North Dakota Water Resources Research Institute Annual Technical Report FY 2004

Introduction

This report describes the activities of the North Dakota Water Resources Research Institute (NDWRRI) during the period of March 2004 to February 2005.

The ND WRRI is one of the 54 institutes known collectedly as the National Institutes for Water Resources (NIWR). The NDWRRI was founded in 1965, by authority of Congress (Water Resources Research Acts of 1964, 1972, 1984, and 1990), and is administrated through the United States Geological Survey. Section 104 of the Water Resources Research Act requires the NDWRRI to apply its Federal allotment funds to:

1. Plan, conduct or otherwise arrange for competent research that fosters: (A) the entry of new research scientists into the water resources field, (B) training and education of future water resources scientists, engineers, and technicians; (C) the preliminary exploration of new ideas that address water problems or expand understanding of water and water-related phenomena; and (D) the dissemination of research results to water managers and public.

2. Cooperate closely with other college and universities in the state that have demonstrated the capability for research, information dissemination and graduate training, in order to develop a statewide program designed to resolve State and regional water and related land problems.

3. Cooperate closely with other institutes and other organizations in the region to increase the effectiveness of the Institute and for the purpose of promoting regional cooperation.

This year, NDWRRI once again allocated its 104(B) resources to fund research projects that are coupled to the Gradate Research Fellowship (GRF) program. The upgraded GRF program meets the requirements of Section 104 of the Water Resources Act effectively in the following respects:

Often it is junior faculty as well as graduate students who perform competent research that fosters the entry of new research scientists into the water resources field; The modest 104(B) federal allotment is focused on training and education of future water resources scientists, engineers, and technicians; Graduate students thesis and dissertation topics foster the preliminary exploration of new ideas that address water problems or expand understanding of water and water-related phenomena; Through the newsletter, website, plus student and faculty presentations and peer-reviewed publications, the dissemination of research results to water managers and the public is accomplished; The NDWRRI cooperates closely with other colleges and universities in the state that have demonstrated the capability of research, information dissemination and graduate training by offering competitive fellowships at both research universities in North Dakota; and The NDWRRI cooperates closely with other institutes and other organizations in the region to increase the effectiveness of the institute and for the purpose of promoting regional cooperation by encouraging faculty to seek in-kind and cash matching support form those institutes and organizations, and its external seminar program.

The institute also continued its efforts to enhance communications between the State and Federal agency personnel and university faculty and students. Advisors and fellows presented their research results to State and Federal professionals.

Program Management

The Institute continued the same administrative mechanism with a director managing the institute program with the help of a State Advisory Committee. Dr. G. Padmanabhan, Professor of Civil Engineering, is the director. Dr. Wei Lin, Associate Professor of Civil Engineeing, has been serving as the interim director during the period (August 2004 July 2005) that Dr. Padmanabhan is on sabbatical leave from the university. Linda Charlton, a NDSU employee, has been working part-time for the Institute to assist the director with Institute finances, communications and information transfer. The State Advisory Committee consists of three members representing the three principal water agencies in North Dakota: State Water Commission, State Department of Health, and the USGS North Dakota District. In addition, the Institute also has a Technical Advisory Committee consisting of faculty form two universities.

Efforts have been directed to seek state appropriation and other support sources in the past few years. As a result of this continuous effort, the State Water Commission provided 15% matching to the 2005 2006 federal 104(B) funding for the GRF program of NDWRRI. The North Dakota State University and the University of North Dakota administrations consider the NDWRRI activities important and are supportive of its efforts.

The Institute is located in the Administrative Building of the College of Engineering and Architecture of North Dakota State University in Fargo, North Dakota, The directors may be reached at:

ND Water Resources Research Institute North Dakota State University Department of Civil Engineering Fargo, ND 58105 Phone: (701) 231-7043 Dr. G. Padmanabhan, or (701) 231-6288 Dr. Wei Lin Fax: (701) 231-6185

State Advisory Committee

The State Advisory Committee provided guidance in the determination of water resources research priorities, and participated in the evaluation of research proposals and projects. The current committee members are:

Gregg Wiche, District Chief, U.D. Geological Survey, Water Resources Division, Bismarck, North Dakota

William Schuh, Water Appropriation Division, North Dakota State Water Commission, Bismarck North Dakota

David Leo Glatt, Chief, Environmental Health Section, North Dakota Department of Health, Bismarck, North Dakota

Mike T. Sauer, Environmental Health Section, North Dakota Department of Health, Bismarck, North Dakota

These members are senior officials in the three agencies in North Dakota responsible for much of the water resources research done outside of NDSU and UND in North Dakota.

Research Program

RESEARCH PROGARM

For the last several years NDWRRI has offered competitive fellowships to NDSU and UND graduate students for research on water resources topics. The Graduate Research Fellowship (GRF) program effectively uses the modest amount of allotment from the 104(B) Institute based grant in perceived to meet the requirements of Section 104 of the Water Resources Research Act of 1984. The fellowship program encourages entry of young university faculty and new research scientists into the water resources field; provides training and education to future water resource scientists and engineers; promotes exploration of new ideas that address water problems or expand understanding of water quantity, quality and related phenomena; and engages university faculty in collaborative research programs and seeking supports from entities concerned with water problems.

This year, the NDWRRI continued the GRF program and applied bulk of the federal allotment to it. The GRF program is administrated and monitored by the director. Applications are invited from the graduate students and their advisors of the two research universities of the State. A rigorous review by the State Advisory Committee and other water professionals in the state determines the awards. Active participation of the academic advisors of the students in meeting matching requirement and seeking co-funding from local, state and other sources is a positive aspect of the program. Periodical review of the progress of the students in meeting the fellowship expectations is ensured by seeking reports from the students and by encouraging them to make presentations in local and regional technical seminars and conferences.

Guidelines for the 2004-2005 Graduate Research Fellowship competition were posted on the Institute website in September 2003, and the competition was announced in October. The following is the request for application that was published on the UND and NDSU campus newsletters, and distribute by e-mail lists:

NDWRRI Calls for Applications for Graduate Research Fellowships The ND Water Resources Research Institute announces its 2004 Graduate Research Fellowship program. NDSU and UND Graduate students who are conducting or planning research in water resources areas may apply for fellowships varying from three summer months to a full year in duration. Stipends may be requested in the range of $800 to $1,400 per month. The fellowship funds must be applied between March 2004 and February 2005. Projects proposed for fellowship support should relate to water resources research issues in the state or region. Regional, state, or local collaborations or co-funding will strengthen an application. Applications are due in the office of the director not later than 5:00 p.m., November 14, 2003. The proposals will be reviewed by a panel of faculty and state water resources research professionals. Announcement of awards will be made by early January. Before preparing your application consult the guidelines for preparation of applications. Fellowships have matching requirements. Applicants and advisors who are new to the program are urged to contact ND WRRI Director, G. Padmanabhan, at 231-7043. Send your applications to Dr. G. Padmanabhan, Director, ND Water Resources Research Institute, North Dakota State University, CIE 201D, Department of Civil Engineering and Construction, P.O. Box 5285, Fargo, ND 58105-5285.

Comparative Study of Fossil and Extant Fish Growth: Including Analyses of Mean Annual Temperature in the Geologic Record

Basic Information

Title:	Comparative Study of Fossil and Extant Fish Growth: Including Analyses of Mean Annual Temperature in the Geologic Record
Project Number:	2003ND25B
Start Date:	3/1/2004
End Date:	2/28/2005
Funding Source:	104B
Congressional District:	1
Research Category:	None
Focus Category:	Surface Water, Wetlands, Climatological Processes
Descriptors:	None
Principal Investigators:	Allan Ashworth, Allan Ashworth

Publication

1. Newbrey, M.G., A.C. Ashworth, and M.V.H. Wilson (2005) Geographic trends in North American Freshwater Fishes from the Cretaceous to the Pliocene: A climatic effect? Presented at Northern Plains Biological Symposium, Fargo, North Dakota.
2. Newbrey, M.G., A.C. Ashworth, and M.V.H. Wilson (2004) Geographic trends in North American Freshwater Fishes from the Cretaceous to the Pliocene, Society of Vertebrate Paleontology 64th Annual Meeting. Journal of Vertebrate Paleontology 24(supplement to 3):98A.
3. Newbrey, M.G. and A.C. Ashworth. 2004. A fossil record of colonization and response of lacustrine fish populations to climate change. Canadian Journal of Fisheries and Aquatic Sciences 61(10):1807-1816.

COMPARATIVE STUDY OF FOSSIL AND EXTANT FISH GROWTH: INCLUDING ANALYSES OF MEAN ANNUAL TEMPERATURE IN THE GEOLOGIC RECORD
(Full Renewal)

DESCRIPTION OF THE REGIONAL WATER PROBLEM

It is important to consider the implications of climatic change on surface water resources in light of potential consequences of global warming. North Dakota boasts some of the best long-term data sets in the form of a fossil record to measure the effect of climatic warming on a single population of fish. A fossil lake bed near Jamestown, ND will provide perhaps thousands of years of continuous data of fish growth during a warming climate. This research will provide insight for fishery biologists and wetland ecologists concerning the long-term response of contemporary fish growth in North Dakota given potential climatic changes.

LITERATURE SUMMARY AND PRIOR WORK

Population dynamics have rarely been studied from ancient ecosystems. However, fossils can provide information about growth, mortality, and numerous other ecological processes that have been examined in contemporary systems (Ricker 1975). A recent study, which detailed the ageing of *Joffrichthys triangulpterus* scales and the subsequent modeling of their growth, provided insight into the population dynamics of an extinct osteoglossid fish (Newbrey and Bozek 2000; 2003). However, there are no contemporary species within the genus *Joffrichthys* to use as a reference for a comparative growth analysis. More recently, I have conducted research with an extinct form of pike (*Esox tiemani*)(Wilson 1980) and compared its growth to living forms of *Esox* (i.e., northern pike and muskellunge). The procedure has since bee repeated for yellow perch in the fossil record. The research details a correlation between growth and mean annual temperature and introduces a new procedure to estimate mean annual temperature in the fossil record. Much of the methodology presented in this proposal is derived from the pike and yellow perch growth research.

Climatological processes strongly influence growth rates of fish. For example, growth can vary depending on aquatic and ambient mean annual temperatures (Gillooly et al. 2002). Air temperature strongly influences surface water temperature (McCombie 1959; Livingstone and Lotter 1998) and therefore fish growth. Temperature has a strong influence on metabolic rate (Q_{10} relationship) and growth on ectothermic taxa; a temperature increase of 10°C increases the metabolic rate two to three fold and reaction rates increase 100-200% (Cossins and Bowler 1987). The pike and yellow perch research indicates that temperature is correlated with latitude. Pike and yellow perch grow more slowly in northerly latitudes because of cooler and shorter growing seasons and more quickly in the warmer-longer growing seasons of southern latitudes. The relationship between growth and temperature will provide a greater understanding of the effects of climatic warming on fish.

My dissertation research will focus on a comparative growth of several groups of fish. Specifically, I will contrast growth of fish in the fossil record to that of living fish to determine mean annual air temperature change in the geologic record. The analyses are important for fishery biologists and ecologists in North Dakota who are interested in the implications of climatic change on surface water resources and fish. For example, I will study a fossil glacial lake site in North Dakota that has produced fossil specimens of contemporary fish species. The environment of the fossil lake changed from a cool wet climate with tamarack, black spruce, birch and aspen to a contemporary prairie-pothole region. The change occurred over a period of about a thousand years thus giving us insight into ecological processes that are affected by current climate changes.

A site of particular interest in North Dakota represents a glacial, 11,000 year old fossil lake bed containing extremely well preserved fish (yellow perch, *Perca flavescens*), which are still living in ND today. Some of the best-preserved late Pleistocene/early Holocene fossils ever reported, come from a 11,000 calendar year-old site (Seibold site) underlying an ephemeral wetland on the Missouri Coteau, near Buchanan, North Dakota. Cvancara et al. (1971) described the geology and paleolimnology of one lake deposit called the Seibold site (SW¼ NW¼ Sec. 21, T141N, R67W), Stutsman County, North Dakota. The Seibold site represents the remains of a small basin (100m in diameter), which was probably part of large lake complex during the late Pleistocene /early Holocene. The site has excellent preservation of terrestrial and aquatic plants and animals, which permits taxonomic assignments of the fossil remains to the generic and specific levels. Study of plant specimens have revealed that the lake was initially surrounded by a spruce-dominated assemblage that was replaced by a mixed assemblage of deciduous trees, shrub, herbs, and grasses (Cvancara et al. 1971). Animals recovered from the site include five species of fish, frogs, muskrat, and evidence of beaver (Cvancara et al. 1971)(see fossils http://www.ndsu.nodak.edu/instruct/ashworth/SEIBOLD.pdf).

The changes in pollen indicate this site is ideal for a long-term study of fish growth in a North Dakota lake, where all data can be gathered in one excavation. During the period of lake sediment deposition, while the climate was warming and the glacier was retreating to Canada, the botanical environment around the lake changed (Cvancara et al. 1971). Fossil pollen indicates that the plant community changed from a forest to prairie ecosystem around 9,500 calendar years ago. As the lake warmed over a few thousand years, measurable change in patterns of growth should be detectable for yellow perch. Numerous studies have modeled growth of individual populations of yellow perch (i.e., Scott and Crossman 1973; Becker 1983; etc.) and, in all publications combined, from a variety of latitudes and ambient mean annual temperatures providing a spectrum of growth curves to assemble and analyze. The combined growth curves will provide a correlation between growth and mean annual temperature and thus provide an index to estimate mean annual air temperature change in the fossil record. This study site and others in my dissertation will provide insight to fishery biologists and surface water ecologists about the effects of temperature change on fish populations in North Dakota and other areas.

SCOPE AND OBJECTIVES

The overall objective of this Fellowship research is to describe changes in the paleoclimate and fossil fish growth by comparing fossil specimens to extant fish populations. For example, some site-specific objectives include: 1.) to conduct an excavation at the Seibold site near Jamestown, ND to collect fossil yellow perch; 2.) to describe growth of fossil yellow perch; 3.) to compile and analyze contemporary yellow perch growth data in order to contrast growth in relation to the fossils; and 4.) to analyze contemporary yellow perch growth in relation to ambient mean annual temperature in order to calculate a chronological series of estimates of ambient mean annual temperature.

These objectives will be repeated for numerous other localities, represented in museum collections, and containing the following taxa: bowfin, *Amia calva*; the mooneyes and goldeyes of *Hiodon*; and the members of the pikes, *Esox*. These genera are represented in the present North American fish assemblage, in the fossil record from the Cretaceous to the present, and in museum collections.

