Lake McCarrons

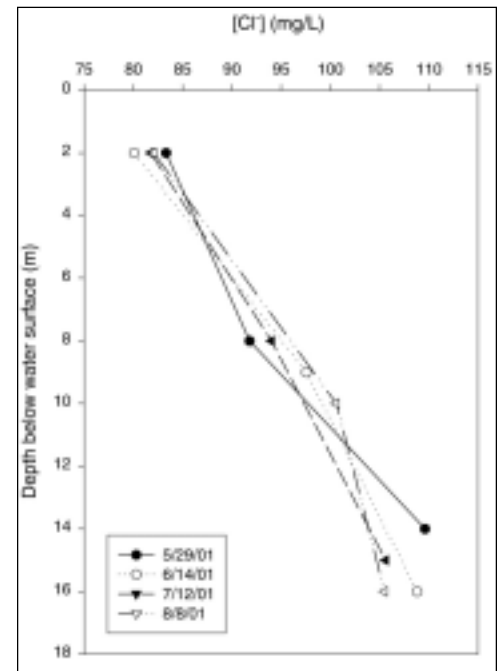


Figure 2. Chloride concentrations in Lake McCarrons

the “fit” and utility of the sediment record for reconstructing prehistoric changes. One important task remaining is the transformation of the percentage data (organic carbon, calcite, and biogenic silica) to accumulation rate data, based on bulk density measurements and incorporation of the “non-v” (unlaminated section) samples of the core. This analysis provides a more realistic

picture of changes in style of sedimentation, as percentage changes may be caused simply by dilution of one component by another. From the data in hand, it is apparent that the lake has undergone cyclic swings in biological productivity over the past century, as shown by variations in the carbon isotopic signature of calcite, and that the

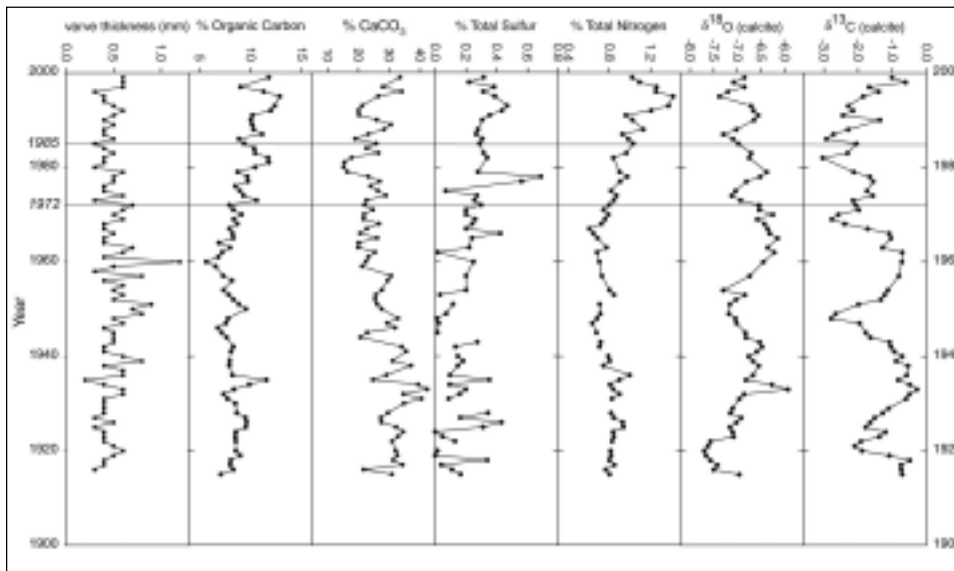


Figure 5. Geochemical and isotopic data from varved section of Lake McCarrons core McC-01-IMP

biogenic silica data (measuring diatom abundance) and the $\delta^{13}\text{C}$ of organic matter (measuring phytoplankton productivity), or both, will show a response to these forcings. As noted above, these analyses are underway.

Student training

Amy Myrbo, Geology and Geophysics Ph.D. candidate, conceived of and wrote the proposal, and is responsible for conducting the project. Two undergraduates, Chris Merkes, a University of Minnesota genetics major, and Aimee Wendt, a St. Cloud State geology major who worked as an intern in the Limnological Research Center during the summer of 2002, have been involved in both field and laboratory work, and Aimee presented a poster on the project at an intern poster session in the geology department in August 2002.

Publications/presentations to date

- LiMNology Retreat February 2001 presentation: “Sedimentary-Historical Context of Eutrophication and Remediation in Urban Lake McCarrons: Would Your Granny Care?”
- Upcoming poster at 3rd International Limnogeology Congress, Tucson, late March 2003, working title “Sedimentary-Historical Context of Eutrophication and Remediation in Urban Lake McCarrons.”

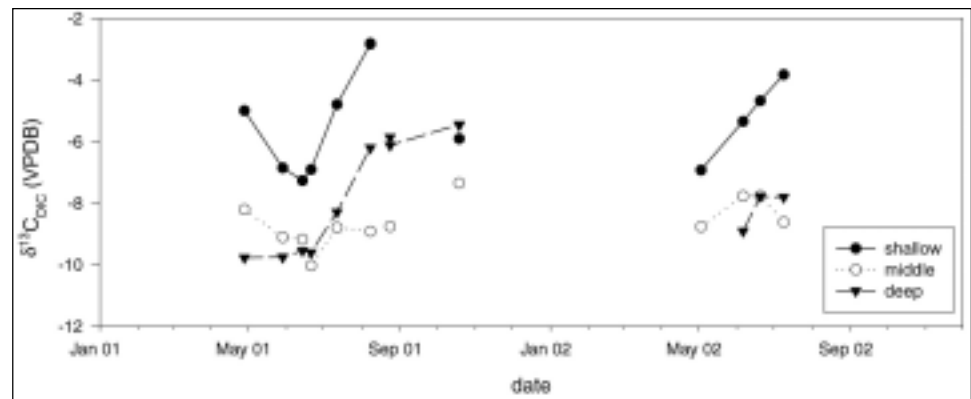


Figure 4. Seasonal changes in carbon stable isotopic value of dissolved inorganic carbon in Lake McCarrons

$\delta^{13}\text{C}$ values are as high in the most recent sediments of the core as the highest values recorded during the century. Note that neither the passage of the Clean Water Act in 1972 (which in some other lakes is a significant event in the sedimentary record) nor the installation in 1985 of a detention pond to trap inflowing nutrients appears to have had any immediate effect on the state of the lake as recorded in the sedimentary components plotted here. This apparent lack of response warrants further study, but it is likely that the

- Informal presentation on thesis research, of which this project is a major component, at evening Quaternary Paleoecology seminar, April 2001.

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A Novel in situ technology for the treatment of groundwater contaminated with agriculturally-derived nitrate

Basic Information

Title:	A Novel in situ technology for the treatment of groundwater contaminated with agriculturally-derived nitrate
Project Number:	2001MN3382B
Start Date:	3/1/2001
End Date:	2/28/2002
Funding Source:	
Congressional District:	5
Research Category:	
Focus Category:	Nitrate Contamination, Treatment, Groundwater
Descriptors:	Biodegradation, Denitrification, Autotrophic, Membranes, Gas Transfer
Principal Investigators:	Paige J Novak, Michael J Semmens

Publication

A novel in-situ technology for the treatment of groundwater contaminated with agriculturally-derived nitrate

Paige Novak, Assistant Professor and PI, **Michael J. Semmens**, Professor, **Katrina Haugen**, Research Assistant, Department of Civil Engineering, University of Minnesota

Funding source: USGS-WRRI 104B National Grants Competition and the Center for Agricultural Impacts on Water Quality

Project duration: March 1, 2000 to February 28, 2002

Summary

A novel *in situ* membrane technology was developed to remove nitrate (NO_3^-) from groundwater. Membrane-fed hydrogen gas (H_2) was used as an electron donor to stimulate denitrification. A flow-through reactor fit with 6 hollow-fiber membranes (surface area = 93 cm^2) was designed to simulate groundwater flowing through an aquifer with a velocity of 0.3 m/day . This membrane technology supported excellent NO_3^- and nitrite (NO_2^-) removal once H_2 and carbon limitations were corrected. The membrane module achieved a maximum H_2 flux of $1.79 \times 10^{-2} \text{ mg H}_2/\text{m}^2\text{-s}$, which was sufficient to completely remove 16.4 mg/L NO_3^- -N from a synthetic groundwater with no NO_2^- accumulation. In addition, this model *in situ* treatment process produced a high quality water containing less than 0.5 mg/L total organic carbon.

Introduction

The experiments described within this report were designed to evaluate the use of *in situ* hydrogenotrophic denitrification for remediating NO_3^- -contaminated groundwaters. Denitrifying bacteria were cultured from soil from the University of Minnesota St. Paul agricultural station. Denitrifying cultures were started June 23, 2000 by adding 50 grams of soil to 100 ml of anoxic synthetic groundwater media. A series of microcosm experiments were performed to develop denitrifying cultures that could use H_2 to reduce NO_3^- .

To evaluate hydrogenotrophic denitrification *in situ* using hollow fiber membranes, a flow-through box reactor was constructed as shown in Figure 1. The box was designed to simulate groundwater flow through an aquifer. The central rectangular test section measured 2.5 cm in width, 1.83 m in length, and 0.304 m deep and was packed with aquarium rocks (Estes' Ultrastone) and soil from the University of Minnesota to simulate *in situ* conditions. Additional tapered inlet and exit sections measuring 0.3 m in length were designed to promote uniform flow in the

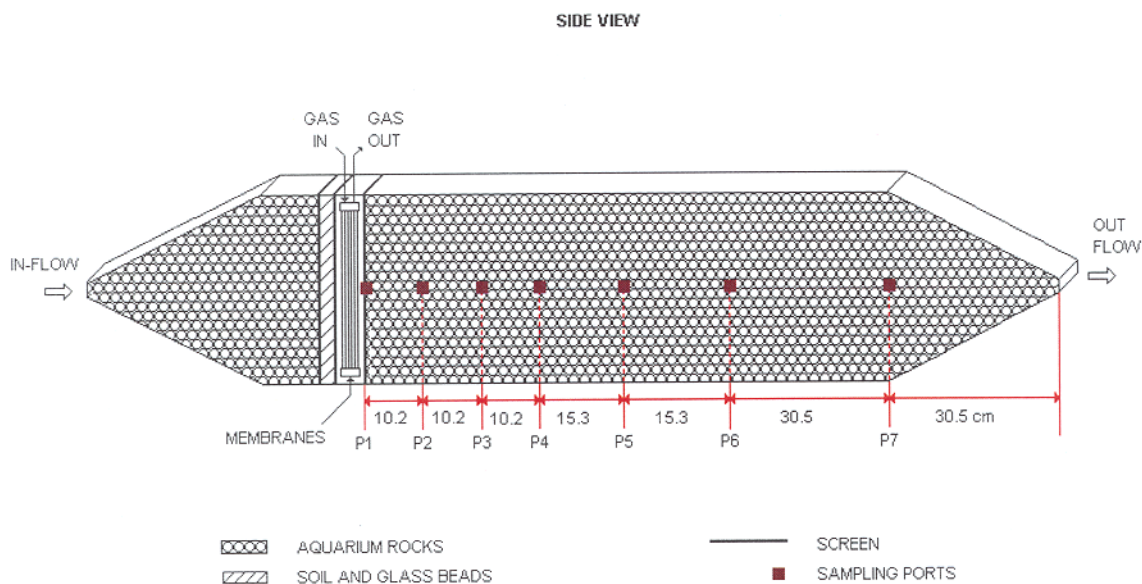


Figure 1. Schematic of flow-through reactor

central test section. The 14.2L reactor was equipped with a removable lid. The lid contained two holes to supply H_2 to the membrane module. The membrane module consisted of six reinforced silicone hollow fiber membranes. Seven gas-tight sampling ports were installed at mid-depth along the length of the reactor for sample collection.

Methylene blue tracer studies were conducted on the box and it was shown that the water moved through the box uniformly in a plug-flow manner.

Prior to the flow-through experiments the reactor was seeded with buffered synthetic groundwater containing an active culture of denitrifying bacteria was allowed to stand for a week. A synthetic, slightly oxic ($2 \text{ mg O}_2/\text{L}$) groundwater flow was then pumped through the reactor at a rate of 1.6 ml/min . For three weeks medium was pumped through the reactor without the addition of H_2 . After three weeks the membrane module was supplied with 100 % H_2 at a gas flowrate of 0.5 ml/min .