METHODS, PROCEDURES, AND FACILITIES

Numerous publications contain the information needed to locate specimens (e.g., Grande, 1984; Grande and Bemis, 1998; Grande, 1999; Li et al., 1997; Wilson, 1980, 1981, 1984; etc.) suitable for data. Typically, hard structures (i.e., scales, otoliths, cleithra, fin rays, spines, and vertebrae) from captured fish are aged and growth is calculated using the relation between growth of these structures and fish total length (Van Oosten, 1941; Carlander, 1969). Total length is the distance from the anterior-most tip of the head to the vertical plane of the posterior caudal fin tips. For this study, fossil scales and vertebrae will be aged in the lab and from museum collections by counting annulus marks or light and dark pairs of bands on bones. Fishery biologists use Von Bertalanffy growth curves (Von Bertalanffy, 1938) to assess growth rates. The curve is fit to the maximum total lengths for each age class:

$$TL_t = L_\infty[1-e^{-K(t-t_0)}]$$

where:
- TL_t = Total length (cm) at t (age in years);
- L_∞ = maximum total length;
- K = the Brody growth coefficient;
- t = time (i.e., age in years);
- t_0 = time at age zero (time at theoretical zero length).

Yellow perch growth data will be taken from Scott and Crossman (1973), Becker (1983), and a list of other sources to contrast extant growth curves. Because male and female yellow perch have different growth rates and life spans all data from extant populations will be combined for both sexes. This is done to standardize error to match that of the fossil material. Site specific mean annual temperature (MAT) data rounded to the nearest 0.1°C will be taken from the WorldClimate© web site and when possible checked for accuracy with Northern Oceanic and Atmospheric Administration (NOAA) data. Ambient MAT will be used in a linear regression analysis and regressed to the natural log transformed total lengths (cm) of age three of yellow perch to obtain a correlation between MAT and growth:

$$\mathrm{Ln}\left(TL_{\mathrm{Age\,3}}\right) = m \times \sqrt{\mathrm{MAT}_E + 10°\mathrm{C}} + b$$

where:
- $\mathrm{Ln}(TL_{\mathrm{Age\,6}})$ = natural log transformed total length (TL cm) at 3 years of age;
- m = slope parameter of linear regression;
- MAT_E = mean annual temperature (MAT) at sites of extant (*E*) populations;
- b = intercept parameter of linear regression.

Von Bertalanffy total length will be used because it includes the growth parameters and describes more variation in growth than individual equation parameters alone. Age three total lengths will be used for analysis because this age represents a stable portion of the curve where the effects of the parameters L_∞ and t_0 are reduced while still providing a range of sizes to contrast prior to asymptotic length. To estimate the ambient MAT of the fossil site, the linear regression equation was algebraically rearranged:

$$\mathrm{MAT}_F = \left(\frac{\mathrm{Ln}(TL_{\mathrm{Age\,3}}) - b}{m}\right)^2 - 10°\mathrm{C}$$

where:
- MAT_F = mean annual temperature (MAT) of the fossil (*F*) site;
- $\mathrm{Ln}(TL_{\mathrm{Age\,3}})$ = natural log transformed total length (TL cm) at age three;
- b = intercept parameter of linear regression;
- m = slope parameter of linear regression.

ANTICIPATED RESULTS

As the glacial lake matured to a modern pothole wetland and as the climate changed from a cool moist environment to a dry warmer environment there were quantifiable changes occurring in fish growth. Because there is a correlation between ambient air temperature and water temperature within the first meter of depth (McCombie 1959; Livingstone and Lotter 1998), we hypothesize that growth of fossil yellow perch will initially be slow in the cool climate and then increase as the climate warmed. Mean annual temperature change will be modeled from contemporary fish growth by a mathematical relation to temperature. The correlation will then be used to predict mean annual temperature change over a few thousand years. This information will provide a better understanding of evolution of natural processes to biologists studying the pothole region in North Dakota. New climatic information will be of interest to researchers studying changes in temperature and wet/dry cycles. The information and analyses obtained from the glacial lake will be presented at a scientific meeting and will ultimately be submitted to a peer-reviewed journal for publication. The procedures will be repeated for the other taxa of fish being examined in my dissertation in order to better understand relations between changes in MAT and fish growth.

REFERENCES

Becker, G. C. 1983. Fishes of Wisconsin. University of Wisconsin Press, Madison, Wisconsin. 1052 pp.

Carlander, K. D. 1969. Handbook of freshwater fishery biology, volume one. Iowa State University Press, Ames, Iowa. 752 pp.

Cossins, A. H. and K. Bowler. 1987. Temperature Biology of Animals. Chapman and Hall, London. 339 pp.

Cvancara, A. M., Clayton, L., Bickley, W. B., Jacob, A. F., Ashworth, A. C., Brophy, J. A., Shay, C. T., Delorme, L. D., and Lammers, G. E. 1971. Paleolimnology of Late Quaternary deposits: Seibold site, North Dakota. Science 171:269-306.

Gillooly, J. F., Charnov, E. L., West, G. B., Savage, V. M., and J. H. Brown. 2002. Effects of size and temperature on developmental time. Nature 417:70-73.

Grande, L. 1984. Paleontology of the Green River Formation, with a review of the fish fauna. The Geologic Survey of Wyoming, Bulletin 3:1-334. (2nd ed.)

--------- and W. E. Bemis. 1998. A comprehensive phylogenetic study of amiid fishes (Amiidae) based on comparative skeletal anatomy. An empirical search for interconnected patterns of natural history. Society of Vertebrate Paleontology Memoir 4:i-x, 1-690; supplement to Journal of Vertebrate Paleontology 18(1).

King, J. R., B. J. Shuter, and A. P. Zimmerman. 1999. Empirical links between thermal habitat, fish growth, and climate change. Transactions of the American Fisheries Society 128:656-665.

Li G.-q., M. V. H. Wilson, and L. Grande 1997. Review of Eohiodon (Teleostei: Osteoglossomorpha) from western North America, with a phylogenetic reassessment of Hiodontidae. Journal of Paleontology 71:1109-1124.

Livingstone, D. M. and A. F. Lotter. 1998. The relationship between air and water temperatures in lakes of the Swiss Plateau: a case study with palaeolimnological implications. Journal of Paleolimnology 19:181-198.

McCombie, A. M. 1959. Some relations between air temperatures and the surface water temperatures of lakes. Limnology and Oceanography 4:252-258.

Newbrey, M. G., and M. A. Bozek. 2000. A new species of *Joffrichthys* (Teleostei: Osteoglossidae) from the Sentinel Butte Formation, (Paleocene) of North Dakota, USA. Journal of Vertebrate Paleontology 20:12-20.

Newbrey, M. G., and M. A. Bozek. In Press. Age, growth, and mortality of *Joffrichthys*

triangulpterus (Teleostei: Osteoglossidae) from the Paleocene Sentinel Butte Formation, North Dakota, USA. Journal of Vertebrate Paleontology 00:00-00.
Ricker, W. E. 1975. Computation and interpretation of biological statistics of fish populations. Bulletin of the Fisheries Research Board of Canada Bulletin 191:1-382.
Van Oosten, J. 1941. The age and growth of freshwater fishes; pp. 196-205 *in* A symposium on hydrobiology. University of Wisconsin Press, Madison, Wisconsin. 405 pp.
Scott, W. B. and E. J. Crossman. 1973. Freshwater fishes of Canada. Research Board of Canada Bulletin 184.
Von Bertalanffy, L. 1938. A quantitative theory of organic growth. Human Biology 10:181-213.
Wilson, M. V. H. 1980. Oldest known *Esox* (Pices: Esocidae), part of a new Paleocene teleost fauna from western Canada. Canadian Journal of Earth Sciences 17:307-312.
---------- 1981. Eocene Freshwater fishes from the Coalmont Formation, Colorado. Journal of Paleontology 55:671-674.
---------- 1984. Year classes and sexual dimorphism in the Eocene catostomid fish *Amyzon aggregatum*. Journal of Vertebrate Paleontology 3:137-142.

PROGRESS OF RESEARCH

I have accumulated data on growth of contemporary bowfin, mooneye, goldeye, northern pike, muskellunge, and yellow perch from about 65 populations/publications representing a variety of latitudes. Museum collections contain about 39 fossil fish populations related to the candidate taxa from a range of geologic ages. Recently, I have been focusing my efforts on yellow perch in order to publish the methods to aid in procuring funding.

Contemporary yellow perch growth responds significantly to air temperature variation across their range from central Manitoba to North Carolina. This not only shows that growth will respond to climatic warming but also that yellow perch can be used as paleothermometers. I have used fossil yellow perch, recovered from the Seibold site, as indicators of temperature. The mean annual air temperature estimates include values from –5° to 0°C, which correspond with the types of fossil vegetation from the site. This research was presented at the International Union for Quaternary Research in July 2003 and in part at the Society of Vertebrate Paleontology annual meeting in October 2003. I am currently working on a manuscript describing growth of yellow perch in relation to changes in climate and their use as paleothermometers.

When the Seibold site was originally excavated data was collected on the types and abundance of fish, which has been analyzed to gain a better understanding of the effects of climate on fish. Fossil fish abundance, stratigraphy, pollen, and charcoal were analyzed to provide information about postglacial colonization and subsequent population fluctuations during a time of climatic warming. The sequence of colonization for each species was correlated with individual thermal and relative water velocity tolerances. Fish abundance fluctuated six times during an approximate 1000 year depositional history. Charcoal abundance, representing fires, was inferred to represent episodic droughts during which nutrient levels were reduced and fish abundance declined. The fluctuations followed an overall trend to increased abundance during a time when the lake-marginal vegetation changed from a spruce to a deciduous forest in response to climatic warming. This information was submitted in manuscript to the Canadian Journal of Fisheries and Aquatic Sciences, which is a contemporary fisheries journal.

I am attempting to use the analyses and the manuscript described to demonstrate in an NSF proposal that a re-excavation of the site will provide a greater understanding of the effects of climate change on the Seibold fish and other biota found associated with them.

I will be running an analysis for another taxa after I finish the yellow perch, either bowfin (Amiidae) or the mooneyes (Hiodontidae). The amiids are a very primitive group and they are represented by only one living species. The amiid range extends north to about the US/Canadian border and are relegated to relatively warmer climates. The hiodontids are more derived and they are represented by two living species. The hiodontids range north to the Northwest Territories, Canada.

Modeling Groundwater Denitrification by Ferrous Iron Using PHREEQC

Basic Information

Title:	Modeling Groundwater Denitrification by Ferrous Iron Using PHREEQC
Project Number:	2003ND27B
Start Date:	3/1/2004
End Date:	2/28/2005
Funding Source:	104B
Congressional District:	At large
Research Category:	None
Focus Category:	Groundwater, Models, Nitrate Contamination
Descriptors:	None
Principal Investigators:	Scott Korom

Publication

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MODELING GROUNDWATER DENTRIFICATION BY FERROUS IRON USING PHREEQC

(Full Renewal)

PROBLEM DESCRIPTION

Nitrate is one of the most common groundwater contaminants (Gillham and Cherry, 1979, Fetter, 1994). Denitrification converts nitrate irreversibly into harmless nitrogen gas (Korom, 1992). It is a natural process that requires an anaerobic environment, denitrifying bacteria, and sufficient and reactive electron donating species (Korom, 1992; Starr and Gillham, 1993). Numerous researchers show that the availability of electron donors within aquifer sediments limits the denitrification potential of aquifers (Trudell et al., 1986; Robertson et al., 1996). Korom (1992) explained that the three common electron donors for denitrification are organic carbon, sulfide (usually as pyrite), and ferrous iron. Reduced manganese may also contribute to denitrification (Korom, 1992), but it has never been shown to be a significant electron donor for denitrification in an aquifer. Efforts by members of the UND denitrification research team show organic carbon and sulfide are active electron donors for denitrification in North Dakota and Minnesota. We also believe ferrous iron is an active electron donor; however, the geochemical evidence for ferrous iron is more difficult to demonstrate and requires comprehensive knowledge of the hydrogeochemistry of the research sites.

SCOPE AND OBJECTIVES

Denitrification in aquifers involves numerous hydrogeochemical processes with both the water and sediment phases. Theses include dilution, ion exchange, dissolution, precipitation, and oxidation-reduction reactions (Tesoriero et al., 2000). Knowledge of the above reactions will enable us to decipher the denitrification capacity of aquifers, particularly when ferrous iron minerals are involved. Therefore, our objective is to use PHREEQC in order to gain a more comprehensive understanding of the hydrogeochemical environment that governs denitrification by ferrous iron and associated aquifer reactions.

KEY LITERATURE AND PRIOR WORK

Figure 1 shows the nine sites in North Dakota and Minnesota currently being studied by the UND Denitrification Research Team.

Figure 1. The nine in situ denitrification sites (indicated by stars) in Minnesota and North Dakota.

At each site stainless steel chambers partially isolate a portion of aquifer sediments, forming in situ mesocosms (ISMs). Tracer tests are performed in the ISMs and the resulting changes in the groundwater geochemistry in the chambers provides evidence for denitrification rates and what electron donors caused the denitrification. Schlag (1999) and Korom et al. (in review) describe how these sites are installed and how the tracer tests are performed. Results from the first tracer test done at the Larimore illustrate how an ISM tracer test is interpreted (Schlag, 1999; Korom et al., in review).

Figure 2 shows the trends of several major anions during the first tracer test at the Larimore site. Note that the nitrate concentrations decrease at a faster rate than the bromide concentrations. The latter decreases due to dilution with native groundwater during the tracer test. Only the nitrate lost beyond that explained by dilution of bromide is attributed to denitrification. Denitrification is commonly estimated by measuring the reaction products. The steep increase in sulfate indicates that sulfide was an electron donor for denitrification. Schlag (1999) and Korom et al. (in review) showed that about 60% of the denitrification can be explained by the oxidation of sulfide as pyrite.

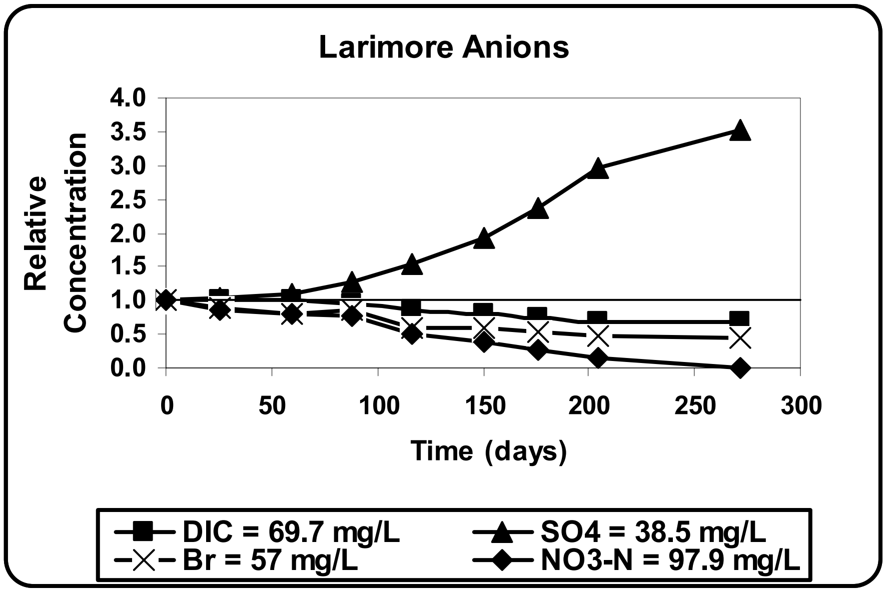

Figure 2. Anion concentrations during the first tracer test at the Larimore site. Initial concentrations are given in the box at the bottom of the figure.

Korom et al. (in review) also showed that organic carbon was likely responsible for most of the remaining denitrification observed. This process is illustrated by noting the decreasing dissolved inorganic carbon in Figure 2 and the steep loss of calcium and magnesium in Figure 3.

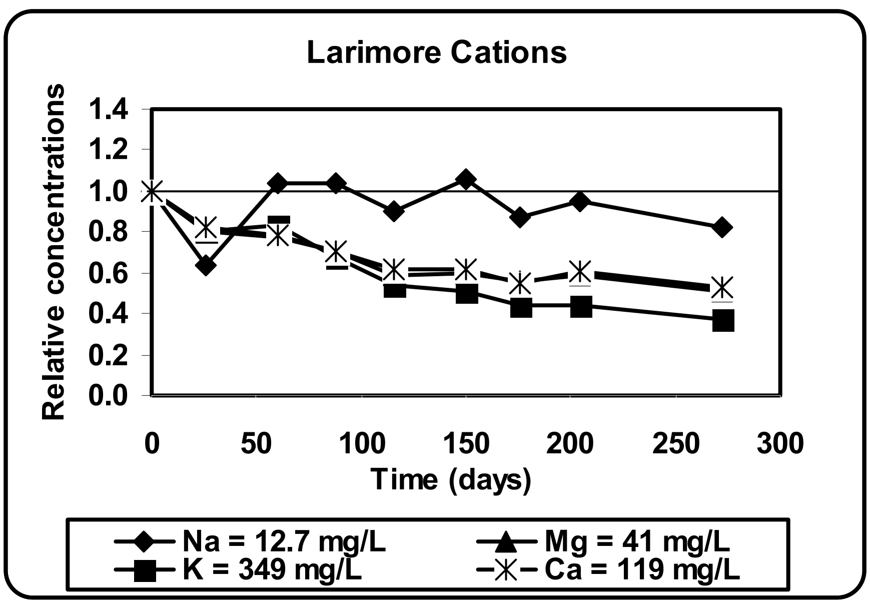

Figure 3. Cation concentrations during the first tracer test at the Larimore site. Initial concentrations are given in the box at the bottom of the figure.

Denitrification by organic carbon produces inorganic carbon. We expected DIC to increase in Figure 2. It would have, except the increase in inorganic carbon was masked by the precipitation of a magnesium-rich calcite ($CaCO_3$). Therefore, denitrification by sulfide results in an increase in sulfate; denitrification by organic carbon results in an increase in inorganic carbon, unless it is accompanied by a decrease in calcium (and possibly magnesium). In the latter case, the DIC will decrease, as well. (The decrease in potassium is mostly attributed to dilution because potassium bromide and potassium nitrate were added to the ISMs.)

We see these patterns in the groundwater in many of the ISMs. In fact the geochemical evidence in five of the research sites shows that organic carbon and inorganic sulfides play a major role in converting nitrates to nitrogen gas. However, both electron donors do not account for all the nitrate lost. Likewise, the reaction products of two sites, Robinson, ND and Akeley, MN, do not indicate the significant involvement of organic carbon or sulfides in the denitrification processes. Our hypothesis is that ferrous iron is the major electron donor causing reduction of nitrates in the latter two aquifers. (The tracer tests in the two ISMs near Minot just began this summer; it is too early to interpret the results).

Scope and Objectives

Mixing of nitrate polluted water and reduced waters at depth trigger important multiphase aquifer hydrogeochemical reactions. Some of the common aquifer geochemical reactions are ion exchange, dissolution and/or precipitation of dominant minerals, and redox reactions (Tesoriero et al., 2000). Knowledge of the above reactions, which is the main reason behind this proposal, enables us to decipher the denitrification capacity of aquifers. Therefore, our objective is to use PHREEQC in order to understand the hydrogeochemical environment that governs denitrification and other associated aquifer reactions, particularly with respect to the involvement of ferrous iron

Methods, Procedures and Facilities

Denitrification reactions require consideration of multiple thermodynamic and kinetic factors. Considering the net effects of these factors requires the application of realistic and relatively complex hydrogeochemical models. In this project PHREEQC (Parkhurst and Appelo, 1999) will be used to couple the regulating geochemical factors involved in the denitrification at the various ISM sites.

To study the controlling multiphase geochemical reactions both forward and inverse modeling schemes will be used. Forward modeling is constrained by equilibrium thermodynamics and the unknown variables are determined by solving the mass action equations. Inverse modeling is based on the net mass transfer among the interacting mineral phases in the initial and the final solutions. Mass balance modeling and cation exchange reactions are given special emphasis in the project. Since the results of inverse modeling are not unique, equilibrium and kinetic factors can be used to sort out improbable results.

Input files for the modeling are geochemical data of the native and injected waters as well as mineralogical data of the aquifers. Fortunately, substantial aqueous geochemical data including major anions, major cations, pH, and temperature, dissolved organic and inorganic carbon, of the study sites are available from previous work. Supplementary data required for the modeling are mineralogical composition, texture description, cation exchange capacity, organic carbon, inorganic sulfide and ferrous iron content of the sediments. Aquifer sediment samples from the nine sites have been collected. Physical and geochemical analyses of the samples are ongoing and should be done by February, 2004. Analytical instruments in the UND Environmental Analytical Research Laboratory and the Department of Geology and Geological Engineering will be used for the water, sediment, and mineral analyses. Finally, modeling output will be compared with the field and laboratory results in order to verify both the numerical procedures as well as the hydrogeochemical reaction schemes.

ANTICIPATED RESULTS

The proposed analytical and modeling results are expected to provide insights into the denitrification capacity and electron donors involved at all the ISM sites. However, the particular focus herein is to provide further evidence whether ferrous iron is the major electron donor for denitrification at the Robinson, ND, and Akeley, MN, ISM sites.

PROGRESS TO DATE

Funding has been secured to repeat the tracer tests at the ND sites. In total, over half a million dollars in funding and in-kind matches has been provided thus far for this research. All data will be made available to me for this investigation. Preliminary interpretation of all the completed tracer tests has been done. Aquifer sediment samples of all the sites and much of the physical and geochemical analyses of the sediment samples are done. Of particular note are the preliminary results of the analyses of the iron coating the surface of the sediments shown below. The surface component is the most reactive fraction of the total ferrous iron in the sediments.

Site	Ferrous Iron (%)
Akeley	0.07
Hamar	0.006
Larimore	0.19
Perham2	0.02
Robinson	0.07

At the Hamar site, we observe little denitrification. However at the Perham2 site we have as much denitrification as at the Akeley and Robinson sites. Organic carbon appears to be the major electron donor for denitrification at the Perham2 site. We can not explain the denitrification at the Akeley and Robinson sites by either organic carbon or sulfide; our hypothesis is that ferrous iron is the electron donor. My preliminary analyses indicate that both of these sites have relatively high concentrations of reactive ferrous iron (3.5 times that of the Perham2 site), which supports our hypothesis. The Larimore site has even more ferrous iron, but it also has higher concentrations of organic carbon and sulfides, which may be used preferentially before the ferrous iron as an electron donor for denitrification.

In addition, PHREEQC has been shown to be effective in interpreting the denitrification reactions in the ISMs during the tracer tests (Skubinna, in preparation).

REFERENCES

Fetter, C.W., 1994. Applied Hydrology. 3rd ed. Prentice-Hall, Inc. Upper Saddle River, New Jersey. p. 321-325.

Gillham, R.W., and J.A. Cherry, 1978. Field evidence of denitrification in shallow ground water flow systems. Water Pollution Research in Canada 13:53-71.

Korom, S.F., 1992. Natural denitrification in the saturated zone: A review. Water Resources Research 28, no. 6: 1657-1668.

Korom, S.F., A.J. Schlag, W.M. Schuh, and A.K. Schlag. In situ mesocosms: Denitrification in the Elk Valley aquifer. In review with Ground Water Monitoring and Remediation.

Lowenstern, J., Janik, J., Fournier, R. O., Tesfay, T., Duffield, W. A., Clynne, M. A., Smith, J. G., Woldegiorgis, L., Weldemariam, K., Kahsai, G., 1999. A geochemical reconnaissance of the Alid volcanic center and geothermal system, Danakil Depression, Eritrea. Geothermics, V. 28, P. 161-187.

Parkhurst, D.L. and Appelo, C.A.J., 1999, User's guide to PHREEQC (version 2)--A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations: U.S. Geological Survey Water-Resources Investigations Report 99-4259, 312 p.

Robertson, W.D., B.M. Russell, and J.A. Cherry, 1996. Attenuation of nitrate in aquitard sediments of southern Ontario. J. Hydrol. 180:267-281.

Schlag, A. J., 1999. In-site measurements of denitrification in the Elk Valley aquifer, M.S. thesis, 104 pp., University of North Dakota, Grand Forks, ND.

Starr, R.C., and R.W. Gillham, 1993. Denitrification and organic carbon availability in two aquifers. Ground Water 31:934-947.

Tesfay, T., Bolles, A.B., Korom, F. S., 2001. Laboratory study of denitrification by recently formed sulfides. American Geophysical Union, Spring Conference 2001, AN: H31C-07.

Tesfay, T., Durbin, H., Korom, F. S., 2002. Predicting denitrification capabilities of Karlsruhe aquifer sediments based on data provided from a Network of In-situ Mesocosms. Midwest Groundwater conference.

Tesoriero, A.J., H. Liebscher, and S.E. Cox. 2000. The mechanism and rate of denitrification in an agricultural watershed: Electron and mass balance along ground water flow paths. Water Resour. Res. 36:1545–1559.

Trudell, M.R., R.W.Gillham, and J.A. Cherry, 1986. An in-situ study of the occurrence and rate of denitrification in a shallow unconfined sand aquifer. J. Hydrol. 83:251-268.

A Study of Microbial Regrowth Potential of Water in Fargo, North Dakota and Moorhead, Minnesota

Basic Information

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Focus Category:	Water Supply, Treatment, Water Quality
Descriptors:	None
Principal Investigators:	Khan Eakalak

Publication

A STUDY OF MICROBIAL REGROWTH POTENTIAL OF WATER IN FARGO, NORTH DAKOTA AND MOORHEAD, MINNESOTA
(Full Renewal)

BACKGROUND

In recent years, water quality scientists and engineers have emphasized on the biodegradability of dissolved organic matter in both raw and treated waters. This is because the biodegradable organic matter (BOM) in treated water can induce the growth or regrowth of microorganisms in the distribution system of drinking water. Residual BOM is usually the most important limiting factor responsible for bacterial regrowth in the water distribution system (Rittmann and Snoeyink, 1984). One of the most effective methods in controlling the bacterial growth in the distribution system is to limit the amount of BOM required for the growth of heterotrophic bacteria in treated water (Servais *et al.*, 1993). Water containing BOM less than a minimum concentration that supports the bacterial growth is usually biologically stable.

BDOC has been used as one of the parameters for quantifying the amount of BOM in water. Servais *et al*. (1989) defined BDOC as the fraction of dissolved organic carbon (DOC) which can be metabolized by bacteria within a period of time. The BDOC test measures the reduction of DOC in a water sample, which is exposed to microorganisms in a period of time (Servais *et al.*, 1987 and 1989). The first BDOC measurement was introduced by Servais *et al*. (1987). It was developed as a batch procedure. A mixed microbial culture from the same environment as the sample was used as an inoculum. Incubation occurred in the dark at 20 ± 0.5°C for a period of 10 to 30 days, and the BDOC was determined by the difference between the initial and final DOCs.

The first BDOC procedure was used specifically for testing the quality of raw water and for designing and monitoring, and optimizing operating conditions of biological activated carbon (ozonation + granular activated carbon) systems. Occasionally, it was used to examine the BDOC removal of other treatment processes such as coagulation and filtration. Interest in BDOC of finished water started to grow when BDOC was linked to the microbial proliferation in the distribution systems. As a result, BDOC is a widely used parameter in the drinking water field.

An alternative to the BDOC procedure called AOC, was invented by van der Kooij *et al*. (1982). AOC is the portion of the organic carbon that can be synthesized to cellular material by a single bacterial strain. In the AOC determination method, a preheated water sample is seeded with a pure strain of *Pseudomonas fluorescens* P17. The sample is incubated at 15°C, and bacterial growth is monitored daily by colony counts (spread plate techniques) until the maximum growth is reached. The incubation period (the number of days to reach the maximum yield) can be from 3 to 30 days depending on the type of the water sample. By concurrently determining the growth yield of bacteria in solutions of known acetate concentration, the maximum growth can be converted into AOC and expressed as μg of acetate-C equivalents/L.

van der Kooij (1987) and van der Kooij *et al*. (1989) included a *Spirillum* strain, NOX, into the procedure as an alternative seed or a dual strain seed due to the inability of *Pseudomonas fluorescens* P17 to metabolize oxalic acid, which is one of the products frequently formed during ozonation. Unlike BDOC, AOC only accounts for the organic carbon used for cell synthesis.

Since the AOC test measures cell growth of a single or dual strain, the test does not guarantee that all the assimilable carbon is measured. The inoculum may not be capable of metabolizing all contaminants. Therefore, the reported AOC value is normally less than the reported BDOC value for the same sample. The AOC method has been widely adopted when the regrowth is a concern.

BDOC has also been related to the regrowth of microorganisms. High BDOC in finished water indicates poor quality and a potential of microbial multiplication. Maintaining a free chlorine residual to prevent the regrowth along the distribution system is a common solution; however, a large amount of chlorine is required. Also, chlorine residual cannot completely inactivate fixed bacteria (Le Chevallier *et al.*, 1988). Controlling microbial dynamics by limiting available substrate (BDOC) is a new and interesting approach (Rittmann and Snoeyink, 1984, Huck, 1990, and Servais *et al*., 1993). Biologically stable water should contain less than 0.15 mg of BDOC/L. At this threshold level, microbial growth is very limited (Servais *et al.*, 1993).