Liquid samples were collected weekly from the reactor sample ports P1 – P7. P1 was located 1 cm downgradient of the membranes. P7 was approximately 93 cm downgradient of the membranes. NO_3^- and NO_2^- concentrations were measured using ion chromatography. Dissolved H_2 concentrations were determined by gas chromatography. Influent and effluent samples were also analyzed weekly for total organic carbon (TOC), pH, redox potential and protein content.

Results

The study successfully demonstrated that the membrane modules could supply H_2 to groundwater in sufficient concentration to effectively remove NO_3^- and NO_2^- at concentrations as high as 16.4 mg N/L . The dissolved H_2 concentration is shown as a function of operating time in Figure 2. The H_2 concentration dropped to very low level between days 25 and 60, indicating that the system was probably H_2 -limited during this period, but after the H_2 gas pressure was elevated to 1.44 atm, high residual dissolved H_2 concentrations were observed.

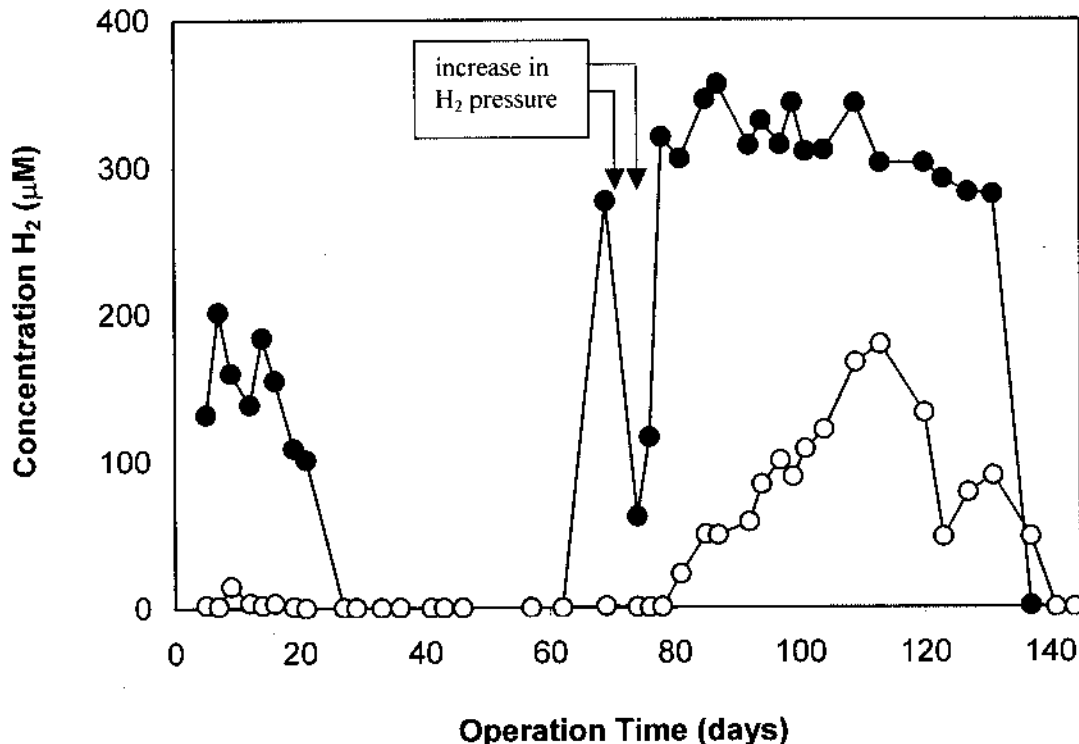


Figure 2. Dissolved H_2 concentration at sampling ports 1 and 7. Symbols are: ● port 1 and ○ port 7.

The reactor required time to develop a microbial population capable of effective NO_3^- and NO_2^- removal (Figure 3). Nevertheless, in this study we were able to demonstrate that both NO_3^- and NO_2^- were effectively

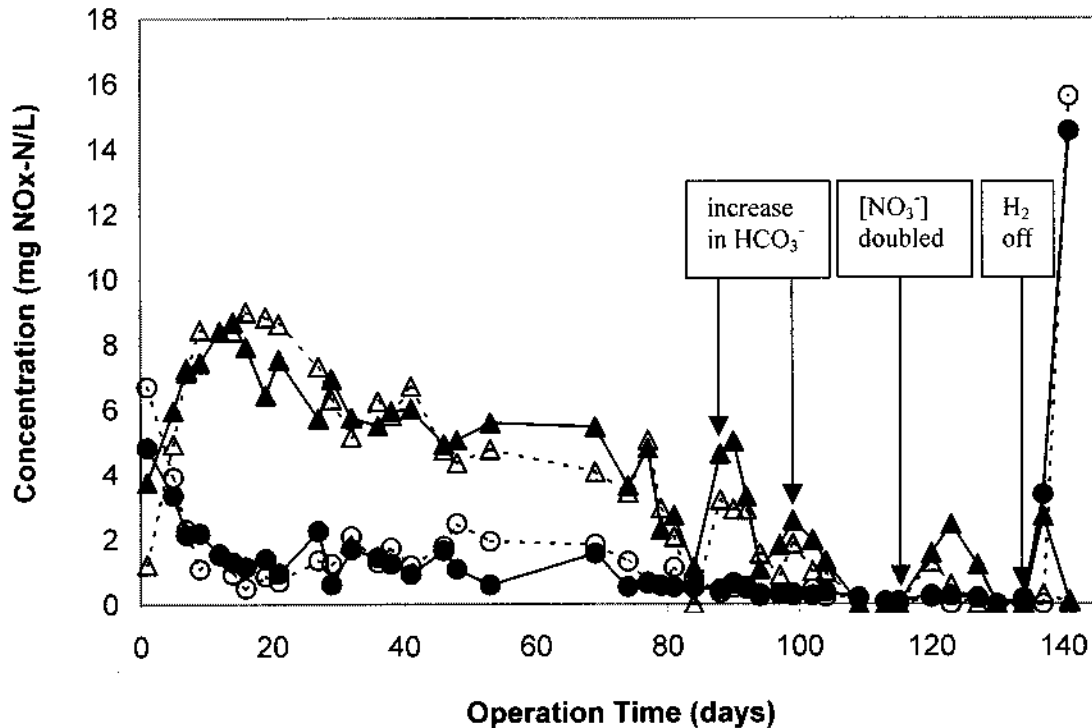


Figure 3. NO_3^- and NO_2^- concentration at sampling ports 1 and 7. Symbols are: ● NO_3^- at port 1, ○ NO_3^- at port 7, ▲ NO_2^- at port 1, △ NO_2^- at port 7.

removed *in situ* by biological denitrification. The majority of the NO_3^- degradation occurred within a few centimeters of the membrane module, removing 169 mg N/h per m^2 of membrane. The variability in performance and the time required to achieve full removal was influenced by operating conditions, namely the H_2 pressure and the concentration of HCO_3^- in the reactor. The system was H_2 and carbon dioxide limited for some time. Once this was recognized and corrected, excellent performance was achieved. This implies that in the field a carbon source (such as carbon dioxide) may need to be added for effective remediation, although in most situations adequate alkalinity (>90 mg/L as CaCO_3) would be present.

The aquarium rock media in the test reactor provided a support for biological growth as well as filtration capacity. Effluent water analyses indicated that the TOC rose by only about 0.5 mg/L as a result of denitrification. This low effluent TOC likely resulted from soluble microbial products and transported biomass. It is reasonable to expect that the product water would improve even more if it had a longer travel path through real aquifer material, which should be more effective in adsorbing and filtering organic matter and biomass than aquarium rocks.

These results indicate that there is merit in pursuing the use of membranes for the *in situ* injection of H_2 gas as a NO_3^- remediation technology. The membranes can deliver sufficient H_2 to stimulate *in situ* denitrification in a safe and controlled fashion. In addition, as the denitrified water flows through the aquifer to a water supply well, processes such as filtration, adsorption and continued biological action will serve to improve the water quality further.

Summary and future research

This seed research project was extremely successful. We were able to demonstrate that the process works effectively and has little impact on groundwater quality. Drs. Novak and Semmens used these early results to apply for follow-on funding from the State of Minnesota, Legislative Commission on Minnesota's Resources. They received \$230,000 in funding in July, 2001 for a field trial. The field trial is currently in progress in Becker Minnesota. The funding obtained from the State of Minnesota was due in part to the successful completion of this WRRI project.

Publications/ presentations

Katrina Haugen, a civil engineering graduate student, conducted this research for her MS thesis project. She graduated in June, 2001 after defending her thesis, titled "A Novel *In Situ* Technology for the Treatment of Nitrate Contaminated Groundwater." Her thesis research has been accepted for publication and is currently in press (Haugen, K. S., Semmens, M. J., and Novak, P. J. 2002. "A Novel *In Situ* Technology for the Treatment of Nitrate Contaminated Groundwater." *Water Research*, in press).

Paleohydrologic response of the Mississippi Headwaters watershed to Holocene climate change

Basic Information

Title:	Paleohydrologic response of the Mississippi Headwaters watershed to Holocene climate change
Project Number:	2001MN3421B
Start Date:	3/1/2001
End Date:	2/28/2003
Funding Source:	
Congressional District:	8th
Research Category:	
Focus Category:	Hydrology, Climatological Processes, None
Descriptors:	paleoclimatology, Mississippi Headwaters, sediment cores, Paleohydrology
Principal Investigators:	howard.d.mooers.1

Publication

Paleohydrologic response of the Mississippi Headwaters Watershed to Holocene climate change

H.D. Moors, Associate Professor and PI, (hmoors@d.umn.edu) and **P.C. Larson**, Research Assistant, Department of Geological Sciences, College of Science and Engineering, University of Minnesota, Duluth

Project duration: March 1, 2001 to June 30, 2003

Funding source: USGS-WRRI 104B National Grants Competition and the Water Resources Center

Summary

This study examines the sedimentary record of major changes in the hydrologic budget of three large lakes in the Mississippi Headwaters area (Cass, Leech, and Winnibigoshish) resulting from multiple diversions of the Mississippi River and its tributaries. Sediment cores collected from Cass and Leech Lakes, in combination with a core previously collected from Lake Winnibigoshish, provide a record of the effects of regional-scale climate-driven changes on the hydrology of the Mississippi Headwaters watershed. The lakes' hydrologic budgets were affected by a series of diversion events that altered the main course of the Mississippi, and altered the watershed areas and throughflow rates of the three lakes.

One of the diversion events is recorded as a prominent, abrupt change in the nature of carbon sedimentation in Lake Winnibigoshish. However, this and other diversion events are not apparently discernable in Cass and Leech Lake sediments. The cause of the radically different response of Winnibigoshish to a diversion event is still enigmatic; however, it implies the existence of an as yet unidentified control on the nature of lacustrine carbon sedimentation.

Ongoing geochemical, stable isotope, and diatom-nutrient calibration work will help distinguish the effects of climate-forced hydrologic variability from those of nutrient loading on sedimentation in the large Headwaters lakes.

Introduction

Most previous paleolimnological investigations in Minnesota have focused on interpreting the sedimentary records of relatively small lakes in small watersheds (Bradbury and Dean 1993, Winter 1997). While the high-resolution records found in these lakes are of undoubted value in interpreting past climatic and vegetation history, they are to some extent extremely sensitive to local conditions not reflective of the region as a whole (c.f. Schwab and Dean 2002). In contrast, the sedimentary records of the largest lakes in a drainage basin might be expected to record a regional-scale signal of climate change. This study examines the sedimentary record of major changes in the hydrologic budget of three large lakes in the Mississippi Headwaters area due to multiple diversions of the Mississippi River and its tributaries.

During the late Holocene, drainage patterns in the Mississippi Headwaters underwent a number of realignments. Prior to circa 3000 years before present (3 ka bp), the main stem of the Mississippi River flowed from Lake Bemidji to Leech Lake, thence down the present-day Leech Lake River. The outlet of Lake Winnibigoshish flowed southward to the Leech Lake River, and Cass Lake's outlet flowed south to Leech Lake. After this time, three stream piracy events led to diversion of major portions of the watershed into a new Mississippi River channel. The Mississippi now flows from Lake Bemidji through Cass and Winnibigoshish, exiting Winnibigoshish by a new eastern outlet. Leech Lake lies in a much diminished watershed, and continues to drain toward the east.