In order minimize AOC and BDOC in finished water, some water treatment plants employ biological filtration in their treatment trains. The biological filtration usually consists of ozonation and filtration. The purpose of ozonation is to destruct complex organic to simpler molecules which can be used by microorganisms in the filter. For some treatment plants, the ozonation portion of the biological filtration also serves as primary disinfection, and taste and odor control. Increases in BDOC and AOC after ozonation have been well documented (Janssens *et al.*, 1984, Servais *et al.,* 1987, and Volk *et al.*, 1993). The BDOC and AOC increases during ozonation are removed in the filter which contains media (activated carbon or sand) covered by attached microorganisms (biofilm).

DESCRIPTION OF THE CRITICAL STATE OR REGIONAL WATER PROBLEM

BDOC and AOC have been used to examine the regrowth potential of water throughout the world. Furthermore, AOC is included in the latest *Standard Methods* (1998). However, the regrowth potential of water in Fargo, North Dakota and Moorhead, Minnesota has never been evaluated; BDOC and AOC values of water in Fargo and Moorhead have not been reported. The ultimate goal is to minimize the concentrations of these two parameters in treated water provided by the Fargo and Moorhead water treatment plants which in turn will benefit public health by limiting the number of microorganisms in tap water. Collecting BDOC and AOC data is a first step to achieve the ultimate goal. The data will also indicate the degree of susceptibility of drinking water of Fargo and Moorhead to microbial proliferation.

It is crucial that BDOC and AOC of water in Fargo and Moorhead are studied because of the nature of high total organic concentrations in the influent and effluent and the use of ozonation at both treatment plants (Figure 1). BDOC and AOC tend to be high with these two conditions. The influent (from the Red River for the Fargo plant and the Red River blended with groundwater at 85%:15% for the Moorhead plant) and effluent total organic carbon (TOC) concentrations at both plants are sometimes as high as 8 to 10 mg/L and 1 to 2 mg/L, respectively. BDOC is a portion of total organic concentrations. Although water with high total organic concentrations does not necessarily contain large amounts of BDOC, positive linear relationships have been frequently observed between the two parameters (Servais *et al.*, 1987 and Khan *et al*. 1998b). As stated previously, ozonation of water with organics results in BDOC and AOC increases and their removal relies on the performance of subsequent treatment which normally is filtration. Currently, BDOC and AOC removal abilities of the filtration units at the Fargo and Moorhead plants are not known because the two parameters have not been measured.

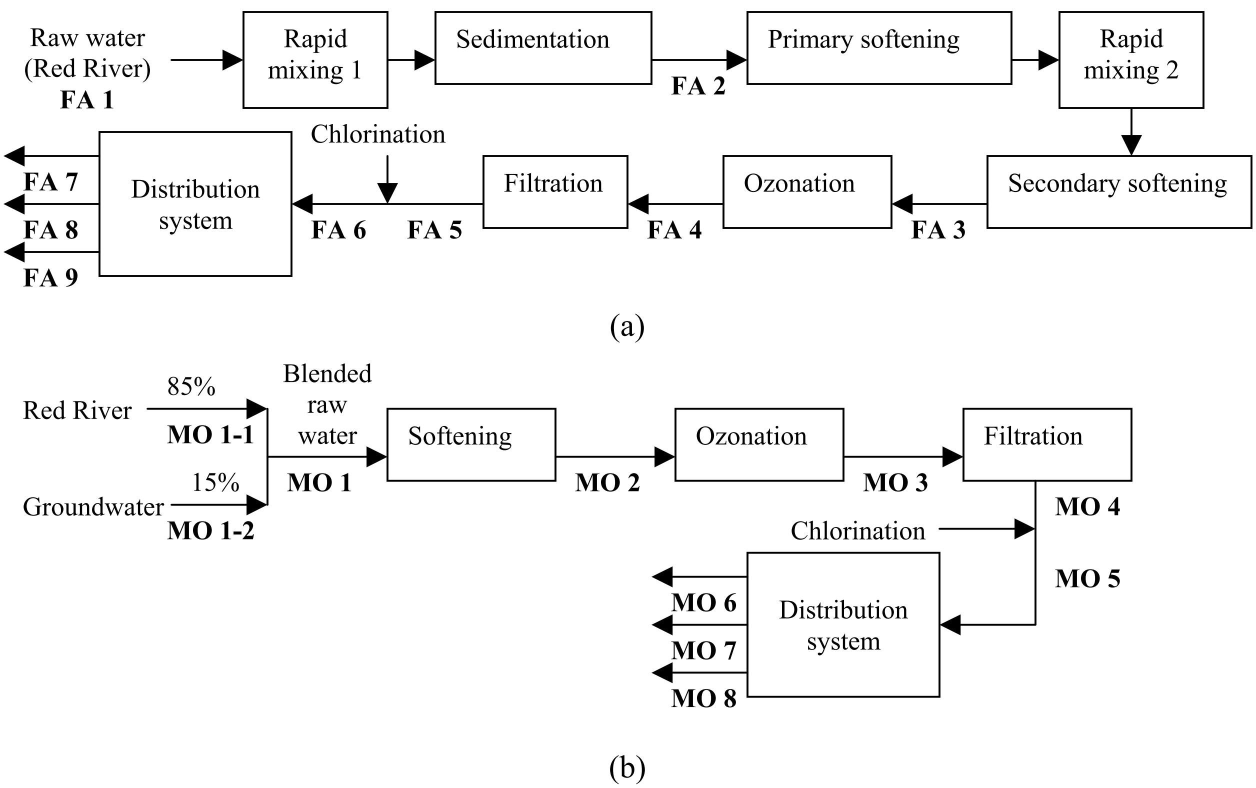

Figure 1 Simplified schematic diagrams for (a) the Fargo Water Treatment Plant and (b) the Moorhead Water Treatment Plant.

SCOPE OF STUDY AND OBJECTIVES

The main scope of this study is to collect BDOC and AOC data of water in Fargo and Moorhead in order to achieve the following objectives:

1) To evaluate the microbial regrowth potential of water especially finished water and tap water,
2) To predict the regrowth occurrence in the distribution systems by comparing AOC and BDOC in finished water and those in tap water, and
3) To compare BDOC and AOC removal of the Fargo and Moorhead plants which are different mainly in the presence and absence of the rapid mixing-sedimentation process.

METHODOLOGY

Sampling

Sampling began since November 1, 2003 and will continue until October 31, 2004. Samples are collected from one treatment plant and accompanying distribution system biweekly. The plants are alternated weekly. Sampling locations are listed in Table 1 and the samples are analyzed for AOC, BDOC, UV_{254}, TOC and pH.

Parameter tested

Each sample will be analyzed for pH, ultraviolet absorbance at 254 nm (UV_{254}), TOC, DOC, BDOC, and AOC. UV_{254} is used to relatively measure the amount of organic compounds that are aromatic in structure or have conjugated unsaturated bonds. It is known that a decrease in UV_{254} indicates less refractory organics (more BDOC).

Table 1 Sample identification and collection locations.

Fargo water systems		Moorhead water systems	
Sample no.	Sampling location	Sample no.	Sampling location
FA 1	Raw water (Red River)	MO 1	Blended raw water
FA 2	After sedimentation	MO 1-1	Raw water (Red River)
FA 3	After secondary softening	MO 1-2	Raw water (Groundwater)
FA 4	After ozonation	MO 2	After softening
FA 5	After filtration	MO 3	After ozonation
FA 6	After chlorination (treated water)	MO 4	After filtration
FA 7	Holiday Inn Hotel	MO 5	After chlorination (treated water)
FA 8	North Dakota State Universtiy	MO 6	Stop and Wash Convenience Store
FA 9	Hector International Airport	MO 7	Busch Agricultural Resources Inc.
		MO 8	Oasis Convenience Store

* Sample will only be collected when utilized as a source for raw water

Analyses

pH is measured using a pH meter (Orion model SA520). UV_{254} is determined following the procedure listed in *Standard Methods* (1998), using a spectrophotometer (Thermo Spectronics model Genesys 10 UV Scanning). TOC and DOC is analyzed according to the procedure described in *Standard Methods* (1998), using a TOC analyzer (Tekmar-Dohrmann model Phoenix 8000). For DOC analysis, the samples are filtered through a glass fiber filter (Whatman, GF/F) prior to TOC determination. BDOC is evaluated in accordance with a modified protocol by Khan *et al.* (1998a) which is simpler and more accurate than the original method (Servais *et al*., 1987). AOC is determined according to *Standard Methods* (1998).

FACILITIES, EQUIPMENT AND INSTRUMENTS

Facilities

This research will be conducted mainly in the Environmental Engineering laboratory facilities of the Department of Civil Engineering and Construction, North Dakota State University. The main laboratory facility occupies about 2,650 square feet of the second floor of the Civil and Industrial Engineering Building. An additional laboratory with an approximate area of 240 square feet is located on the first floor of the Engineering Technology Building. These two facilities have general apparatus (glassware) basic support services (gas, water, air, fume hoods, distilled and deionized water). Included in the main facility are offices for research assistants and storage spaces.

Laboratory equipment and instruments

The facilities contain most basic instruments and are well-equipped for conducting the proposed research. Examples of the basic instruments available are turbidimeters, pH meters, dissolved oxygen (DO) meters, ozone generators, a respirometer, phase contrast microscopes, conductivity meters, ion selective probes, vacuum pumps, ovens, furnaces, incubators, an autoclave, centrifuges, balances, refrigerators, water baths, cooling units, distillation and digestion systems for chemical oxygen demand (COD), nitrogen, and phosphorus analyses. Available major instruments in the main facility include a purge and trap gas chromatograph, with a mass selective detector (GC/MSD), two scanning UV-VIS spectrophotometers, and a TOC analyzer.

PROGRESS TO DATE

Literature review has been performed to learn background information about the topic. The background information that has been reviewed assisted in the experiment design and processes that need to be followed. Preliminary testing has been performed and results of the BDOC analysis can be seen in Figure 1 below. The preliminary AOC data are not available due to problems with the test method. The test method for AOC is very meticulous and leaves a lot or room for error and contamination. The problems that occurred have been corrected and I am confident that the results will be correct in the near future. The sampling and testing will continue until October 31, 2004. From October 31, 2004 to March of 2005 a thesis will be written and defended. In the original proposal sampling was to start on March 1, 2002, but was delayed due to my inexperience with test procedures and equipment that was required to complete each method. Also, more time was spent on practice testing and literature reviews than originally planned for.

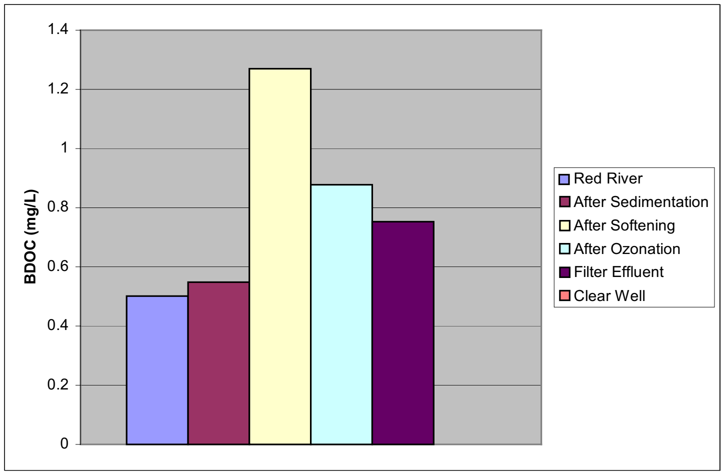

Figure 1: BDOC, Fargo Water Treatment Facility

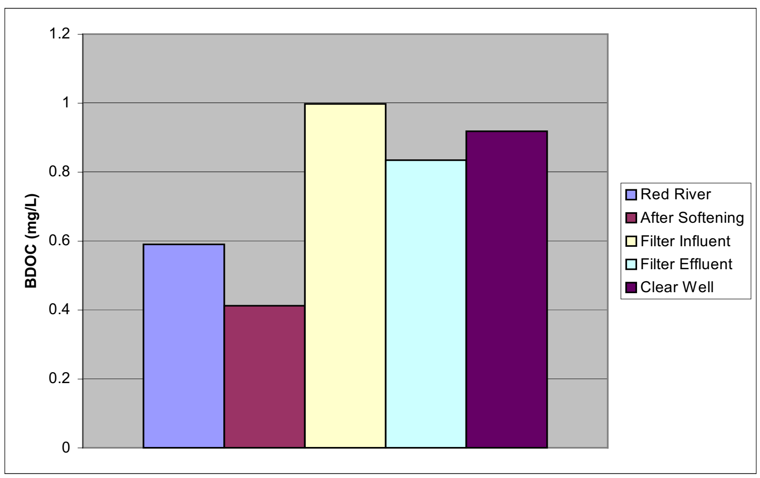

Figure 2: BDOC, Moorhead Water Treatment Facility

ANTICIPATED RESULTS AND BENEFITS ("DELIVERABLES")

This research will greatly benefit the water treatment facilities and public health because it will indicate how biologically stable the water in Fargo and Moorhead is. If the finished water produced by the Fargo and Moorhead plants has high regrowth potential (containing high BDOC and AOC), first it has to be known and then studied in more detail on strategies to minimize BDOC and AOC which will help to protect water consumers more from possible microbial contact that may cause adverse health effects. Furthermore, the results of this research will indicate whether blending the Red river water with groundwater as practiced at the Moorhead plant and the rapid mixing-sedimentation process used by the Fargo plant have any effect on BDOC and AOC in finished water.

In addition to the synopsis, abstract, and summary of progress, the findings on this project will be presented at a national or regional conference and will be submitted for publication in a peer review journal. The M.S. thesis generated from this research, which will also make available to public electronically on the internet, will contain all the information on the project including raw data and will serve as a final report.

REFERENCES

Huck, P. M. (1990) Measurement of Biodegradable Organic matter and bacterial growth potential in drinking water. *J. Am. Water Works Assoc.*, **82** (7), 78.

Janssens, J. G., Meheus, J., and Dirickx, J. (1984) Ozone enhanced biological activated carbon filtration and its effect on organic matter removal and in particular on AOC reduction. *Water Sci. Tech.*, **17**, 1055.

Khan E., Babcock R. W., Suffet I. H. and Stenstrom M. K. (1998a) Method development for measuring biodegradable organic carbon in reclaimed and treated wastewater. *Water Environ. Res.* **70**(50), 1025.

Khan E., Babcock R. W., Viriyavejakul S., Suffet I. H. and Stenstrom M. K. (1998b) Biodegradable dissolved organic carbon for indicating wastewater reclamation plant performance and treated wastewater quality. *Water Environ. Res.* **70**(5), 1033.

Le Chevalier, M. W., Cawthon, C. D., and Lee, R. G. (1988) Inactivation of biofilm bacteria. *Appl. Environ. Microbiol.*, **54**, 2492.

Rittmann B. E. and Snoeyink V. L. (1984) Achieving biologically stable drinking water. *J. Am. Water Works Assoc.* **76**(10), 106.

Servais P., Billen G. and Hascoet M. C. (1987) Determination of the biodegradable fraction of dissolved organic matter in waters. *Water Res.* **21**(4), 445.

Servais P., Anzil A. and Ventresque C. (1989) Simple method for determination of biodegradable dissolved organic carbon in water. *Appl. Environ. Microbiol.* **55**(10), 2732.

Servais P., Laurent P. and Randon G. (1993) Impact of biodegradable dissolved organic carbon (BDOC) on bacterial dynamics in distribution systems. In *Proc. AWWA Water Qual. Tech. Conf.*, Miami, FL, 963.

Standard Methods for the Examination of Water and Wastewater (1998) 20th ed., APHA, AWWA, and WEF, Washington, D.C.

van der Kooij, D., Visser, A., and Hijnen, W. A. M. (1982) Determining the concentration of easily assimilable organic carbon in drinking water. *J. Am. Water Works Assoc.*, **74** (10), 540.

van der Kooij, D. (1987) The effect of treatment on assimilable organic carbon in drinking water. In *Proc. Second Natl. Conf. on Drinking Water.* P. M. Huck and P. Toft (Eds.), Permagon Press, NY.

van der Kooij, D., Hijnen, W. A. M., and Kruithof, J. C. (1989) The effects of ozonation, biological filtration, and distribution on the concentration of easily assimilable organic carbon in drinking water. *Ozone Sci. Engrg.*, **11** (3), 297.

Volk C., Roche P., Renner C., Roche P., Pailard H. and Joret J. C. (1993) Effects of ozone on the production of biodegradability dissolved organic carbon (BDOC) during water treatment. *Ozone Sci. Engng.* **15**(5), 389.

Effects of West Nile Virus Infection, Immune Function, and Age on Female Yellow-headed Blackbird (Xanthocephalus xanthocephalus) Reproduction.

Basic Information

Title:	Effects of West Nile Virus Infection, Immune Function, and Age on Female Yellow-headed Blackbird (Xanthocephalus xanthocephalus) Reproduction.
Project Number:	2004ND46B
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Focus Category:	Wetlands, Ecology, Conservation
Descriptors:	None
Principal Investigators:	Wendy Reed, Wendy Reed

Publication

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EFFECTS OF WEST NILE VIRUS INFECTION, IMMUNE FUNCTION, AND AGE ON FEMALE YELLOW-HEADED BLACKBIRD (*XANTHOCEPHALUS XANTHOCEPHALUS*) REPRODUCTION
(Partial Renewal)

DESCRIPTION OF THE CRITICAL WATER PROBLEM

Recent high water levels and canalization of water resources (i.e., Garrison Diversion) in North Dakota have resulted in an increase of aquatic habitats for many wildlife species. Current water conditions correspond with increased numbers of wetland breeding birds and increased habitat for breeding mosquitoes. Because birds often serve as intermediate hosts for mosquito borne diseases, increased populations of birds and mosquitoes could impact the ecology, rate of emergence, and persistence of diseases in humans and wildlife. The recent spread of WNV into the state has produced a need for research to study the influence of the virus on wetland wildlife in North Dakota.

The North Dakota Department of Health reported the first cases of WNV in the state in the summer of 2002. The first bird to test positive for WNV was an American crow (*Corvus brachyrhynchos*) found on July 14th, and the first positive human cases were reported on August 28th. There were 19 human cases of WNV and 2 deaths in the state in 2002. In 2003, the virus was much more widespread, with 422 human cases and 4 deaths. This year alone, 788 bird carcasses have been tested in the state and 189 were WNV positive.

Because stagnant water in wetlands is ideal breeding habitat for mosquitoes, wildlife associated with these habitats may suffer high rates of WNV infection. The recent arrival of WNV into the state necessitates a study of the prevalence and immunological impact of WNV on native North Dakota wetland species. Most research on the virus has focused on using carcasses of birds as a surveillance system for detecting the spread of WNV across North America. No published research has been conducted on a living population of free-ranging birds. Failure of biologists to adequately address disease emergence in free-ranging wildlife may lead to diminished geographic distributions and populations declines (Friend et al. 2001).

The Missouri Coteau of central North Dakota has many small prairie wetlands, which provide essential foraging and breeding habitat for many species of birds. Yellow-headed blackbirds are an ideal species to study WNV infection because they breed in high-density wetland colonies throughout the Coteau. Establishing rates of WNV infection in yellow-headed blackbirds is necessary to determine the vulnerability of this wetland dwelling species and the influence of WNV infection on reproduction. Information gathered on WNV for this study can also be used to model and predict potential impacts of the virus on other species of wetland birds.

KEY LITERATURE

West Nile virus is a mosquito-borne virus that was first diagnosed in North America in 1999 (Rappole et al. 2000). Since that time, the virus has spread across the United States and into Canada. Because the virus can cause fatal meningitis, it has become a national health concern for human populations, an economic concern for domestic animal losses, and a concern for the status of free-living bird populations (Campbell et al. 2002). Birds are one of the principal hosts of WNV (Rappole et al. 2000), with more than 138 species of wild birds diagnosed with the virus in the United States since 1999 (CDC unpub. data). Most of the information we have on the prevalence and distribution of the virus is based on information from symptomatic birds (i.e., sick or dead), which can bias estimates of potential outbreaks if asymptomatic birds have survived infection or act as carriers of the virus. By testing for the presence of antibodies to WNV in yellow-headed blackbirds and monitoring reproductive performance, I will be able to assess the degree to which a free-living population has been exposed to the virus, the non-lethal effects of WNV infection on reproduction, and the potential for blackbirds to serve as carriers of WNV.

WNV could influence yellow-headed blackbird reproduction by compromising female immunity. When a bird suffers immune system stress, resources are allocated away from nonessential processes, such as growth and reproduction, and are reallocated to activities directly related to survival (Lochmiller and Deerenberg 2000). For example, depressed female immunity is known to decrease the diversity and concentration of carotenoids in egg yolks (Saino et al. 2002). Carotenoids are biologically active, lipid-soluble pigments synthesized by plants and photosynthetic microorganisms, which animals must obtain from their diet (Blount et al. 2000). In developing avian embryos, carotenoids in the yolk protect vulnerable tissues against damage caused by free radicals, by-products of normal metabolism and immune defense, which can cause extensive DNA, protein, and lipid damage (Surai et al. 2001). Because carotenoids are derived solely from the female, they reflect the quality of the maternal diet prior to egg laying.

As powerful antioxidants and immunostimulants, carotenoids are also incorporated into the sexual signals of many animals and are thought to indicate individual health (Blount et al. 2000). Yellow-headed blackbirds depend on carotenoids for their brightly colored yellow plumage. Second year (SY) female yellow-headed blackbirds can be distinguished from older, after second year (ASY) females because they have smaller patches of yellow feathers and are paler in their head, neck and breast regions (Crawford and Hohman 1978). These differences in plumage may reflect a female's ability to obtain carotenoids from surrounding habitats and therefore reflect her ability to deposit carotenoids into her eggs (Royle et al. 2001). Female age could also have substantial impacts on resource allocation and immune function. Young females may allocate more physiological resources to growth than mature females, and therefore allocate less to reproduction and immunity.

Maternal tradeoffs exist between the use of carotenoids for physiological functions, the expression of sexual signals, and investment into eggs (Saino et al. 2002). Yellow-headed blackbirds are an ideal species to study maternal tradeoffs between reproduction and self-maintenance, because females can easily be separated into 2 age classes and they allocate carotenoids both to plumage and eggs. Also, the high density of conspicuous, easily accessible nests in small North Dakota wetlands makes yellow-headed blackbirds an ideal species for study of WNV infection, immune response, and carotenoid concentrations in breeding females and their offspring.

SCOPE AND OBJECTIVES

The overall objective of this project is to determine the effects of female age and infection with West Nile virus on yellow-headed blackbird (*Xanthocephalus xanthocephalus*) maternal investment into eggs. The specific objectives of this project are to identify the prevalence of WNV in a free-living population of yellow-headed blackbirds, to quantify variation in immune function of female blackbirds, and to measure the relationship between female immune function and age on carotenoid allocation to eggs. These objectives will allow us to evaluate potential relations between wetland bird WNV infection and increased aquatic habitat for breeding mosquitoes in North Dakota.

METHODS, PROCEDURES, AND FACILITIES

Female yellow-headed blackbirds will be captured using mist-nets in order to collect blood samples to assess WNV antibody production and to measure variation in immune function using non-lethal immune challenges. Blood serum will be tested for WNV antibodies using competitive enzyme-linked immunoabsorbent assay (ELISA). We will follow protocol specifically designed to detect WNV antibodies in blood serum from avian species (Dr. Barry Beaty, Colorado State University, pers. comm.). We will quantify variation in female immune function at both the cell-mediated (i.e., white blood cell) and humoral (i.e., antibody production) levels using the methods described in Casto et al (2001). To assess cell-mediated immunity, we will measure differential-cutaneous swelling between wings of 30 females injected with a harmless plant protein (phytohemaglutinin - PHA) in the right wing and saline solution in the left. We will assess variation in humoral immune response by quantifying the antibody production of 30 females injected with sheep red blood cells (a novel, non-lethal antigen). Prior to release, each female will be categorized as either SY or ASY and will be banded with a standard Fish and Wildlife Service aluminum band along with a unique color-band combination for individual field identification.

We will locate and monitor nests of marked females to assess maternally allocated carotenoids in eggs and offspring survival and growth. The third-laid egg will be removed from each nest for carotenoid analysis, which insures the detection of differences among females and not variation in carotenoid allocation due to egg laying order. Yolks will be separated from the egg and the carotenoids will be extracted from the yolk using the methods described in Surai and Speake (1998). We will analyze carotenoids with High Performance Liquid Chromatography (HPLC) using a reverse-phase column. We will assess the concentration of carotenoids by comparing my samples to a calibration curve obtained from known concentrations of carotenoids. After sampling the third egg, we will monitor each nest at 3-day intervals to determine hatching success and nestling growth rates (i.e., body mass, tarsus length, and wing length).

This study is being conducted on several wetlands located within a five square mile area of the Missouri Coteau region of central North Dakota (Stutsman County). Central North Dakota has one of the highest concentrations of yellow-headed blackbirds in North America (Twedt and Crawford 1995). In addition, Stutsman County has one of the highest numbers of positive avian West Nile virus cases in central North Dakota (CDC unpub. data).

My advisor, Dr. Wendy Reed will provide field facilities in Stutsman County for all field data collection (i.e., equipment storage, animal care, and lodging for myself and my assistant). Lab analysis of WNV antibodies and carotenoid concentrations will be conducted at NSDU.

ANTICIPATED RESULTS AND DELIVERABLES

This study will provide essential information on the prevalence and immunological impact of WNV on a North American avian species. Infection with the virus can be lethal, however, the degree to which birds are adversely affected varies across species and even between individuals within a species (Rappole et al. 2000). By testing for the presence of antibodies to WNV in yellow-headed blackbirds, we will be able to assess the vulnerability and degree of virus exposure in a free-living population of wetland dwelling birds. We will also be able to evaluate potential influences of current high-water conditions on breeding populations of mosquitoes and avian WNV infection rates.

Many wildlife pathogens cause non-lethal physiological and reproductive effects that remain poorly understood. This study will quantify the immunological costs and maternal tradeoffs associated with exposure to a non-lethal antigen. Because female birds allocate essential resources to eggs, exposure to pathogens can shift maternal resources away from reproduction. This seemingly small, non-lethal effect influences the survival of offspring and can therefore cause population level effects in the next generation.

The research conducted for this study will comprise a Ph.D. dissertation. Results will be presented at an American Ornithologist Union conference and will ultimately be submitted for publication to a prestigious peer-reviewed journal.

PROJECT PROGRESS

During my first field season from May to August of 2003, I collected 51 eggs and 20 feather samples to use for yellow-headed blackbird carotenoid quantification. I conducted immune challenges on five females, but the majority of the immunity and nest performance data will be collected in upcoming field seasons. I also collected blood samples for WNV antibody detection from 44 yellow-headed blackbirds, 18 grackles, two red-winged blackbirds, and one western meadowlark. This fall I have tested the 65 blood samples for WNV antibodies and I detected antibodies in only two individuals, one red-winged blackbird and one western meadowlark.

I have two hypotheses to explain why I did not find WNV antibodies in yellow-headed blackbirds or common grackles. The first is that WNV could be lethal in free-living individuals of these two species. In a recent study by Komar et al. (2003), experimentally infected common grackles were shown to have a 33% death rate within four days of being infected with WNV. Perhaps death rates are closer to 100% in less hospitable natural conditions and that is why I was unable to detect individuals with antibodies. In contrast to common grackles, all of the red-winged blackbirds that were experimentally infected with WNV survived infection, indicating that the species is able to survive WNV infection by producing antibodies (Komar et al. 2003).

High death rates in yellow-headed blackbirds and common grackles due to WNV infection could influence human health. Bird species that suffer high death rates associated with WNV have been found to have high viremia levels circulating in their blood streams (Komar et. al. 2003). They also have the highest probability of passing the virus to a mosquito vector and therefore to a human. If the virus is lethal in yellow-headed blackbirds and common grackles, infected individuals may act as virus reservoirs in central North Dakota.

The loss of large numbers of yellow-headed blackbirds and common grackles due to lethal WNV infection would have ecological ramifications in the food-web dynamics of the prairie wetlands of North Dakota. Eggs, young, and adult birds of both species are an invaluable food source to predatory birds and mammals. In addition, WNV induced yellow-headed blackbird population crashes could result in a population explosion of red-winged blackbirds. As the most abundant songbird in North America, red-winged blackbirds cause extensive crop damage in North Dakota annually. Yellow-heads help to control red-winged blackbird numbers by excluding red-wing breeding pairs from their colonies and competing for natural food sources.

My second hypothesis is that WNV infection rates are low in yellow-headed blackbirds and common grackles. If infection rates are low, perhaps I did not have a large enough sample size to detect WNV infected individuals. This hypothesis seems unlikely since one out of two red-winged blackbirds and the only western meadowlark sampled had WNV antibodies. Since all sampled birds were collected within a five square mile area, it would seem infection rates were actually high in my study area.

I am very intrigued by my preliminary findings and will continue to collect more information on WNV infection in yellow-headed blackbirds and common grackles in my upcoming field seasons. I also hope to collaborate with another university to experimentally infect yellow-headed blackbirds with WNV in captivity to better understand how the species responds to infection.