During the mid-Holocene, Cass and Leech Lakes were characterized by large watershed:lake area ratios, while Winnibigoshish had a small one. This condition led to evaporation-forced hydrologic closure of Winnibigoshish, lower lake levels, eolian erosion of bottom sediment, and development of a dunefield on the eastern shore of the lake. These geomorphic relationships, and their implications for the paleohydrologic budgets of the lakes, indicates strong linkages exist between climate, hydrology, landforms, and the sedimentary records of the lakes.

Methods

Coring

Cass and Leech Lakes were cored in August 2001 using the University of Minnesota Limnological Research Center's ETH-Kullenberg system, a raft-mounted piston corer designed for use in deep water. Recovered cores are

9-cm in diameter. On both lakes, the coring location was the deepest part of the lake.

A 640-cm core was recovered from 44-m water depth in Walker Bay of Leech Lake. Sediment in this portion of the lake has a relatively high clastic component and corresponding high density, resulting in incomplete penetration of the coring device. However, the key late Holocene portion of the sediment record was completely sampled.

A 351-cm core was recovered in 34-m water depth in the northern portion of Cass Lake. Although short, this core terminates in glaciofluvial gravel and likely represents a complete postglacial section.

Lake Winnibigoshish was previously cored using a modified Livingston corer. A 575-cm core was recovered in 20-m water depth. Similar to Leech Lake, sediment in the lower portion of the sequence has a relatively high clastic component and corresponding high density, resulting in the inability to recover a complete postglacial section. However, the key late Holocene portion of the sediment record was completely sampled.

Sediment dry bulk density

Sediment dry bulk density was determined by weighing 1-cm³ samples of water-saturated sediment, freeze-drying, and weighing of the dried sediment. Sediment water content (porosity) corresponds to water loss during drying, and dry bulk density to the mass of dried sediment divided by the original volume.

Magnetic susceptibility

Whole-core magnetic susceptibility for all three cores was measured at the Limnological Research Center, University of Minnesota. Magnetic susceptibility is a proxy measurement for the relative amount of clastic material in the sediment.

Carbon analyses

Inorganic carbon and total carbon content of sediment from the recovered core was determined by coulometry at the Large Lakes Observatory, University of Minnesota Duluth. The organic carbon content of sediment is calculated by subtracting the inorganic from the total carbon content.

CHNS analyses

Sediment total carbon, nitrogen, sulfur, and hydrogen contents are being analyzed using a LECO at the Large Lakes Observatory, University of Minnesota Duluth. Results of these analyses will allow assessment of the origin of organic carbon stored in the lakes' sediments.

Diatom nutrient calibration

Diatom analysis of sediment samples from all three lakes is being conducted by J. Kingston at the Natural Resources Research Institute, University of Minnesota Duluth.

Results to date

Core stratigraphy

The Lake Winnibigoshish core consists of 300 cm of silty marl in the basal (pre-diversion) interval. The diversion event is recorded as the abrupt appearance of fine-grained sand in the sediments, marking the beginning of a 28-cm thick clastic-rich fining-upward sequence. The upper 247 cm of the core are black sapropel.

The Leech Lake core recovered 640 cm of silty marl occasionally interrupted by minor beds rich in detrital organic material, and thin sand lenses. The Cass Lake core recovered 351 cm of organic-rich marl. No abrupt changes in the nature of sedimentation were recorded in either lake's sediments.

Carbon coulometry

Cass and Leech Lake sediments have relatively low organic carbon contents, while the pre-diversion interval in the Winnibigoshish core has very low organic carbon, contrasted by very high organic carbon in the post-diversion interval (Figure 1a). Cass and Leech Lake sediments are characterized by relatively high carbonate contents, while Winnibigoshish has high carbonate in the pre-diversion interval succeeded by relatively low carbonate contents (Figure 1b).

Magnetic susceptibility

Leech Lake sediments have the overall highest magnetic susceptibility of the three lakes, reflecting relatively abundant influx of silt to Walker Bay (Figure 2). Of particular interest are peaks at 260, 434, 450, 480, and 501 cm core depth. These coarser-grained, clastic-rich intervals likely represent mass flows, perhaps in response to lake level instability.

Cass Lake sediments have very low magnetic susceptibility, reflecting the very low input of clastic sediment to the northern basin of the lake through the Holocene. This is despite evidence that mid-Holocene lowstands may have resulted in significant sediment redistribution from the littoral zones of the lake.

Lake Winnibigoshish sediments have relatively high magnetic susceptibility in the pre-diversion interval, suggest-

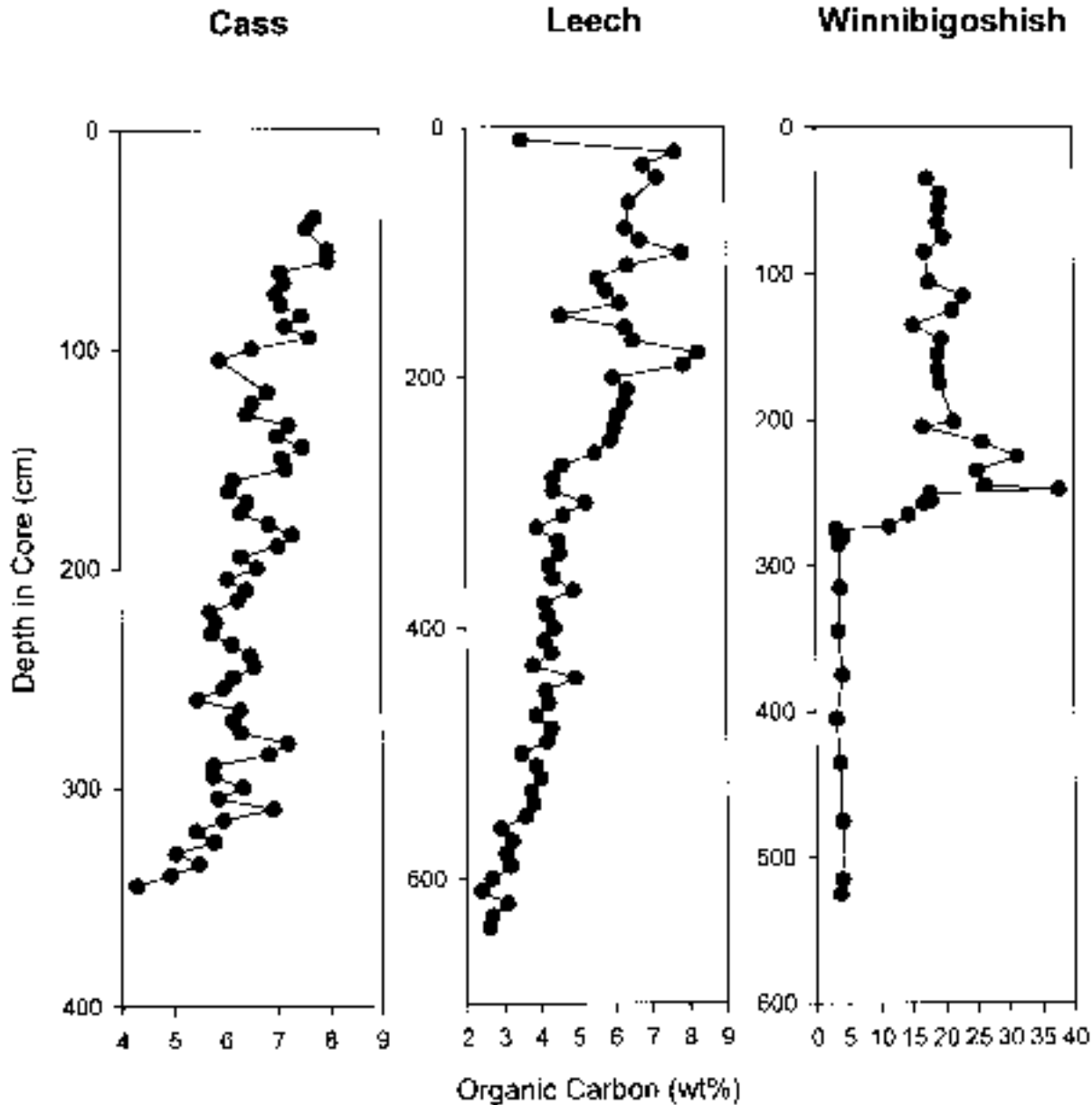


Figure 1a. Organic carbon content profiles for Cass, Winnibigoshish, and Leech Lakes.

ing fluctuating lake levels may have resulted in a small, but steady, influx of silt from the littoral zone to the deep basin. These magnetic susceptibility peaks are absent in the post-diversion interval, suggesting lake level, and therefore the shoreline, was stable through this period.

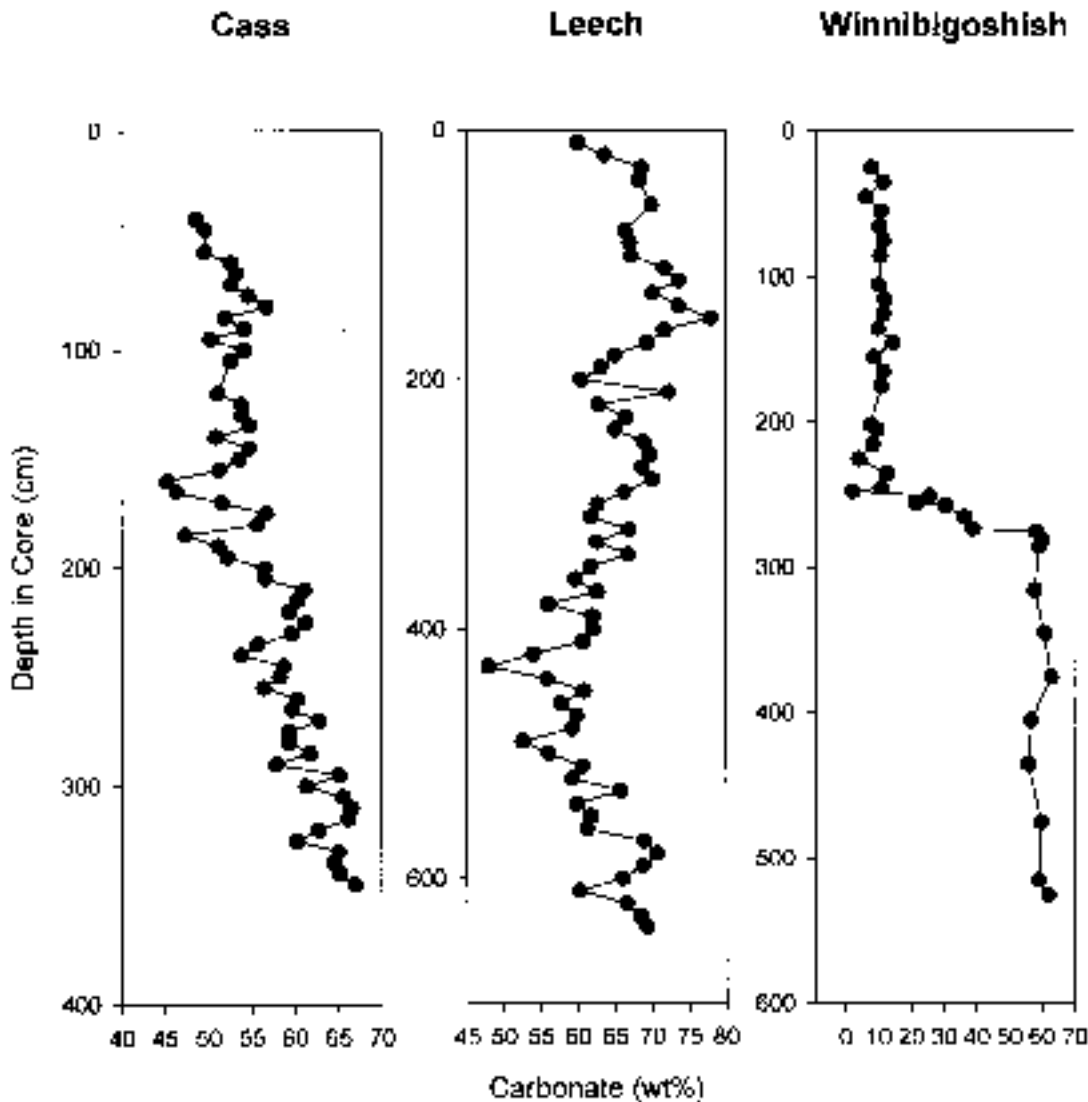


Figure 1b. Carbonate content profiles for Cass, Winnibigoshish, and Leech Lakes.

Description of ongoing work

As described above, results of diatom-nutrient calibration and CHNS analyses are pending. In addition, some of the radiocarbon dates for the sediment cores are still pending. Final results will complete the geochemical picture of the evolution of these large lakes during the Holocene.

Stable isotope analyses

The carbon and oxygen stable isotope compositions of ostracod and marl carbonate found in the lake sediments will be performed in 2003.

Diatom-nutrient calibration

Diatom population concentration and taxa will be counted, and the resulting data integrated with existing and ongoing diatom-nutrient calibration data for the Minnesota region (Kingston et al. 1990, Ramstack 1999, Kingston 2002). This diatom-nutrient calibration set references diatom abundance and taxa in modern bottom sediments to a variety of water-quality parameters, including water turbidity, Secchi transparency, color, and dissolved silica, chlorophyll-a, phosphorus, and nitrogen contents. The results of these analyses will be used to assess long-term changes in the nutrient status of the three Headwaters lakes. Particular emphasis is being placed on quantifying changes in nutrient status corresponding to transitions in the nature of sedimentation recognized in the cores.

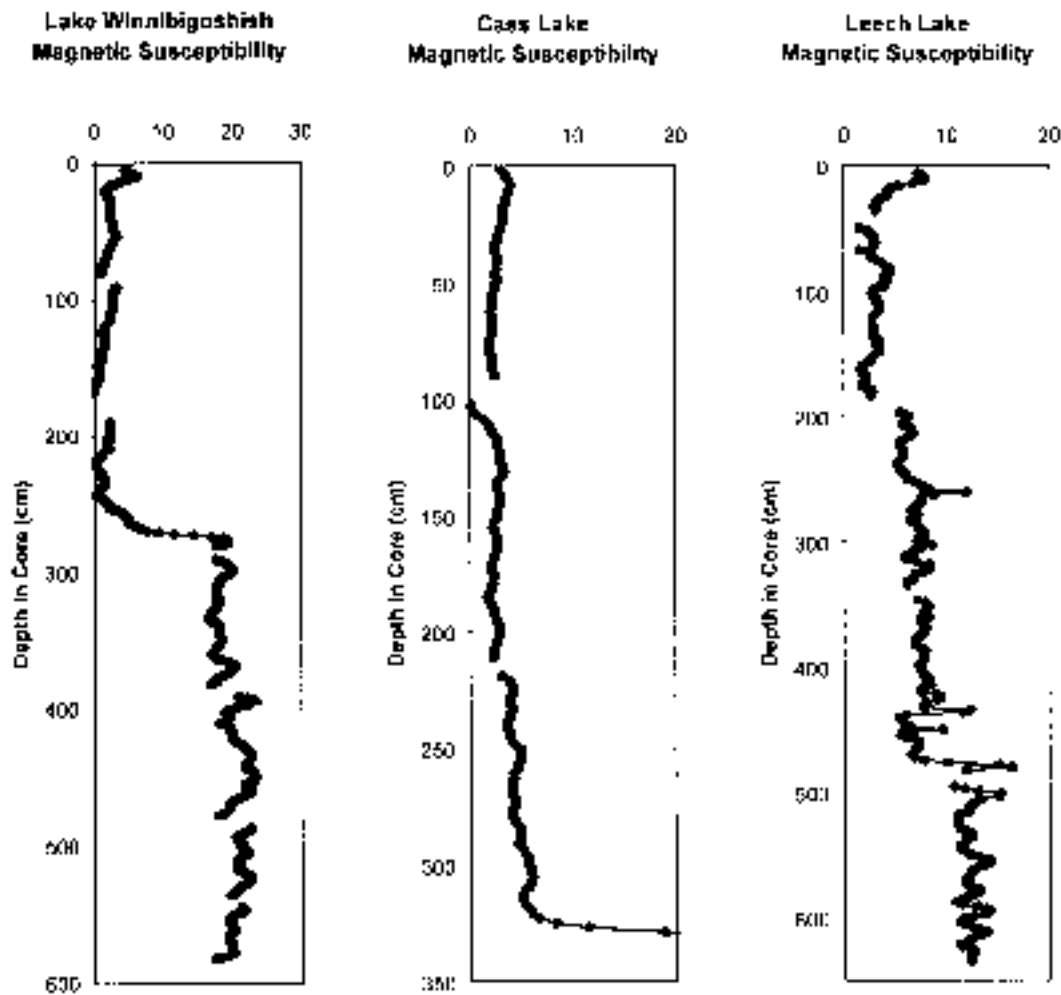


Figure 2. Magnetic susceptibility profiles for Cass, Winnibigoshish, and Leech Lakes. Units SI.

Sedimentology

Two undergraduate research projects by University of Minnesota- Duluth students investigating the sedimentology of Lake Winnibigoshish and its surroundings have been initiated in conjunction with this project:

K. Smith will examine the carbonate mineralogy of the lower portion of the Lake Winnibigoshish core by X-ray diffraction in an effort to determine if evaporative controls on carbonate sedimentation were present. The carbonate mineralogy of lacustrine sediment is often a function of salinity; low-salinity waters precipitate low-Mg calcite, while increasing salinity favors precipitation of high-Mg calcite or aragonite. Presence of high-Mg calcite or aragonite in Winnibigoshish's sediments will provide strong evidence of hydrologic closure and evaporative concentration of the lake prior to diversion of the Mississippi River into its watershed.

R. Smith is examining the sedimentology of eolian sediments in the Headwaters area to determine the extent of eolian activity in the mid-Holocene Winnibigoshish Dune Field. While Grigal and others' (1976) radiocarbon dates have firmly established the presence of eolian activity adjacent to Lake Winniboshish during the mid-Holocene, the areal extent of this activity is unknown. Comparing sediment characteristics and dune morphology of known mid-Holocene and known early Holocene (immediate post-glacial) dunes will allow assessment of the area of the Winnibigoshish Dune Field and volume of sand active during the mid-Holocene. This, in turn, will allow a more

precise reconstruction of the effects of mid-Holocene aridity on the lake's hydrologic budget.

Summary of important findings

In Lake Winnibigoshish, diversion of the Mississippi River into the basin and the corresponding increased throughflow rate is accompanied by a radical shift in the nature of carbon sedimentation in the lake, from entirely carbonate to entirely organic carbon. Pre-diversion sediments in the core have very little organic carbon (3-4%) and carbonate contents of 60%. Post-diversion sediments have organic carbon contents of ~20% ranging up to 37%, and carbonate contents generally <12%.

However, a similar diversion and increase in throughflow rate of Cass Lake is not reflected in its carbon sediment record. Similarly, complementary decreases in the throughflow rate of Leech Lake are not reflected in its carbon sediment record. Cass Lake sediments record a gradual increase in organic carbon content from 5-8%, and a complementary decrease in carbonate from 65-50%. In Leech Lake, sediments record a gradual, steady increase in organic carbon from 2-8%, while carbonate varies from 48-78%. This pattern is similar to those reported by Dean (1999) in numerous lakes in Minnesota.

Dean (1999) has suggested that the shift from carbonate to organic carbon preservation in lake sediments is driven by increasing primary productivity. The transition in Lake Winnibigoshish is the most rapid reported in any lake in Minnesota. A 1-cm thick layer of nearly pure organic material in the core immediately following the diversion event suggests diversion was accompanied by increased nutrient loading. However, while the instantaneous increase in watershed area may have delivered increased nutrients to the lake, the presence of Cass Lake serving as a nutrient sink just upstream argues against this hypothesis. Alternately, pre-diversion carbonate sedimentation in Winnibigoshish may have been forced by evaporative concentration of lake water, a condition that was relieved with the initiation of increased throughflow. Results of the diatom-nutrient calibration study will help distinguish between these two hypotheses.

Our results suggest that the nature of lacustrine carbon sedimentation is controlled in part by a threshold condition, one which has not been reached in most lakes in Minnesota, including Cass and Leech Lakes. The incremental increase and decreases in throughflow experienced by Cass and Leech during the late Holocene were apparently not of sufficient magnitude to trigger radical change in carbon sedimentation, while the increase experienced by Winnibigoshish was. This suggests that future climate-induced hydrologic changes in the Mississippi Headwaters basin, rather than being gradually manifested, may be characterized by rapid onset of perturbation of lacustrine ecosystems.

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Fluorochemicals in Minnesota Waters: An Emerging Environmental Issue

Basic Information

Title:	Fluorochemicals in Minnesota Waters: An Emerging Environmental Issue
Project Number:	2001MN3441B
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End Date:	2/28/2003
Funding Source:	
Congressional District:	4th, 5th
Research Category:	
Focus Category:	Toxic Substances, Water Quality, None
Descriptors:	environmental levels and sources, water, PFOS, perfluorooctanesulfonate
Principal Investigators:	matt.f.simcik.1

Publication

Fluorochemicals in Minnesota waters: An emerging environmental issue

Matt F. Simcik, Assistant Professor and PI, (simci001@umn.edu), **Kelly J. Dorweiler**, Research Assistant, Division of Environmental & Occupational Health, School of Public Health, University of Minnesota

Funding source: USGS-WRRI 104B National Grants Competition and the Center for Agricultural Impacts on Water Quality

Project duration: January 31, 2001 to January 30, 2003

Summary

Perfluorochemicals are an emerging class of global concern. To date the only established methods for their determination in environmental samples have been LC/MS/MS and ^{19}F NMR, requiring expensive equipment. In order to open the field of investigation to a broader range of environmental laboratories, we developed a single quadrupole LC/MS method for the determination of perfluorochemicals in environmental samples employing a fluorinated silica gel column for the removal of chromatographic interference. This method has been validated for fish tissue and surface water samples. In addition to method development we have collected water, sediment and fish tissue samples to test several hypotheses. Our overall hypothesis is that the global distribution of perfluorochemicals is due to atmospheric transport. We therefore sampled a group of small lakes that are expected to only be subject to atmospheric sources. Preliminary results indicate the presence of one perfluorochemical, perfluorooctane sulfonate (PFOS), in livers from northern pike from Agnes Lake, supporting our hypothesis that atmospheric deposition is responsible for transport of perfluorochemicals to the environment. We have also collected water samples from several lakes, rivers and waste water treatment plants to determine spatial distributions in Minnesota waters and identify specific sources such as waste water treatment plants and/or urban areas.

Introduction

Fluorochemicals represent an emerging issue of environmental concern due to their global distribution, persistence and bioaccumulation. It is the hypothesis of this project that their global distribution is a result of atmospheric transport. The objectives of this project are to establish baseline data on the concentrations of these chemicals in surface waters and sewage treatment effluent around the state of Minnesota, and use spatial heterogeneity to infer source areas and transport mechanisms. A group of lakes under study are located in Voyageurs National Park with no industry or surface water inflow from industrial areas. By detecting fluorochemicals of interest in these lakes, where the only possible source is atmospheric deposition, we will directly test our hypothesis.

Table 1.

Lake	County	Geographic Region	Media	Date Sampled
Locator	St. Louis	remote	water & fish	5/24/01
Loiten	St. Louis	remote	water	5/24/01
Shoepack	St. Louis	remote	water	5/23/01
Jorgens	St. Louis	remote	water	5/23/01
Agnes	St. Louis	remote	water & fish	5/23/01
Little Trout	St. Louis	remote	water & fish	5/24/01
Fish Trap	Morrison	agricultural	water	8/18/01
Itasca	Clearwater	remote	water	8/22/01
Minnetonka	Hennepin	suburban	water	6/3/01
			water	7/12/01
			water	8/16/01
			water	5/19/02
Mississippi River	Hennepin	urban	water	6/24/02
Lake Calhoun	Hennepin	urban	water	6/24/02
Lake of the Isles	Hennepin	urban	water	6/24/02

Results to date

To date, we have sampled several surface waters in Minnesota (Table 1), and sampled the remaining lakes, rivers and sewage treatment plants from our original list in the fall of 2002. At this time we have analyzed water from Lake Minnetonka, and fish from Lake Erie and Agnes Lake in Voyageurs National Park. We have detected both perfluorooctanesulfonate (PFOS) and perfluorooctanoic acid (PFOA) in the water sample and PFOS in most of the fish samples.