LITERATURE CITED

Blount, J. D., D.C. Houston, and A. P. Møller. 2000. Why egg yolk is yellow. Trends in Ecology and Evolution 15: 47-49.

Campbell, G. L., A. A. Marfin, R. S. Lanciotti, and D. J. Gubler. 2002. West Nile Virus. The Lancet Infectious Diseases. 2: 519-529.

Casto, J. M., V. Nolan, Jr., and E. D. Ketterson. 2001. Steroid hormones and immune function: experimental studies in wild and captive dark-eyed juncos (*Junco hyemalis*). The American Naturalist 157: 408-420

Crawford, R. D. and W. L. Hohman. 1978. A method for aging female yellow-headed blackbirds. Bird-Banding 49: 201-207.

Friend, M., R. G. McLean, and F. J. Dein. 2001. Disease emergence in birds: challenges for the twenty-first century. Auk 188: 290-303.

Lochmiller, R. L. and C. Deerenberg. 2000. Trade-offs in immunology: just what is the cost of Immunity? Oikos 88: 87-98.

Rappole, J. H., S. R. Derrickson, and Z. Hubálek. 2000. Migratory birds and spread of West Nile Virus in the Western Hemisphere. Emerging Infectious Diseases 6: 319-328.

Royle, N. J., P. F. Surai, and I. R. Hartley. 2001. Maternally derived androgens and antioxidants in bird eggs: complementary but opposing effects? Behavioral Ecology 12: 381-385.

Saino, N., V. Bertacche, R. P. Ferrari, R. Martinelli, A. P. Møller, and R. Stradi. 2002. Carotenoid concentration in barn swallow eggs is influenced by laying order, maternal infection, and paternal ornamentation. Proceedings of the Royal Society of London. Series B, Biological Sciences 269: 1729-1733.

Surai, P. F. and B. K. Speake. 1998. Distribution of cartotenoids from the yolk to the tissues of the chick embryo. Journal of Nutritional Biochemistry 9: 645-651.

Surai, P. F., B. K. Speake., N. A. R. Wood, J. D. Blout, G. R. Bortolotti, and N. H. C. Sparks. 2001. Carotenoid discrimination by the avian embryo: a lesson from wild birds. Comparative Biochemistry and Physiology Part B 128: 743-750.

Twedt, D. J. and R. D. Crawford. 1995. Yellow-headed blackbird (*Xanthocephalus xanthocephalus*). *In* The Birds of North America, No. 443 (A. Poole and F. Gill, eds.). The Academy of Natural Sciences, Philadelphia, and The American Ornithologists' Union, Washington, D.C.

Analysis and Model Simulation of Stormwater Runoff -- A Study of Land Use and System Design on Discharge Flow Rates and Water Quality

Basic Information

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2. Martin., J.; Somayajula, S. M. K.; Gautam B.; Lin, W.; Fredrick, F.; and Ell, M. (2005) Stormwater Sampling and Analysis for Fecal Coliform and Turbidity Total Maximum Daily Load (TMDL) Development, Presented at the Second International Water Conference Research and Education in an International Watershed: Implications for Decision Making, April 6-7, Winnipeg, Manitoba, Canada.

ANALYSIS AND MODEL SIMULATION OF STORMWATER RUNOFF -- A STUDY OF LAND USE AND SYSTEM DESIGN ON DISCHARGE FLOW RATES AND WATER QUALITY

DESCRIPTION OF THE CRITICAL WATER PROBLEM

In a 1988 report to the Congress, USEPA stated that urban runoff in the U.S.A is the fourth most extensive cause of water quality impairment of rivers, and the third most extensive source of water quality impairment of lakes (USEPA, 1990; Novonty, 1991; Novonty and Olem, 1994).Yields of total suspended solids (TSS), total phosphorus (TP), and total nitrogen (TN) from intensive agriculture and urban areas in the Great Lakes region were 10-100 times greater than from the forested and idle lands (Sonzogani et al.1980).Urban development increases stormwater runoff volumes and pollutant concentrations. Impervious surfaces, such as rooftops, driveways, and roads, reduce infiltration of rainfall and runoff into the ground and degrade runoff quality. Land use and storm sewer system design all have important effects on stormwater runoff quality. $BOD_{5,}$ bacteria and nutrient concentrations in stormwater are typically lower than in raw sanitary wastewater. However, urban stormwater still has relatively high concentrations of bacteria, $BOD_{5,}$ and suspended solids along with high concentrations of many metallic and organic toxicants (Burton, G. Allen et al, 2002).

The Red River is an important resource for water supply and recreational purposes. However, the reach of Red River main stem covering Moorhead, MN and Fargo, ND areas has been identified as impaired for swimming designated use (primary contact recreation) under Section 303(d) of the Clean Water Act (CWA). The main causes contributing to impairment are excessive fecal coliform bacteria and high turbidity. High ammonia concentration in the river is another concern. An analysis of Red River quality data shows that urban runoff is a major source of fecal coliform and suspended solids. Fish kill in this reach of Red River occurred after a storm in August 2003. During the period of fish kill, low dissolved oxygen (DO) was observed in the river. Low flow rate in the river and high BOD concentration in the urban runoff were believed to be the reasons for the low DO and subsequent fish kill.

The impact of urban runoff on the quality of a water body may vary significantly depending upon its existing water quality and the rates at which pollutants are introduced into the system. So we need to study flow of the runoff and major contaminant concentration. The multiple of flow rate and concentration is known as loading rate or simply load. So load of a particular stormwater outfall relates to the impairment of the reach of the receiving water body. Therefore to accurately asses the effect of urban runoff and to propose control measures, load has to be calculated. The first step in the calculation of load is to estimate runoff. Runoff quantity is governed by the hydrological and physical characteristics of the of the drainage area. Simulation models are now days widely used in estimating stormwater flows in urban areas. More advanced models can simulate pollutants concentration in addition to flow and stages. So to find a broader picture of the affect of urban runoff on the Fargo Moorhead reach of Red River, sampling of the runoff and using this data to simulate a model is proposed.

The proposed research will be incorporated and synchronized with other related works going on with the view of analyzing the urban runoff of Fargo-Moorhead area. There is currently study going on to find out the Total Maximum Daily Load (TMDL) for the Fargo-Moorhead reach of the Red River. In this regard samples have been collected by River Keepers, the city of Moorhead and ND Department of Health. A number of samples from different location has been collected and analyzed for fecal coliform analysis and turbidity analysis. The analysis of 2002 data identified that fecal coliform is mainly being discharged from the urban area. The stormwater sampling has been started this year and initial data show high BOD, fecal coliform and turbidity in storm runoff. An initial GIS map of urban reaches of Red river in Fargo – Moorhead area has been developed.

KEY LITERATURE

Hydrological features of a basin govern the storm runoff flow rate. If we analyze the classic 'Rational Formula' for peak runoff estimates, runoff coefficient, rainfall intensity and basin area are the three governing factors. Runoff coefficient is associated with the land use of a particular basin. Increased land use or Urbanization has important role to play in the change of flow rate. According to (Chow, et al. 1988), major change in flow rates in urban watershed are the result of (i) the increase in the volume of water available for runoff because of the increased impervious cover of provided by parking lots, streets, and roofs, which reduce the amount of infiltration and (ii) changes in hydraulic efficiency associated with artificial channels, curbing, gutters, and storm drainage collection systems increase the velocity of flow and the magnitude of flow peaks. The storm duration intensity is another factor which has to be looked carefully while estimating runoff. Usually high discharge of stormwater from urban area in the United States results from high intensity short duration rainfall like thunderstorm. For reducing the increase of peak runoff from urban areas stormwater detention ponds are commonly employed in new developments. Although most detention ponds are designed for flow rate control, they may improve the water quality as result of sedimentation in the ponds.

For the analysis of contaminant level of the pollutant, field analysis and sampling is needed. Most water quality data consist of concentration of various parameters. Some parameters like pH, conductivity, temperature and dissolved oxygen can be measured in site while other parameters like suspended solids, BOD, COD and bacteria counts require laboratory analysis. The type of pollutant load also tends to relates to the type of land use. For example the bacterial quality of runoff especially from residential area can be poor as a result of animal/bird faeces and wrong connection. (Ellis, J.B; 1985)

The computation of combined effect of flow rate and pollutant concentration requires considerable calculations and judgment, which is why simulation models are finding increasing use. As the water quality measurements are costly and time consuming, it may be preferable to use a mathematical model which is verified by limited local measurements and then applied to the system under consideration to obtain an appreciation of the pollution situation. (Huber, C.W, 1986). All models need to be calibrated for local conditions. Calibration usually involves the collection of initial set of data that is used to modify the model for the local characteristics. Validation is an independent check to ensure that the calibrated model produces predictions within an acceptable error range (Burton, G. Allen et al, 2002).

Simulation models have found increasing use from its initial phase in the early 1970. Some of the most popular and comprehensive models are SWMM (Storm Water Management Model) and STORM (Storage Treatment Overflow Model). A widely used simulation model is SWMM which is developed by EPA. SWMM is capable of simulating the movement of precipitation and pollutants from the surface of the ground pipe and channel networks and storage treatment units to receiving water. (Viessman, W and Lewis, 1998)

As stated earlier, this research will be a collaborative effort with the TMDL study going on the department. The analysis of initial data from TMDL study in Red River has given some surprising results. The time – pollution graphs (pollutographs) of some major contaminants are showing variation as regard to peak load. This result in itself is proving to be a challenge and exciting research opportunity. The urban runoff study as proposed in this research proposal will surely help in understanding these results.

SCOPE AND OBJECTIVES

The goal of this proposed research is to determine contaminant loads that are carried by urban runoff to the Red River by field sampling and model simulations. The corresponding objectives to achieve the goal are to:

- Collect samples to determine the flow rates and concentration of major contaminants from selected stormwater outfalls
- Develop hydrographs and contaminant load curves based on the field data
- Study the impact of land use and storm water system design on runoff flow rate and quality
- Determine the pollutant loads from Fargo and Moorhead stormwater outfalls through model simulation

METHODS, PROCEDURES, AND FACILITIES

The methodology for this research consists of different level of activities. The procedure to achieve above mentioned objectives will follow a well directed path.

Literature Review and Model Evaluation

Literature review gives the sound base to research work. Journal articles, conference papers give the background information about the related activities going on field. Literature review as regard to this research will consist of collection of information on methods, calculations, sampling procedures required for the study. As simulation of model is important aspect of this research, evaluation of different models will also be done. Study of application, updates, and manuals as regard to the model would help in gaining through knowledge of the model and help in its future simulation.

Site Selection

Site selection as regard to this research consists of selection of land use pattern and corresponding selection of stormwater outfall. Area to be sampled will be selected with the help of the GIS map which is already prepared as part of the TMDL study. Some of the different land use patterns that will be considered are; residential, industrial, agricultural and institutional. The selection would be representative of the ground condition. Accessibility of the outfall will be another governing factor. The coverage area, population data of the drainage are will be found out from field study and concerned authority. To study the effectiveness of detention ponds as quality control measure, the area draining in to the detention pond will be studied separately.

Runoff Flow Rate Measurement and Quality Sampling

As already mentioned, flow rate is the function of hydrological and physical characteristics of the area so reliable measurement of these functions must be insured. Rainfall data will be collected from corresponding gauging station. With these data hydrographs would be generated which would help in accurately predicting runoff magnitudes. Another important hydraulic feature is the discharge through the drainage channels. Manning's equation will be used to calculate the quantity of the flow. Among input parameters for this equation, slope and channel geometry of outfalls will be collected and pressure transducer will be used to measure the water level. Due consideration will be given while obtaining Manning's coefficient (n).

For the quality parameters of the runoff, continuous monitoring is possible with the use of multi quality measuring instruments. Currently there are 4 number of quality measuring Sonde instruments available for use. It will be calibrated first then placed in the selected outfall. It would collect continuous which would be downloaded with the help of Data logging system.

Logistic support for this research will be provided by Minnesota Pollution Control Agency (MPCA) and NDSU Civil Engineering Department. Computer and GIS software will be used in NDSU. The advisors and faculty of the Department of Civil Engineering would be consulted during the whole research process.

Model Calibration and Simulation

The gathered hydrological, physical data will be used in calibrating the model. After the calibration the model will be used to derive hydrographs and pollutographs. The simulation will give new insights in the affect of land use on urban runoff quality. The whole research and results would be part of the thesis work. The time for this research is expected to take one and half years. So the results would be available in the summer of 2005.

ANTICIPATED RESULTS AND DELIVERABLES

Considering the fact that urban runoff has been identified as a major source of pollution to the receiving water body, there is a growing concern for the analysis of the extent of the problems caused by it and development of a proper management plant suited to the local condition. Hence in this regard this research will help in identifying the level of problem and will provide a better understanding of the urban runoff pollution. A simulated model which would predict runoff load will be one important result of this research.

The main benefits of this research will be that it will provide better understanding of the pollutant concentration of the urban runoff which will eventually lead to the improvement of the quality of the receiving water body, in our case Red River. The result of the study will focus the attention to the critical sections of the urban area, which is contributing more to the pollution of the Red River. Another important aspect of this research is to find out how land use pattern co-relates with the urban runoff load. Now day's detention ponds have found increasing use in stormwater disposal system. Some new areas of the Fargo city have been using them as flood control measures. This research will also test does these ponds act as pollutant control devices or not.

LITERATURE CITED

1. Burton, G. Allen and Pitt, Robert E: (2002), Stormwater Effects Handbook, A toolbox for Watershed Managers, Scientists, and Engineers, Lewis Publishers
2. Huber, C.W: (1986) 'Deterministic Modeling of Urban Runoff Quality', in H.C Torno, J. Marsalek, and M.Desbordes, (eds), NATO ASI Series, Vol G10, Urban Runoff Pollution, Springler-Verlag, Berlin, Heidelberg, pp. 167-241
3. Wolfang F Geiger: (1986) 'Use of Field Data in Urban Drainage Planning', in H.C Torno, J. Marsalek, and M.Desbordes, (eds), NATO ASI Series, Vol G10, Urban Runoff Pollution, Springler-Verlag, Berlin, Heidelberg, pp. 103-127
4. Tsihrintzis, Vassilios A. and Hamid, Rizwan :(1997), Modeling and Management of Urban Stormwater Runoff Quality: A Review, Water Resources Management, pp 137-164
5. Brezonik, Patrick L. and Stadelmann Teresa H.: (2002), Analysis and predictive models of stormwater runoff volumes, loads, and pollutant concentrations from watersheds in the Twin Cities metropolitan area, Minnesota, USA, Water Research, pp 1743-1757
6. Viessman, W,and Leiws, G.L., (1996), Introduction to Hydrology, Harper Collins
7. Novonty, V. and Olem, H: (1994),Water Quality- Prevention, Identification, and Management of Diffuse Pollution, Van Nostrand Reinhold
8. Sonzogni WC, Chesters G, Coote DR, Jeffs DN, Konard JC, Ostry RC, Robinson JB, Pollution from Land Runoff, (1980), Environ Sci TEchonol, 14(2):148-53
9. Chow VT, Maidment DR and Mays LW, (1988), Applied Hydrology, McGraw -Hill

Reliable and Continuous Measurement of Flow Rate in the Red River of The North by means of an Acoustic Doppler Velocity Meter

Basic Information

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Publication

RELIABLE AND CONTINUOUS MEASUREMENT OF FLOW RATE IN THE RED RIVER OF THE NORTH BY MEANS OF AN ACOUSTIC DOPPLER VELOCITY METER

DESCRIPTION OF THE CRITICAL WATER PROBLEM

It has become increasingly significant for government agencies along with private companies to have an accurate real-time discharge data so that proper water management tactics can be promptly instigated for flood control, water distribution, and drought management (Mason and Weiger). This statement holds true to the utilization practices of the Red River of the North. The Red River is a vital resource that numerous cities depend greatly on for their water supply. This river can also be a liability when the water it delivers begins to spill over it banks. During both high and low flow periods, an accurate recording of flow rate is needed to deal with the present and future status of the Red River responsibly.