Significant chromatographic interferences from dissolved organic carbon in the water samples and biological molecules from the fish samples occurred without prior liquid-solid chromatography. These interferences are a problem only with single quadrupole LC/MS because we are unable to monitor the transition from parent to daughter ions, as is possible with more expensive instrumentation used for LC/MS/MS. Therefore we have developed an analytical chemistry method to clean-up environmental samples and make them amenable to single quadrupole LC/MS.

Our inspiration for separating the interferences from the fluorochemicals comes from synthetic organic chemistry where fluorinated compounds are removed from nonfluorinated compounds using fluorous silica gel. The theory is that the fluorous silica gel will selectively retain fluorinated compounds, but release them with the appropriate solvent. We have been successful in our attempts to separate perfluorochemicals from environmental matrices using this technique and have recently submitted for publication the results from the fish samples. Figures 1 and 2 illustrate the efficiency of fluorous silica gel to separate fluorochemicals from environmental interferences. Results of the

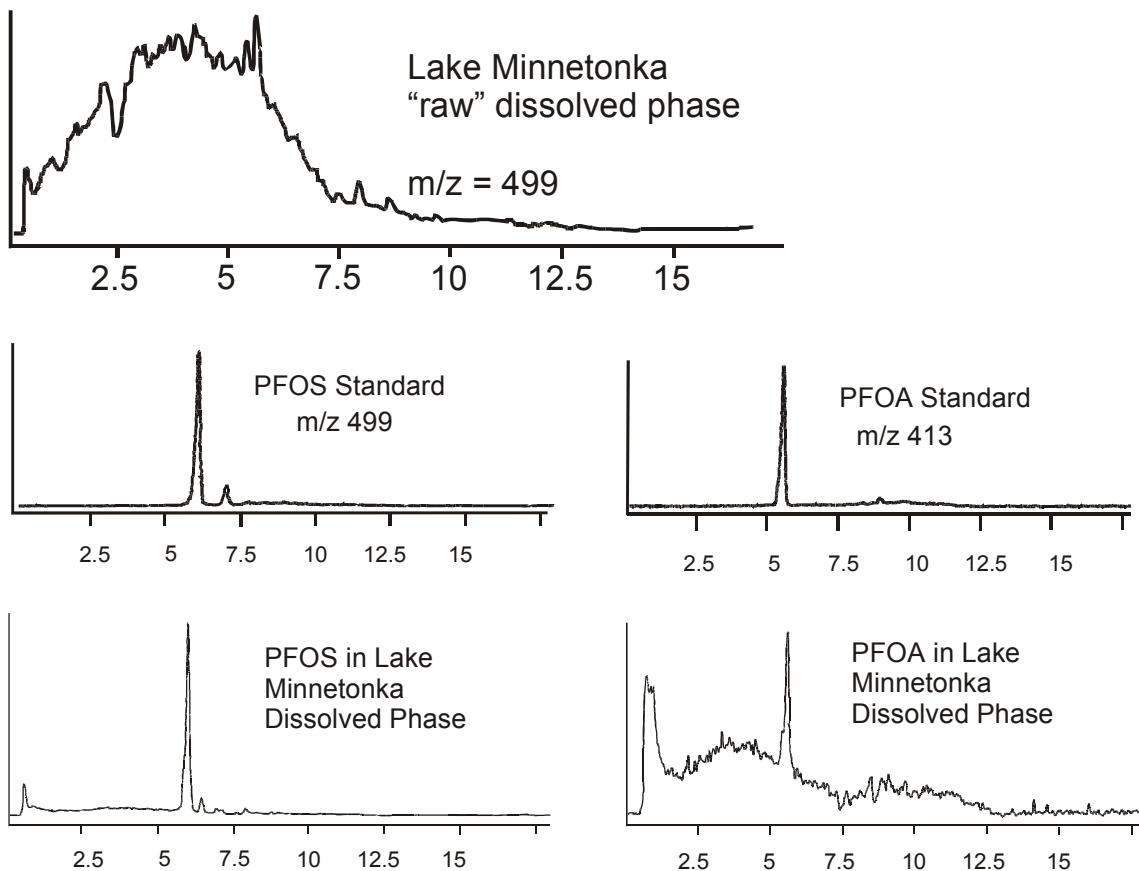


Figure 1. LC/MS chromatograms comparing "raw" water extracts and "cleaned-up" water extracts from Lake Minnetonka.

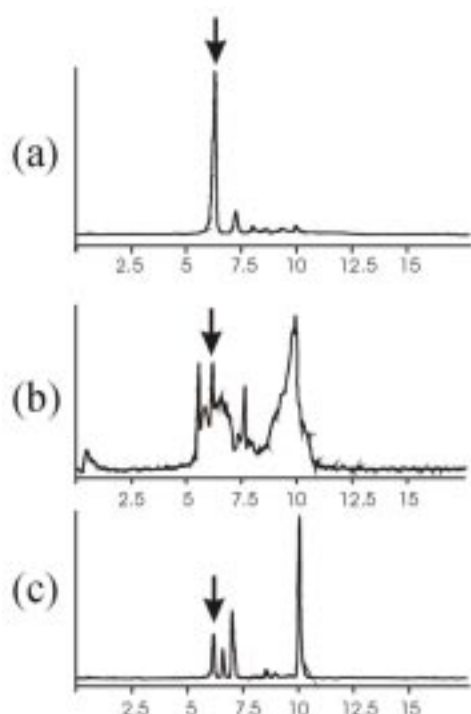


Figure 2. Lake Erie walleye extracts analyzed by HPLC-ES/MS: (a) extracted ion chromatogram of PFOS standard with parent ion 499; (b) extracted ion chromatogram of uncleaned fish extract with m/z of 499; (c) extracted ion chromatogram of cleaned fish extract by fluorour silica gel. Arrows indicate PFOS peaks. From: Dorweiler and Simcik, in review.

samples analyzed to date are summarized in Table 2.

Ongoing work

Our next step is to continue collecting surface water samples from around the state of Minnesota. During fall and winter we will analyze these samples, as well as the associated filters and sediment samples, to determine the partitioning of perfluorochemicals.

Summary of important findings

The successful development of a method conducive to single quadrupole liquid chromatography mass spectrometry (LC/MS) will enable many more investigators to study the environmental chemistry of the emerging contaminant class of perfluorochemicals.

List of publications and presentations

Dorweiler, K.J. and M.F. Simcik. 2002. Detection and Quantitation of Perfluorinated Chemicals in Fish Samples Using Single Quadrupole LC/MS *Environmental Science & Technology* (submitted)

Dorweiler, K.J. and M.F. Simcik. 2002. Detection and Quantification of Perfluorinated Chemicals in Surface Waters, International Association for Great Lakes Research 45th Conference on Great Lakes Research, Winnipeg, MB June 2-6, 2002

Dorweiler, K.J. and M.F. Simcik. 2002. Analysis of Minnesota Surface Water Samples for Fluorinated Surfactants, Minnesota Water 2002 Conference, St. Cloud, MN. April 18, 2002.

Table 2.

Sample	PFOS	PFOA
Lake Minnetonka	3.5 ng/L	3.5 ± .3 ng/L (n=3)
Lake Erie Walleye 1	28 ng/g wet weight	ND
Lake Erie Walleye 2	7.1 ng/g wet weight	ND
Agnes Lake Northern Pike 1	1.1 ng/g wet weight	ND
Agnes Lake Northern Pike 2	0.91 ng/g wet weight	ND
Agnes Lake Northern Pike 3	ND	ND

Related submitted grants

Project Title: Perfluorinated Surfactants in Great Lakes Fish

Current/Pending: Pending

Source of Support: Minnesota Sea Grant

Total Award Amount: \$63,297

Total Award Period Covered: 02/01/03 – 1/31/05

Student training

Kelly J. Dorweiler, Environmental Health, M.S. expected Spring 2003.

Antibiotic Losses in Runoff and Drainage from Manure-Applied Fields

Basic Information

Title:	Antibiotic Losses in Runoff and Drainage from Manure-Applied Fields
Project Number:	2001MN1041G
Start Date:	9/1/2001
End Date:	8/31/2003
Funding Source:	
Congressional District:	4th
Research Category:	
Focus Category:	Agriculture, Non Point Pollution, Water Quality
Descriptors:	
Principal Investigators:	

Publication

Antibiotic losses in runoff and drainage from manure-applied fields

Satish Gupta, Professor and PI, (gupta002@umn.edu), Department of Soil, Water, and Climate; **Ashok Singh**, Veterinary Diagnostic Laboratory; **Kuldip Kumar**, **Anita Thompson**, and **David Thoma**, Department of Soil, Water, and Climate, University of Minnesota

Project duration: September 4, 2001 to September 3, 2003

Funding source: USGS-WRRI 104G National Grants Competition

The objective of this research is to quantify the effects of liquid swine manure application on antibiotic and nutrient (N and P) losses via surface runoff and subsurface drainage under a conventional (moldboard plowing) and a conservation (chisel plowing) tillage system. The field experiment is set up at the University of Minnesota Southwest Research and Outreach Center, Lamberton, Minnesota. The soil at the experimental site is a Webster clay loam soil (fine-loamy, mixed mesic Typic Haplaquoll), a common soil series in the Minnesota River Basin. The experiment is a randomized split-plot design with four replications (Figure 1). The main plots consist of two tillage treatments: (1) fall moldboard plowing followed by two passes of field cultivation before corn planting; and (2) chisel

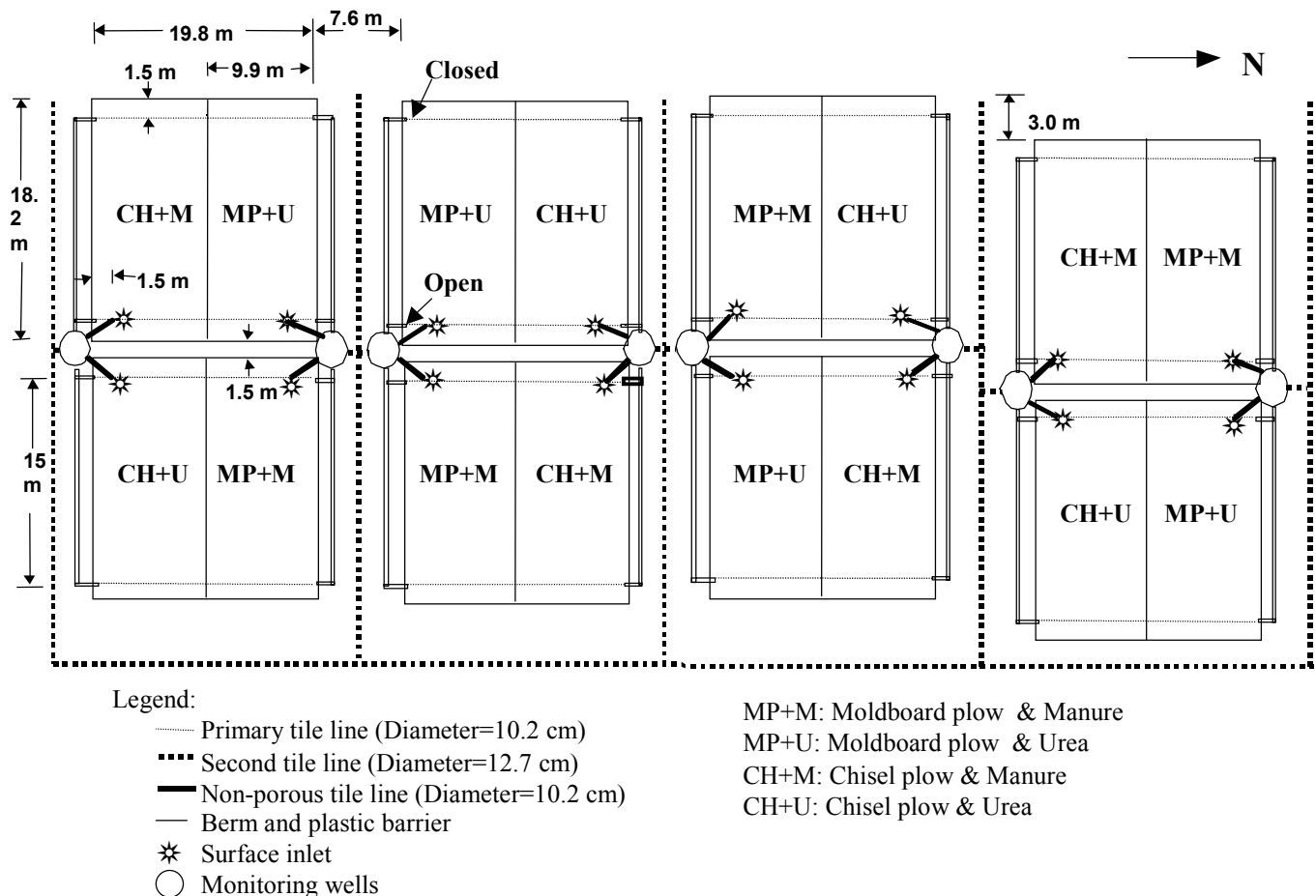


Figure 1. Surf-n-sub plot lay out at the Southwest Research and Outreach Center in Lamberton, MN.

plowing followed by two passes of field cultivation before corn planting. The subplots are two annually applied nutrient management treatments: fall injected (10 cm depth) liquid swine manure *versus* spring-applied and incorporated (5 cm depth) urea.