The United States Geological Survey (USGS) is the government agency that is given the task of monitoring the water resources of the US. One of the USGS gaging stations is located on the Red River at Fargo, ND. The USGS monitors water flowrate at this station by the use of conventional methods that develop a stage-discharge rating. This rating is derived from periodic discharge measurements made by USGS personnel at the gaging site. After numerous measurement readings have been recorded at various water stages, a relation can then be developed between the discharge and the corresponding stage height of the river. This essentially makes the discharge estimation a function of the river's depth. This method can leave some intrinsic flaws in discharge estimation.

A recently developed hydroacousic instrument called an Acoustic Doppler Velocity Meter (ADVM) may be able to provide a more true discharge estimate when properly calibrated (Morlock, et al, 2002). An ADVM is small and easy to install and maintain maintain. They are able to calculate the average velocity of a sample volume within the river. This sample volume velocity is called the "index" velocity and can be related to the channels mean velocity. Proper calibration is needed to supply optimal discharge estimates.

The North Dakota USGS district currently has two ADVMs in operation. There is one on the Red River at Grand Forks, and one on the James River at Jamestown. These meters have been used effectively to increase the real-time accuracy of the flow estimations of each river. The district is now interested in implementing an ADVM flow monitoring system at the Fargo gage-station on the Red River. The ADVM is a newer technology and research is needed for understanding of the technology so that river discharge can be determined for a wide range of conditions.

KEY LITERATURE

The conventional methods of measurement used by the USGS have some parameters that are not fully expanded on and limit the effectiveness of the discharge estimations. One parameter is the changing hydraulic characteristics of a river channel. As the seasons in the Fargo region changes, so do some of the hydraulic factors of the river. One example of this change is the altering of the channel roughness based on the shift of vegetation development through the seasons. Another example is the possibility of temporary debris blockage causing a rise in water level but not in discharge. Discharge estimates can also be skewed by the formation of ice on the river channel during winter time.

An additional parameter that the conventional method has setbacks with is the dealing with situations of backwater. As the Red River flows north, the slope of the channel begins to decrease. During periods of flooding, this decreasing gradient, along with ice jams, cause the Red River's water to begin backing up and increases the stage height leading to a pooling effect as the river's water spills out of its banks. As the river drains the shallow "lake" that was created, there is an over lap between stage heights and the corresponding discharge of the river showing "the discharge for a given stage is greater when the stream is rising than it is when the stream is falling" (Rantz and others, 1982).

The installation and proper calibration of an Acoustic Doppler Velocity Meter (ADVM) can provide a more accurate and continuous estimation of the present flow rate within the river. An ADVM brings velocity into the equation by making the discharge estimation a function of velocity using the continuity equation (Q=VA). This allows for more true flow estimates with a wider range of hydraulic conditions. ADVM measurements will also help to diminish the stage-discharge loop caused by the effects of backwater.

An ADVM provides a noninvasive measurement of the average velocity of a sample volume within a stream on a continuous basis (Cheng and Gartner, 2003). The meter obtains this "index" velocity by means of a pair of monostatic acoustic transducers. These transducers are set at a known orientation and trigonometry is used to determine the index velocity in the sample volume. An ADVM transducer is able to transmit sound pulses known as pings of a given frequency along an acoustic beam. As these pings travel through the water along these beams, they come into contact with the solids suspended in the water known as "scatterers". These scatterers cause some of the sound to be bounced back along the acoustic beam back to the transducers. The returning sound has a shift in frequency which is caused by the Doppler Effect. This shift is related to the velocities of the suspended particles and the water the acoustic beam is sent through. Using the Doppler Effect, the ADVM develops the index velocity which can be related to the mean velocity of the channel (Son Tek).

As of early 2001, it was estimated that the USGS had purchased 150-200 ADVMs to install in streams for flow rate gaging (Morlock, et al, 2002). A study was conducted by the USGS on three rivers in Indiana to investigate the development and accuracy of ADVM measurements. Based on the results of this study, a velocity rating curve was developed for each of the three rivers. The studies showed there to be a linear relationship between the index velocity and the mean velocity for two of the rivers and the third was found to be linear with the effects of stage elevation included. An empirical equation was derived to represent the mean velocity of the channel. The mean velocity equation is represented by

$$V= V_i(X+ YH) +C$$

V is the mean velocity computed

V_i is the velocity measured by the ADVM
X is the velocity coefficient
Y is the stage coefficient
H is the rivers stage.
C is a constant

Even though a linear velocity rating curve was found for all three rivers studied, it can not be assumed this is true for all rivers and other parameters may be involved. Each stream must be done on a case-by-case basis.

The study conducted in Indiana left many parameters untested. For one, the measurements were collected within a small range of stage elevations. Not knowing how the rating curve is affected by high and low flows can drastically increase the error in the flow estimation during these periods. It was mentioned that the roughness of the bottom was identified as a factor affecting the velocity profile and in turn the velocity rating curve. The extent of the impact caused by the roughness of the channel would be difficult to determine without the low flow measurements. Another setback in the study was that it was not explained why stage height was a factor in the determination of the velocity rating for one of the rivers but not the other two. Other parameters that were left untouched were the effects of ice cover on the channel, effects of change in the viscosity of the water, and how the rating curves handled the effects of backwater.

These parameters will need to be further researched to develop the theory and understanding behind the empirical equations that represent the mean velocities. For calibrating an ADVM for the Red River, this theory and understanding is critical in deriving a reliable index velocity rating curve that can be used for a variety of stages. Knowing the effects of these other parameters will help to find an accurate reading for the mean velocity of the channel. The key to having an accurate discharge reading is to develop a solid index velocity rating meaning different curve fitting equations may need to be used.

SCOPE AND OBJECTIVES

The purpose of the project is to install, calibrate, and operate an ADVM in the Red River at Fargo. There is also the need for studying the hydraulic factors in the river that affect the velocity. Using the index velocity given by ADVM and an understanding of the effects of the hydraulic factors, a velocity rating curve can then be developed through numerous measurements at various stages. Developing a good rating curve can than be used to deliver the ultimate goal of an accurate discharge estimate for the Red River of the North at Fargo.

METHODS, PROCEDURES, AND FACILITIES

The first phase of the project will begin with a literature review. This will be conducted to learn more about the ADVM, to understand how it works and the methods it employs to record an index velocity measurement. The factors that effect the ADVM's measurements will also need to be studied and maybe discovered. Along with the ADVM studies, the hydraulic parameters of the Red River will also need to be reviewed. An understanding of flow factors such as channel geometry and roughness and the effects of seasonal changes will need to be researched to view how they affect the mean velocity of the river.

The second phase will consist of selecting a cross-section and installation of the ADVM. This phase will be conducted in the spring under the supervision of the USGS. The first task in this phase is selecting a cross-section that typifies the Red River's flow in Fargo year round. After a desirable cross-section has been chosen, there will be an in depth profile conducted to develop the elevation-area rating curve for this portion of the river. This is so that at any given stage, the area of flow can be estimated. Along with the profiling will be the installation of the ADVM. There are several factors the will need to be taken into consideration. First is the positioning of the ADVM. Placement will need to be in a portion of the channel where the meter will be safe from potential hazards for destruction and yet be able to attain an accurate index velocity measurement. Downstream portion of bridge piers are often a good selection. After the placement of the meter is completed, the sample volume will need to be set so that boundaries (i.e. river bottom, water surface, or turbulent areas) won't interfere with the index velocity measurement. This phase will also include the selection of a data acquisition site that is easily accessed.

Phase three will be the collection of data. Measurements of the rivers mean velocity will be obtained by applying the conventional methods used by the USGS or by the use of an Acoustic Doppler Current Profiler (ADCP). The index velocities recorded by the ADVM at the time of the measurements will also be noted. Numerous measurements of the mean velocity will be record throughout the following year to collect velocities at various stages including periods of high and low flows.

The fourth phase will be analyzing the collected data. This analysis will be used to develop the rating curves that will be used to estimate the mean velocities and areas of the river at various stages. The stage-area rating curve will be developed based on the profile performed on the selected cross-section in phase two. The index velocity curve will be developed using the data collected in phase three and the understanding gained from phase one on how the hydraulic factors affect the velocity of the river. This curve will be developed by use of regressional methods.

After these two curves are developed, discharge estimates will be made using the continuity equation (Q=VA). The discharge measurements obtained from the ADVM will be compared to the discharge measurements made using the conventional method or by use of an ADVM.

The facilities needed for the project will for the most part be supplied by North Dakota State University. NDSU will give access to the computers and computer software that will be needed and also lab facilities if other studies are needed. The USGS will supply the surveying equipment required for the profiling of the cross-section, the ADVM needed, and also the current meters necessary to measure the mean velocities of the river. The USGS will also provide assistance and training in the tasks of selecting a cross-section, installing an ADVM, and collection of index and mean velocities of the river.

ANTICIPATED RESULTS AND DELIVERABLES

Calibrating an Acoustic Doppler Velocity Meter for the Red River at Fargo will aid the USGS in their studies and analysis of the river by providing them with an accurate real-time data collection of the discharge in the Red River at Fargo. Many agencies (i.e. the weather service and engineering firms) rely on the prompt and accurate data obtained from the USGS in their forecasting and planning. In addition to the flood control and water management, a more accurate discharge reading will also help water quality control agencies in determining the capacity of the Red River so proper regulations can be instigated for the regulate the discharges of point and nonpoint sources.

LITERATURE CITED

Cheng, Ralph T., and Gartner, JW, 2003, Complete Velocity Distribution in River Cross-Section: IEEE/OES Working Conference on Current Measurement Technology, pg 21-26

Mason, Robert R., Jr., Weiger, Benjamin A., 1995, Stream Gaging and Flood Forecasting, Fact Sheet - U. S. Geological Survey, FS 0209-95, 8 p.

Morlock, Scott E., 1994, Evaluation of Acoustic Doppler Current Profiler measurements of river discharge, Water-Resources Investigations Report 95-4218, 37 p.

Morlock, Scott E., 1999, Overview of Hydro-Acoustic Current-Measurement Applications by USGS: IEEE Working Conference on Current Measurement, pg. 112-116

Morlock, Scott E., Nguyen, Hieu T., and Ross, Jerry H., 2002, Feasibility of Acoustic Doppler Velocity meter for the production of discharge Records from U.S. Geological Survey Streamflow-Gaging Stations, U. S. Geological Survey Water-Resources Investigations Report 01-4157, 59 p.

Rantz, S.E., and others, 1982, Measurement and Computation of Streamflow: U.S. Geological Survey Water-Supply Paper 2175, 2 v., 631 p.

Son Tek Corporation, 2003, Son Tek Argonaut-SL Expanded Description, http://www.sontek.com/product/asl/aslxdsc.htm, 5 p.

Sample Analysis, Kinetic Studies, and Modeling of a Full-Scale Moving Bed Biofilm Reactor for Ammonia Removal

Basic Information

Title:	Sample Analysis, Kinetic Studies, and Modeling of a Full-Scale Moving Bed Biofilm Reactor for Ammonia Removal
Project Number:	2004ND52B
Start Date:	3/1/2004
End Date:	2/28/2005
Funding Source:	104B
Congressional District:	1
Research Category:	None
Focus Category:	Treatment, Methods, Water Quality
Descriptors:	None
Principal Investigators:	Wei Lin

Publication

SAMPLE ANALYSIS, KINETIC STUDIES, AND MODELING OF A FULL-SCALE MOVING BED BIOFILM REACTOR FOR AMMONIA REMOVAL

DESCRIPTION OF THE CRITICAL WATER PROBLEM

High concentrations of ammonia in wastewater discharges have been shown to be toxic to fish and cause dissolved oxygen (DO) depletion in receiving streams, especially during periods of low river flow. However, when the City of Moorhead Wastewater Treatment Facility (WWTF) was designed in 1983, no ammonia discharge limit was implemented and no treatment process for the removal of ammonia was employed. Since operation began at the Moorhead WWTF, the typical discharge of ammonia to the Red River of the North had been near 19 parts per million (ppm).

In the mid-1990's, the reach of the Red River of the North from the Cities of Moorhead and Fargo to the confluence with the Buffalo River in Minnesota was identified as impaired for both ammonia and dissolved oxygen (i.e. violating water quality standards for these parameters at low river flow). In 1994, a workgroup was formed to address this impairment and establish a Total Maximum Daily Load (TMDL) study to set allowable loadings of $CBOD_5$ and ammonia discharged from each plant and corresponding permit limits for the treated wastewater discharges. To aid that effort, a water quality model (QUAL2E), developed by the EPA, was used to simulate the wastewater discharges. The model was found to be sensitive to the assumed reaeration rate in the river, and therefore, the workgroup concluded that calibration at critical low river flow conditions was necessary to simulate the impacts of $CBOD_5$ and ammonia on dissolved oxygen in the river.

In 1999, the USEPA revised their water quality criteria for ammonia. This criteria is established for ammonia toxicity and unrelated to dissolved oxygen impacts associated with ammonia discharges. The Minnesota Pollution Control Agency subsequently adopted a site specific standard for ammonia for the impaired reach of the Red River of the North based on the new criteria and developed a new discharge limit for the City of Moorhead (equivalent to 8 ppm for the months of June through September when the river flow is less than fifty cubic feet per second). A compliance date of September 30th, 2003 was also established. The City of Moorhead developed a facility plan and, based on that plan, constructed an innovative process, the attached growth moving bed biofilm reactor (MBBR), to meet the new limits at a cost of $3.3 million in 2002.