The drainage plots are 18.2 m long and 9.9 m wide. Each plot is isolated to a depth of 1.8 m by trenching

around plot borders and installing a 0.3 mm plastic sheet (Zhao et al. 2001). A perforated plastic tile drain, 10 cm in diameter, is installed at 1 m depth and 1.5 m away from the plot boundary along its width. This arrangement drains 16.7 m (18.2 m minus 1.5 m) length of the plot, one-half side of tile drains that may be 33.4 m apart. Tile drains empty into a monitoring well. Surface inlets are located at the lowest point in the plots and also drain surface runoff into the monitoring well.

Manure and urea application rates are based on the University of Minnesota recommendations corresponding to a yield goal of 150 bu/acre. Both surface runoff and subsurface tile drainage are measured by tipping bucket devices that are connected to CR-10 data loggers. Volume- distributed (composite water sample over a certain number of tips) runoff samples from surface inlets are taken by automated ISCO® samplers. Time-distributed (composite water sample over a certain time interval) subsurface drainage samples are collected manually once a day. The other details of sampling set-up and protocol are given in Zhao et al. (2001), and Thoma and Gupta (2001).

For the 2001-2002 crop year, primary tillage was done October 4, 2001, and subsequently liquid hog manure was injected on November 5, 2001, in half of the plots @ 4944 gallons/acre. This corresponds to N application of 239 lbs/acre. We had planned to apply manure corresponding to a yield goal of 150 bu/acre. However, our manure analysis from the manure pit before application showed lower N concentration than what was actually applied. The low concentration might have been due to lack of mixing of the manure in the pit prior to collection of the sample used to determine application rate. When we analyzed the actual manure sample injected in the soil, N concentrations were higher, resulting in higher N application rates than needed for the yield goal.

Two passes of secondary tillage were made on May 1, 2002. In the remaining half of the plots, urea was applied at an equivalent of 150 lbs-N/acre just before the secondary tillage. Corn was planted on May 1, 2002, right after secondary tillage. Both runoff and tile line samples were collected as per event. The samples are being analyzed for sediment, nutrients, and antibiotics losses.

Currently, there are no standard methods for analysis of antibiotics in soil and water samples. Therefore, most of our effort this year has gone into the development of analytical methods for antibiotic in manure, water, and soil samples. The farmer supplying manure for our experiment mentioned that he is mixing aueromycin (chlortetracycline) and tylosin in swine feed. Therefore, our methods development was geared towards quantification of chlortetracycline and tylosin. Analysis of the hog manure from the supplier lagoon showed presence of chlortetracycline (5.0 mg/L of manure slurry) and tylosin (5.6 mg/L of manure slurry). At 4,944 gallons/acre, this is equivalent to 92.7 gm/acre of chlortetracycline and 103.8 gm/acre of tylosin. At 150 lbs-N/acre, the manure application rate would have been 3103 gallons/acre and the addition of antibiotics would have been 58.2 g of chlortetracycline and 65.2 g of tylosin. Antibiotic analysis in manure sample was done on HPLC (High Performance Liquid Chromatography).

Subsequent analysis of runoff and tile line samples showed that concentrations of both chlortetracycline and tylosin were too low to detect with HPLC. Therefore, a new method based on immuno assay (ELISA-Enzyme-Linked Immunosorbent Assay) was used to analyze runoff samples. Because the ELISA plates are expensive and our laboratory showed that chlortetracycline is readily and highly adsorbed on soil particles, most of our effort so far has gone into analysis of tylosin. We have detected the presence of tylosin in only a few runoff samples. In most of these runoff samples, tylosin concentrations were generally <1 parts per billion (ppb). There were other samples where tylosin concentration was between 1–3 ppb. In one sample, we detected tylosin concentrations as high as 5.4 ppb (Table 1). These concentrations are relatively low compared to the concentration of tylosin in the manure sample (5.6 ppm). We are in the process of buying the ELISA plates for chlortetracycline. In the next report, we should have results on the concentration of chlortetracycline in runoff and tile line samples and also the concentration of tylosin in the tile line samples.

Other efforts in this project have gone into characterizing the adsorption characteristics of tetracycline, chlortetracycline and tylosin on two different soil types (Webster clay loam and Hubbard sandy loam). Adsorption studies were done both in batch (Figure 2) and in flow-through (Figure 3) set-up. The surface samples of Webster clay loam soil were taken from urea plots of our field experiment at Lamberton. Hubbard sandy loam is a glacial outwash soil and represents a major soil group in Central Sands of Minnesota. Batch experiments showed that tetracycline and chlortetracycline are strongly adsorbed on both soils than tylosin. Among the soils, Webster clay loam has higher adsorption capacity than the Hubbard sandy loam. The differences in soil types are due to differences in clay and

Table 1. Samples Tested Positive for Tylosin.

Sample (Plot-Number) ^a	Sample Date	Manure or Urea ^b	Filtered or Unfiltered ^c	ELISA Test ^d	Tylosin concentration (ppb)
2-1	08/04/2002	M	F	Aug 14 #1	1.77
9-bkt	08/04/2002	M	F	Aug 14 #1	1.14
9-bkt	08/04/2002	M	U	Aug 14 #1	1.46
1-5to8	08/09/2002	U	U	Aug 14 #1	0.17
2-1	08/09/2002	M	F	Aug 14 #1	0.13
2-bkt	08/09/2002	M	F	Aug 14 #1	1.40
2-bkt	08/09/2002	M	U	Aug 14 #1	1.85
8-1	08/09/2002	M	F	Aug 14 #2	1.02
8-1	08/09/2002	M	U	Aug 14 #2	1.68
8-bkt	08/09/2002	M	F	Aug 14 #2	1.75
9-bkt	08/09/2002	M	F	Aug 14 #2	0.05
9-bkt	08/09/2002	M	U	Aug 14 #2	0.81
11-1	08/09/2002	M	F	Aug 14 #2	3.27
11-1	08/09/2002	M	U	Aug 14 #2	0.92
13-bkt	08/09/2002	M	F	Aug 14 #2	0.88
16-1	08/09/2002	M	F	Aug 14 #2	1.92
16-1	08/09/2002	M	U	Aug 14 #2	0.90
16-2	08/09/2002	M	F	Aug 14 #2	0.78
16-2	08/09/2002	M	U	Aug 14 #2	0.49
16-3	08/09/2002	M	F	Aug 14 #2	1.03
16-3	08/09/2002	M	U	Aug 14 #2	0.32
8-1	07/30/2002	M	U	Aug 19	0.44
9-1	07/30/2002	M	F	Aug 19	5.38
1-1	08/04/2002	U	F	Sept 17	0.64
4-1	08/04/2002	M	F	Sept 17	0.50
1-4	8/9/02	U	F	Sept 17	0.52
10-1	8/9/02	U	F	Sept 17	0.20
12-1	8/9/02	U	F	Sept 17	0.34
12-2	8/9/02	U	F	Sept 17	0.41
14-1	8/9/02	U	F	Sept 17	0.12
15-1	8/9/02	U	F	Sept 17	0.06
1-1	8/22/02	U	F	Sept 17	0.04
2-1	8/22/02	M	F	Sept 17	1.21
8-1	8/22/02	M	F	Sept 17	1.36
14-1	8/22/02	U	F	Sept 17	0.25
15-1	8/22/02	U	F	Sept 17	2.91
15-2	8/22/02	U	F	Sept 17	0.03

^abkt refers to samples collected from the tipping bucket^bM=manure plots, U=urea plots^cF=filtered sample, U=unfiltered sample^dDates refers to dates ELISA test was done

organic matter content of soils. Webster clay loam is higher in both clay and organic matter contents (34% & 4.4%) than the Hubbard sandy loam (10.4% & 2.2%). Flow-through experiment with Hubbard sandy loam showed results consistent with the batch experiment; i.e., chlortetracycline and tetracycline are more strongly adsorbed on the soil than tylosin.

Linear sorption coefficients (K_d) of chlortetracycline, tetracycline and tylosin on Webster clay loam were 2386, 2370, and 92 L/kg as compared to 1280, 1147, and 66 L/kg for Hubbard sandy loam. Thus, at saturation, the retardation coefficients of chlortetracycline, tetracycline and tylosin in Webster clay loam will be 6083, 6042, 236, as compared to 4466, 4002, 231

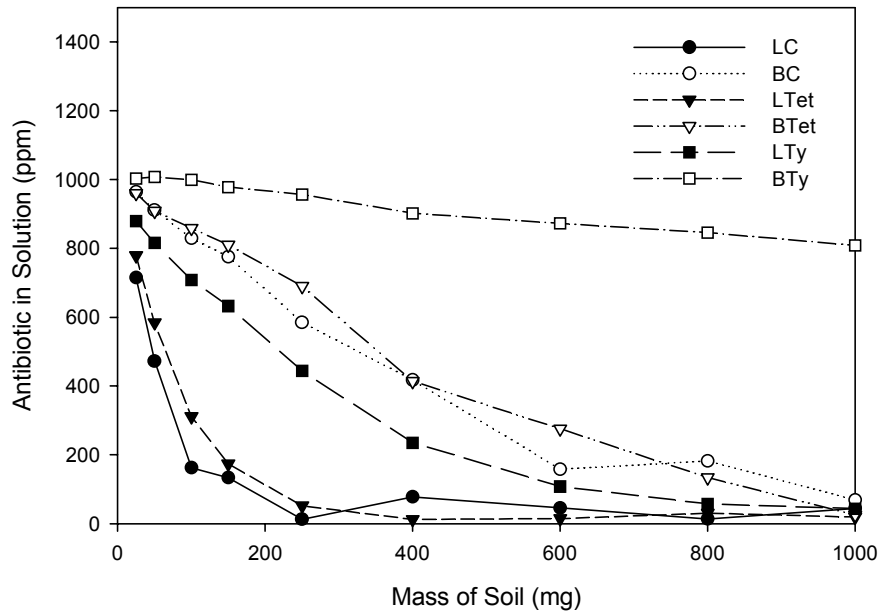


Figure 2. Antibiotic remaining in solution after shaking 1000 ppm of antibiotic solution with various amounts of soil. L= Webster clay loam, B=Hubbard sandy loam, C=chlortetracycline, Tet=tetracycline, Ty=Tylosin. Top three curves are for Hubbard sandy loam soil whereas bottom three curves are for Webster clay loam soils. Tetracycline and chlortetracycline are more strongly adsorbed on both soils than tylosin. Among the soils, Webster clay loam soil has higher adsorption capacity than the Hubbard sandy loam soil.

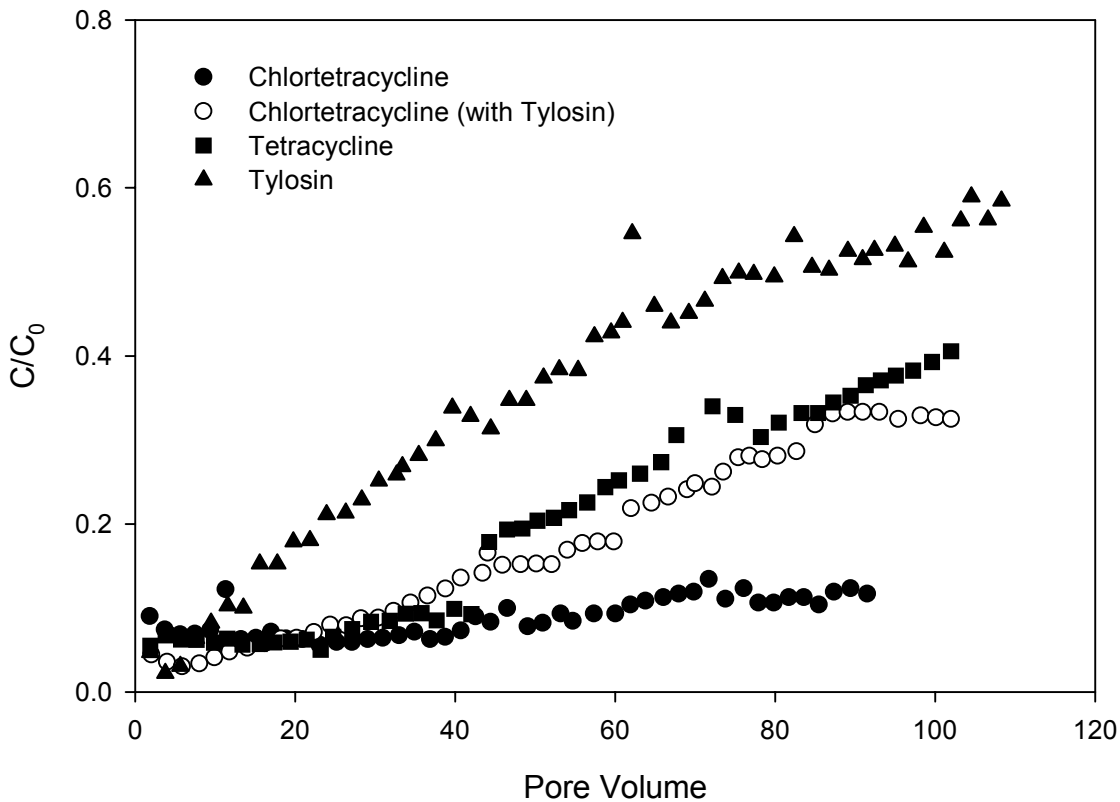


Figure 3. Breakthrough Curves for the Hubbard sandy loam soil for three antibiotics. Each data point is the average of three replicates. As shown by batch adsorption studies, chlortetracycline and tetracycline are more strongly adsorbed on the Hubbard sandy loam soil than tylosin.

for Hubbard sandy loam. The higher the retardation value, the greater is the adsorption potential of that chemical for a given soil. This number also reflects the quantity of water needed to displace a chemical through soil to the same distance as the non-adsorbing chemical. In other words, chlortetracycline will need 6083 times more water to displace than chloride in a Webster clay loam at saturation. The variation in K_d values reduced when it was normalized with clay or organic carbon contents, thus suggesting that clay and organic carbon may be the primary adsorption sites for these antibiotics.

Breakthrough experiments with Hubbard sandy loam also showed similar differences in the mobility of these three antibiotics. At $C/C_0=0.2$, the pore volume needed to displace tylosin was 24 compared to 52 for tetracycline and >100 for chlortetracycline.

We have finished the nitrate and ammonium concentration of tile line samples. We are still processing the runoff samples for sediment and phosphorus. We will report those results along with other antibiotic analyses in our next report.

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Zhao, S. L., S.C. Gupta, D.R. Huggins, and J.F. Moncrief. 2001. Tillage and nutrient source effects on surface and subsurface water quality at corn planting. *J. Environ. Qual.* 30: 998-1008.

Photochemical fate of pharmaceutical compounds discharged and detected in natural waters

Basic Information

Title:	Photochemical fate of pharmaceutical compounds discharged and detected in natural waters
Project Number:	2001MN281G
Start Date:	9/1/2001
End Date:	8/31/2003
Funding Source:	
Congressional District:	Minnesota Fifth
Research Category:	
Focus Category:	Non Point Pollution, Surface Water, Waste Water
Descriptors:	
Principal Investigators:	, Kristopher McNeill

Publication

Photochemical fate of pharmaceutical compounds discharged and detected in natural waters

W.A. Arnold, Assistant Professor and Co-PI, (arnol032@umn.edu), Department of Civil Engineering; **K. McNeill**, Co-PI, Department of Chemistry, University of Minnesota

J.L. Packer, Research Assistant, Department of Civil Engineering; **D.E. Latch**, and **A.L. Boreen**, Research Assistants, Department of Chemistry, University of Minnesota

Funding source: USGS-WRRI 104G National Grants Competition

Project duration: 9/04/2001-9/03/2003

Summary

Recent studies have detected numerous pharmaceuticals and personal care products (PPCPs) in US surface waters. The potential environmental impact of these chemicals will be dictated by their persistence in the environment and the biological activity of any degradation products. One potential loss process for pharmaceuticals and personal care products is photodegradation. In this work, the direct photolysis and indirect photolysis (hydroxyl radical mediated and singlet oxygen mediated) of selected PPCPs was investigated. To date, the fate of the antacids cimetidine and ranitidine hydrochloride and the antimicrobial compounds triclosan and chlorophene have been studied. All the compounds studied react with hydroxyl radical at nearly diffusion limited rates, but given the low concentration of hydroxyl radical in natural waters, other processes appear to be more important. The heterocyclic groups in cimetidine and ranitidine hydrochloride are susceptible to attack by singlet oxygen. Ranitidine hydrochloride is subject to direct photolysis while cimetidine is not. Direct photolysis occurs rapidly for triclosan and chlorophene when these compounds are present in the deprotonated phenolate form. These compounds also react with singlet oxygen, but preliminary results indicate that direct photolysis is the dominant photo-initiated loss process. The direct photolysis of triclosan at pH > 8.0 leads to the formation of 2,8-dichlorodibenzodioxin in yields ranging from 1-10%. This result underscores the importance of identifying the transformation products and not just the degradation rates.

Introduction

Pharmaceuticals and personal care products (PPCPs) are a class of chemicals that are continuously released into the environment through human activities, and, even though they have known biological effects, receive little attention (1,2). Examples of PPCPs include antibiotics, lipid regulators, psychiatric drugs, over the counter medications, and antimicrobial compounds. Most of these chemicals are introduced into the sewage system through their normal course of use. Once in the sewage system, many PPCPs are not completely removed at treatment plants (3) and thus, there is continuous introduction of these compounds to the environment. Numerous PPCPs have been detected in both ground and surface waters throughout the United States and Europe (2,4-12).

The impacts of PPCPs on the environment are unknown. Undesirable effects on non-target aquatic organisms and damage to sensitive ecosystems are possible (2). Furthermore, antibiotic drugs and antimicrobial agents in the environment may aid in the development of resistant bacteria (2,13). The lifetimes of the PPCPs in aquatic systems will partially determine the magnitude of the effects and potential threats to drinking water supplies. Loss processes such as photolysis, therefore, will play an important role in the environmental impact of these compounds. This includes not only direct and indirect photolysis loss processes, but also identifying intermediates and products that are formed through photolysis as transformation products many still have biological activity.

The research objective of this study is to determine the importance of both direct photolysis and indirect photolysis mediated by hydroxyl radical and singlet oxygen as loss processes for common PPCPs (medications cimetidine (Tagamet), ranitidine hydrochloride (Zantac), naproxan sodium (Alleve), ibuprofen (Advil), clofibrac acid, and diclofenac; the antimicrobial agents triclosan and chlorophene, and commonly prescribed antibiotics). Additionally, the research aims to identify major products resulting from the photolysis experiments.

Methods

Direct photolysis

Quartz bottles filled with either 25 or 50 mL aqueous PPCP samples over a range of concentrations and pH values were placed in a merry-go-round reactor and irradiated by a 450 W medium pressure Hg-vapor lamp (Ace Glass) controlled by an Ace Glass 7830 power supply. The lamp was encased in either a borosilicate or quartz cooling well, containing a continuous flow of cold tap water to help maintain constant temperature. For kinetic analyses 0.5 mL samples were withdrawn from the quartz bottles at predetermined intervals and analyzed on either an 1100 Series Hewlett Packard HPLC or a Waters LC Module 1 Plus, each equipped with UV-absorbance detection and a computer driven data acquisition system. Direct photolysis experiments were also performed in natural sunlight. Quartz bottles or borosilicate test tubes were placed in direct sunlight and samples were taken at predetermined intervals. Quantum yields were calculated by comparing the rate constant for the disappearance of the PPCPs with the rate constant for the disappearance of a *p*-nitroacetophenone actinometer as described in Leifer (ref. 14).

Hydroxyl radical

The second-order rate constant for the reaction of PPCPs with hydroxyl radical was determined using Fenton's reagent. Serum bottle reactors contained a 100 mM solution of the PPCP of interest, 100 mM acetophenone, 0.2 mM Fe²⁺, and 5 mM hydrogen peroxide adjusted to pH 3 with sulfuric acid (15). Samples were withdrawn at predetermined intervals and mixed with an equivalent volume of methanol to quench the reactions (16). HPLC analysis for both the PPCPs and the acetophenone was performed.

The hydroxyl radical rate constant was determined using competition kinetics according to:

$$k_{OH}^S = \frac{\ln([S_t]/[S_0])}{\ln([R_t]/[R_0])} k_{OH}^R$$

where *S* is the substrate (the PPCP) and *R* is the reference compound with a known hydroxyl radical rate constant (acetophenone, $k_{OH} = 5.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$).

Singlet oxygen

Singlet oxygen reaction kinetics were measured in one of two ways, directly by laser flash photolysis (LFP) or indirectly by steady-state photolysis (SSP). In both types of experiment the substrate (typically at micromolar concentrations) and $4 \times 10^{-5} \text{ M}$ Rose Bengal (RB), a singlet oxygen sensitizer, were dissolved in either alkaline buffer or EtOH. In the LFP experiments, a pulse of laser light excites the RB, which then produces singlet oxygen. A sensitive Ge-photodiode detector then monitors the phosphorescence emission from singlet oxygen. The rate of disappearance of the singlet oxygen phosphorescence signal is a measure of a substrate's activity toward singlet oxygen. The resulting total quenching rate constant (k_{tot}) is the sum of the chemical reaction and physical quenching rate constants.

In SSP experiments, the samples are photolyzed continuously and small aliquots are removed for analysis by HPLC. In this case, the disappearance of the PPCP is monitored (as decreases in peak area), rather than the singlet oxygen signal. This allows for the determination of the chemical reaction rate constant (k_{rxn}) for the PPCP with singlet oxygen.

Product identification

To analyze the products of various photoreactions, GC-MS and NMR spectroscopy were employed. An Agilent Technologies 6890 Gas Chromatograph with Mass Selective Detector was used to obtain mass spectra of various reaction mixtures. Photolysis samples run in organic solvents were analyzed by GC-MS to identify products. Product peaks were compared to mass spectral libraries to aid in their identification. Authentic samples of the likely products were then run under identical conditions to compare to the photolysis samples. Proper retention times and mass spectra indicated that a peak from the reaction mixture matched the standard solutions.

The NMR analyses were run on Varian Inova 300, 500, or 600 MHz instruments. In most product analysis experiments, a small amount of the reaction mixture was placed in an NMR tube prior to photolysis and an initial NMR spectrum was taken. Following a given period of irradiation, another NMR spectrum was taken. New peaks

that grew in were taken to be emerging product peaks. Whenever possible, these product peaks were compared to spectra obtained from authentic standards of the likely products to aid in their identification.

For triclosan, the direct photolysis experiments yielded the toxic 2,8-dichlorodibenzo-*p*-dioxin (2,8-DCDD). Since this product was also photoreactive, a large batch of triclosan (25 ppm, 500 mL) was irradiated and then extracted into hexanes. Following evaporation of the hexanes, the sample was dissolved in basic methanol- d_4 and analyzed by both 1D and 2D (HMQC) NMR spectroscopy.

Results to date

Direct photolysis

The half-lives of triclosan and chlorophene are dependant on the pH of the aqueous solution. By obtaining the half lives at both high and low pH values (representing fully protonated and unprotonated forms of the PPCPs), we were able use pKa values to extrapolate and determine the half-lives at various pH values. The half-life of triclosan in natural water at 40° latitude in the protonated form is expect to be 2.55 hours in summer, and 5.5 days in the winter. In the unprotonated form, the half-life of triclosan is expected to be 6.15 min in summer and 5.35 hours in the winter. Chlorophene behaves similarly, as the half-life in natural water at 40° latitude in the protonated form is expected to be 2.35 hours in summer, and 5.07 days in the winter. In the unprotonated form the half-life of chlorophene is expected to be 22.75 min in summer sunlight, and 19.77 hours in winter sunlight.

As shown in Figure 1, cimetidine is not subject to direct photolysis under the sunlight irradiation conditions employed so far in this project (mid-winter sunlight in Minneapolis, MN, 44.88° latitude). Ranitidine hydrochloride is photodegraded in these light conditions with a half-life of 5 hours. After correcting for the increase in rate caused by the lens effect of the curved test tubes (approximately a factor of 2), at 45° latitude, the half-life is expected to be approximately 10 h in surface water (17). The rate constant could be expected to increase by a factor of approximately 3-5 under midsummer sunlight conditions, resulting in a half-life of 2-3 hours.

Hydroxyl radical

Antimicrobial agents triclosan and chlorophene are subject to reaction with hydroxyl radicals. The second order rate constants for triclosan and chlorophene are $5.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and $7.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, respectively. Medications cimetidine and ranitidine hydrochloride are also susceptible to this type of indirect photolysis, with hydroxyl radical rate constants of $6.50 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and $1.46 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, respectively.

In natural near-surface waters, hydroxyl radical concentration may range from 10^{-16} M (in agriculturally impacted waters containing high nitrate levels) to 10^{-18} M (pristine waters) (18,19). Based on these steady-state concentrations, the half-life of triclosan may range from 15.14 days to 4.1 years in surface waters. Chlorophene behaves similarly with a half-life ranging from 11.3 days to 3.1 years. The half-life of cimetidine may range from 10.4 days to 2.8 years, and the shortest of these hydroxyl radical mediated half-lives, is ranitidine hydrochloride with an estimated half-life of 5.4 days to 1.4 years.

Singlet oxygen

The antacid medications cimetidine and ranitidine hydrochloride were both highly reactive toward singlet oxygen ($k_{\text{rxn}} = 9.2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ and $2.1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ at pH 8, respectively; Figure 2). Model studies were employed to assess which moieties of each drug were most reactive with singlet oxygen. In both cases, the heterocyclic rings were the reactive groups.

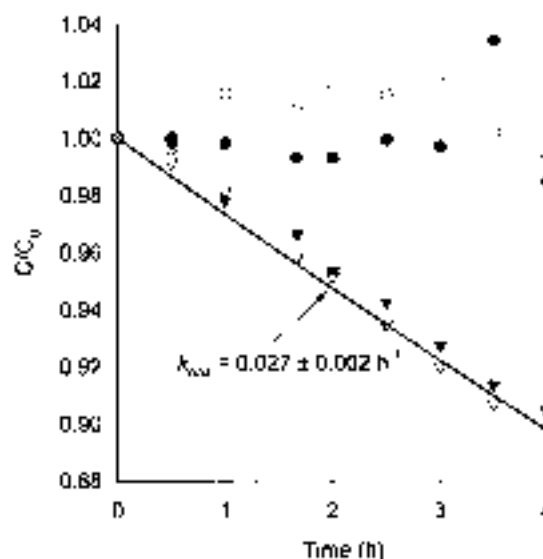


Figure 1. Direct photolysis of ranitidine hydrochloride (triangles) and cimetidine (circles).

Initial studies with chlorophene and naproxan show that the former interacts with singlet oxygen, while the latter does not to any significant extent. The dissociated form of triclosan has been found to quickly react with singlet oxygen ($k_{rxn} = 1.07 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ at pH 10).

Product identification

GC-MS analysis of the reaction between singlet oxygen and triclosan provided insight into the probable reaction mechanism. Phenoxide anions are well known to react with singlet oxygen to produce quinone products (20). As such, the triclosan quinone was independently synthesized and characterized. This product was not observed in any of the triclosan singlet oxygenation reactions. A peak for 2,4-dichlorophenol was evident in both GC-MS and NMR analyses, though. When the triclosan quinone was subjected to the same alkaline conditions that the triclosan reaction mixtures were, the quinone quickly broke down to yield 2,4-dichlorophenol and some other insoluble product. Thus, it appears likely that the triclosan quinone is being formed in the singlet oxygen reaction of triclosan, but it is readily cleaved, yielding the 2,4-dichlorophenol product.

GC-MS analysis first indicated that 2,8-DCDD may be formed in the direct irradiation of triclosan (Figure 3). A peak displaying the proper 2,8-DCDD mass spectrum was evident in the reaction mixture. When compared to an

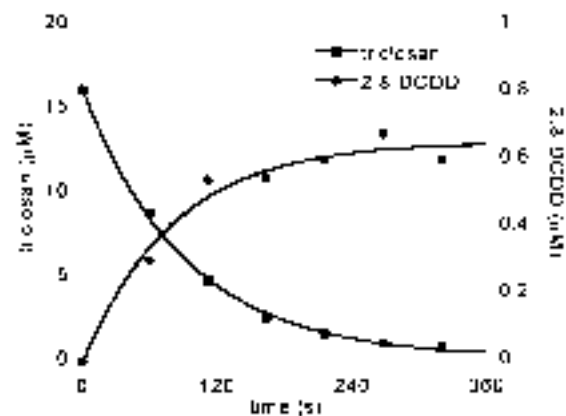


Figure 3. Photochemical conversion of triclosan to 2,8-DCDD, a member of the dioxin family, in Mississippi River water.

authentic sample of 2,8-DCDD, the retention times and mass spectra matched. This seemed to confirm that 2,8-DCDD was indeed forming in the photolysis experiments. It has been shown, however, that the perchlorinated analogue of triclosan forms octachlorodibenzo-*p*-dioxin at the heated inlet of GCs (21). Additional measures were thus taken to ensure that 2,8-DCDD was being formed in the direct photolysis samples and is not just an interference arising from the analysis method. First, the sample was compared to the 2,8-DCDD standard by HPLC. The retention time of one of the product peaks matched that of the standard. Second, the reaction mixture was compared to the standard solution by NMR spectroscopy. Following photolysis of a large batch of triclosan, the dioxin was concentrated and analyzed by 1D and 2D (HMQC) NMR spectroscopy. The spectra that were obtained compare favorably to that of the authentic sample, confirming the presence of 2,8-DCDD as a photoproduct.

Ongoing work

Current work is focusing on the direct and hydroxyl mediated photolysis of naproxan sodium, ibuprofen, clofibric acid, and diclofenac. Also under investigation is the photochemical fate of the sulfa drugs. Product identification studies are also underway as is expansion of the target chemical list.

Summary of findings

The over-the-counter antacids ranitidine and cimetidine are both rapidly degraded by singlet oxygen. Only the ranitidine is susceptible to direct photolysis. Degradation by hydroxyl radical appears to be of lesser importance for these species. The degradation of the antimicrobial compounds triclosan and chlorophene by direct photolysis and by reaction with singlet oxygen are pH dependent, with the phenolate forms of the compounds being more reactive in

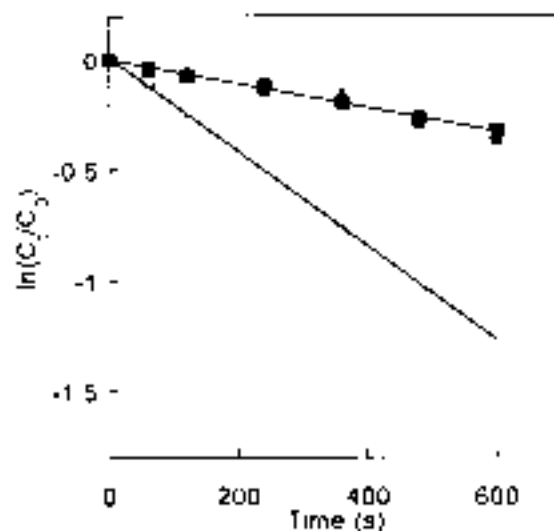


Figure 2. Logarithmic kinetic decay traces for rate for the singlet oxygenation of ranitidine hydrochloride (filled symbols) and FFA (open symbols).

each case. The direct photolysis of triclosan results in the formation of 2,8-DCDD in 1-10% yield depending on the experimental conditions. This result emphasizes the importance of identifying reaction products in environmental systems.

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List of publications & presentations resulting from this project

Stender, B.L., D.E. Latch, J.L. Packer, W.A. Arnold, and K. McNeill (2002) *Photochemical Fate of Pharmaceuticals in the Environment: Reactions of Singlet Oxygen and Hydroxyl Radical with Cimetidine and Ranitidine Hydrochloride*. Environmental Science and Technology, in revision.

Latch, D.E., J.L. Packer, W.A. Arnold, and K. McNeill (2002) *Photochemical Conversion of Triclosan to 2,8-Dichlorodibenzo-p-dioxin in Aqueous Solution*. Submission planned July 2002.

Latch, D.E., W.A. Arnold, and K. McNeill (2002) *The Photochemical Fate of Triclosan*. Poster presentation at the 2002 Great Lakes Regional Meeting of the American Chemical Society, June 2-4, 2002, Minneapolis, MN.

Boreen, A.L., W.A. Arnold, and K. McNeill (2002) *Kinetics of the Reaction Between Singlet Oxygen and Sulfa Drugs*. Poster presentation at the 2002 Great Lakes Regional Meeting of the American Chemical Society, June 2-4, 2002, Minneapolis, MN.

Latch, D.E., W.A. Arnold, and K. McNeill (2002) *Singlet Oxygen and the Photochemical Fate of Triclosan*. Paper presentation at the 2002 national meeting of the American Chemical Society, April 7-11, 2002, Orlando, Florida.

Packer, J.L., K. McNeill, and W.A. Arnold (2002) *Direct and Indirect Photolysis of Triclosan*. Paper presentation at the 2002 national meeting of the American Chemical Society, April 7-11, 2002, Orlando, Florida.

VanOverbeke, J.L., and K. McNeill (2002) *Photochemical fate of chlorophenol antibacterials in the environment*. Poster presentation at the 2002 national meeting of the American Chemical Society, April 7-11, 2002, Orlando, Florida. (CHED-474)

Latch, D.E., B.L. Stender, and K. McNeill (2001) *Singlet oxygen and the photochemical fate of pharmaceuticals*. Poster presentation at the 2001 national meeting of the American Chemical Society, August 26-30, 2001, Chicago, Illinois. (ENVR-135)

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Dr. Arnold and Dr. McNeill have submitted grants to the Camille & Henry Dreyfus Foundation, the Minnesota Sea Grant Program, and the Legislative Commission on Minnesota Resources (LCMR) to study PPCP fate in aquatic systems.

Description of student training provided by project:

Name: Jennifer L. Packer

Program: Department of Civil Engineering, University of Minnesota

Degree being sought: Masters of Science

Name: Douglas E. Latch

Program: Department of Chemistry, University of Minnesota

Degree being sought: Ph.D.

Name: Anne L. Boreen

Program: Department of Chemistry, University of Minnesota

Degree being sought: Ph.D.

Name: Jennifer L. VanOverbeke

Program: Dept. of Chemistry, Univ. of Minnesota Summer, Undergraduate Research Program

Degree being sought: B.S. (Northwestern University)

Supported by the Summer Undergraduate Program of the Department of Chemistry

Information Transfer Program

Student Support

Student Support					
Category	Section 104 Base Grant	Section 104 RCGP Award	NIWR-USGS Internship	Supplemental Awards	Total
Undergraduate	0	0	0	0	0
Masters	1	5	0	0	6
Ph.D.	0	0	0	0	0
Post-Doc.	0	0	0	0	0
Total	1	5	0	0	6

Notable Awards and Achievements

Publications from Prior Projects