This process is the only full scale separate stage nitrifying MBBR in the country. The MBBR process utilizes floating media placed in an aeration basin. In the basin, an aeration system supplies oxygen and provides mixing for the process while the media supply the necessary surface area for attached growth of nitrifying bacteria

In 2003, low river flows were experienced in the Red River of the North. In response, a sampling plan was carried out by the USGS and state agencies from North Dakota and Minnesota to determine the reaeration coefficient of the Red River at low flow conditions. The results of this study will be used to reassess the Red River's capacity for receiving $CBOD_5$ and ammonia at low flow conditions while maintaining proper water quality. If an appropriate water quality can not be maintained, the permit limits will be reduced even further.

An evaluation of this new, innovative process is necessary in order to determine the most critical operational parameters. A better understanding of the process gained by studying the key parameters via a kinetic model will result in improved operational efficiency and reduced effluent concentrations of ammonia, thus improving the overall water quality of the Red River of the North.

KEY LITERATURE

Nitrification is the conversion of ammonia to nitrate mainly by autotrophic bacteria. This process consumes alkalinity and oxygen. As a result, pH and dissolved oxygen are two important parameters in nitrification process selection and system operation (Tchobanoglous and Schroeder, 1987). The two major nitrifying bacteria are known as Nitrosomonas and Nitrobacter. Carbon dioxide is utilized as the only source of carbon for cell synthesis while energy is obtained by oxidizing ammonia to nitrate.

Nitrification can be achieved in single or separate sludge processes. In a single sludge system, nitrification occurs concurrently with the removal of organic matter (i.e. BOD) in combined carbon oxidation-nitrification reactors (Grady and Lim, 1980). In a separate stage system, nitrification is accomplished in a separate reactor after the majority of BOD is removed in the first stage. Both single and separate sludge systems can be designed as suspended growth or attached growth processes. Because of the low specific growth rate of nitrifying bacteria, certain design complications are presented. One aspect of importance is the influence of sludge retention time on the rate of nitrification (Hamoda, 1996). Additionally, the efficiency of nitrification in an attached growth system is affected by biofilm thickness, biomass density, DO level, and water temperature (Bonomo, 2000).

The issue of ammonia removal has been studied extensively by the City of Moorhead WWTF and at NDSU. Jayme Klecker (1998) studied the feasibility of using the existing polishing ponds at the Moorhead WWTF for nitrification. The polishing ponds provided an appropriate detention time, but a low biomass concentration in the ponds limited the removal efficiency of the nitrification process. Klecker recommended that modified operation be evaluated in order to achieve nitrification on a full-scale.

Based on Klecker's study and research by Dr. Robert A. Zimmerman, one of the existing polishing ponds at the Moorhead WWTF was later converted to the MBBR process. Feasibility of the full-scale nitrification process was evaluated by a pilot-scale study using the separate stage attached growth MBBR process. Addition of the media allowed for the development of a suitable biomass population (Zimmerman, 2003).

Zimmerman and his collaborators suggested that the nitrification rate of the MBBR process can be modeled as a 1st order decay model. The equation implies that nitrification is primarily dependent on the influent loading. However, a number of other parameters were recognized as affecting the process. Further research of the new MBBR process was recommended in order to resolve unanswered questions regarding the nitrification rate and its relationship to ammonia concentration, dissolved oxygen concentration, and detention time, as well as influent loading. Developing definitive relationships require evaluation where these parameters are maintained as independent variables.

SCOPE AND OBJECTIVES

The objectives of the proposed research include (1) monitoring the system operation under various flow and ammonia loading conditions and (2) developing and calibrating a kinetic model to further evaluate and optimize critical design and operational parameters for the separate stage nitrifying MBBR. Improved understanding of this process will enhance operational efficiency of the facility and further reduce effluent ammonia concentration discharged into the Red River. This objective becomes particularly important if, in fact, the permit limits are reduced based on the results of the USGS calibration of the water quality model. The research will also be widely applicable to the MBBR process in general, and thus, expand the body of current knowledge associated with this new process.

METHODS, PROCEDURES, AND FACILITIES

The proposed research will be conducted at the Moorhead WWTF laboratory and the NDSU Environmental Engineering laboratory. A literature review will be conducted to gather available information specific to the kinetic modeling of a separate stage nitrification process (i.e. model equations, key parameters to consider, etc.). A vendor search will also be conducted for commercially available software with the capabilities required for the research objectives. Software packages will be evaluated with regard to the specific objectives of this research and the most suitable package will be purchased. The model will be studied in detail to gain a full understanding of the software requirements such as influent wastewater characteristics, kinetic model equations employed, key kinetic parameters involved, and effluent wastewater characteristics. This information will be used to establish data collection requirements.

A significant amount of full-scale operational data has been collected since the process began operation in April, 2003. However, based on the model requirements, it is anticipated that additional specific data collection (i.e. actual biomass characteristics which may include thickness and mass) will be required in conjunction with the on-going operational data collection. A sampling and analysis protocol will be established to collect the additional required information. Utilizing this information, in conjunction with the historical operational data collected, the model will be calibrated. Following calibration, the model will be verified by additional data collection to determine the usefulness of the calibrated model.

An understanding of the factors that affect the kinetics of nitrification in the MBBR process will be gained through experimentation and analysis of key parameters in the model. These parameters include but are not limited to temperature, dissolved oxygen, pH, residence time, loading, and other environmental considerations. Substrate growth on the media will be predicted as well as measured in-situ.

Once the model is calibrated and verified, key parameters relating to operation and optimal design of the process will be determined through sensitivity analysis. This analysis will involve examining changes in key operational parameters and the corresponding changes in process performance predicted from the verified model. If appropriate, a simplified model may be presented for design and operational consideration.

ANTICIPATED RESULTS AND DELIVERABLES

This study will result in a calibrated and verified kinetic model for the MBBR process. In addition, an analysis of important operational and design parameters for the system will be reported. If possible and/or appropriate, a simplified model will be proposed for design and operational considerations with regard to the process. Improved understanding of the MBBR will optimize operation which will, in return, reduce ammonia concentrations in the Red River of the North.

Other benefits included in the study are related to the uniqueness of the process. As mentioned earlier, this is the only separate stage nitrifying moving bed biofilm reactor in the country. Attention has been growing with regard to the MBBR process. As a separate stage system, an opportunity is presented to study and evaluate this full-scale system, and thus, provide valuable operational and design information which may be utilized in similar systems; not only for separate stage systems, but also in combination with activated sludge. In conclusion, this endeavor will provide valuable information to improve the water quality of the Red River of the North as well as establish an important kinetic model for the MBBR process that has a potentially wide application.

LITERATURE CITED

1) Bonomo, L., et. al., *Tertiary Nitrification in Pure Oxygen Moving Bed Biofilm Reactors.* Water Science and Technology, 2000, Volume 41 Issue 4, pp. 361-368, Milano, Italy.

2) Grady, Leslie C. P. Jr., and Henry C. Lim, Biological Wastewater Treatment. New York: Marcel Dekker, Inc., 1980.

3) Hamoda, M. F., et. al., *Biological Nitrification Kinetics in a Fixed-Film Rector.* Bioresource Technology, October 1996, Volume 58 Issue 1, pp. 41-48, UAE University, Al-Ain.

4) Klecker, Jayme J., *Feasibility Study of Achieving Ammonia Removal by Nitrification in Polishing Ponds.* Master of Science Thesis, May 1998, North Dakota State University, Fargo, ND.

5) Tchobanoglous, George, and Edward D. Schroeder, Water Quality. University of California at Davis, CA: Addison-Wesley, Inc., 1987.

6) Zimmerman, Robert A., et. al., *Pilot-Scale Evaluation of Separate Stage Nitrification Utilizing an Attached Growth Moving Bed Media Process.* Water Environment Research, September/October 2003, Volume 75 Number 5, pp. 422-433, Alexandria, VA.

Study of Denitrification in the Karlsruhe Aquifer Using Stable Isotopes of N and O in Nitrate

Basic Information

Title:	Study of Denitrification in the Karlsruhe Aquifer Using Stable Isotopes of N and O in Nitrate
Project Number:	2004ND54B
Start Date:	5/16/2004
End Date:	8/15/2004
Funding Source:	104B
Congressional District:	At Large
Research Category:	None
Focus Category:	Groundwater, Nitrate Contamination, Water Quality
Descriptors:	None
Principal Investigators:	Scott Korom

Publication

STUDY OF DENITRIFICATION IN THE KARLSRUHE AQUIFER USING STABLE ISOTOPES OF N AND O IN NITRATE

DESCRIPTION OF THE CRITICAL WATER PROBLEM

Denitrification is a natural process exhibited in some aquifers by which bacteria reduce NO_3^- to N_2 through the oxidation of organic or inorganic electron donors. One very distinct trait of denitrification is the resulting increase of the heavier isotopes of nitrogen and oxygen in the un-denitrified fraction of the nitrate. During denitrification bacteria prefer to attack the bonds of the lighter isotopes because they are easier to break. Thus, as denitrification proceeds, corresponding increases in the ratios of ^{15}N to ^{14}N and ^{18}O to ^{16}O in the remaining nitrate result. Other processes that decrease nitrate concentrations, such as dilution, do not change $^{15}N/^{14}N$ and $^{18}O/^{16}O$ ratios in the nitrate. Thus, noting increases in $^{15}N/^{14}N$ and $^{18}O/^{16}O$ groundwater nitrate samples verify that denitrification is occurring. The nitrogen ratio is based on the following:

$$\delta^{15}N = (R_{sample} - R_{standard}) / R_{standard}$$

Where $\delta^{15}N$ is the variation in the isotope expressed in parts per thousand (typically denoted "permil") at a specific time compared to the original amount, R_{sample} is the isotopic ratio ($^{15}N/^{14}N$) some point into the denitrification process, and $R_{standard}$ is the isotopic ratio of atmospheric nitrogen (N_2). A similar relationship exists for $\delta^{18}O$.

Under some idealized conditions, such as in situ mesocosms (ISMs), denitrification results in a linear relationship with $\delta^{15}N$, such as shown on Figure 1 (Schlag, 1999; Korom et al., in review). This is because a known amount of nitrate is put into the ISMs at the beginning of a tracer test and observed in isolation from other sources of nitrate for the duration of the test. Nitrate entering an aquifer, however, may vary in its source, concentration, and time of introduction into the aquifer. With such variability, plots with $\delta^{15}N$ and concentration may not be helpful. Consider Figure 2 from a site in the Assiniboine Delta aquifer in Manitoba (Phipps and Betcher, 2003). It is difficult to see any trend between nitrate-N concentrations and $\delta^{15}N$ with sample depth. Under these conditions, also including $\delta^{18}O$ analyses provides considerable improvement. Consider Figure 3 using the same data for $\delta^{15}N$ as in Figure 2, plus some additional $\delta^{18}O$ data. The resulting enrichment trend was attributed to denitrification (Phipps and Betcher, 2003).

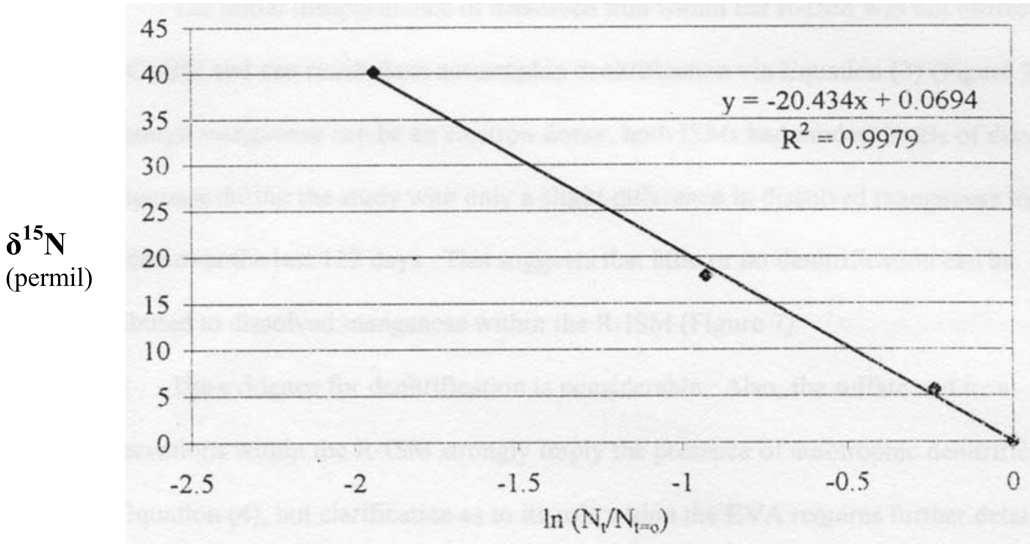

Figure 1. $\delta^{15}N$ versus the natural logarithm of the nitrate concentrations remaining in the in situ mesocosms during the first tracer test at the Larimore site (Schlag, 1999; Korom et al., in review).

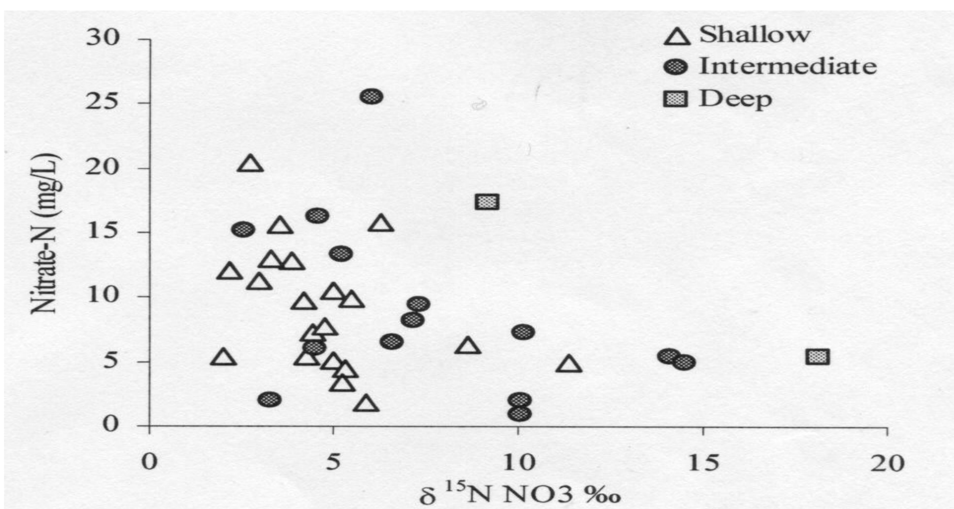

Figure 2. Nitrate-N concentrations versus for selected shallow, intermediate, and deep groundwater samples in the Assiniboine Delta aquifer beneath a field fertilized with hog manure (Phipps and Betcher, 2003).

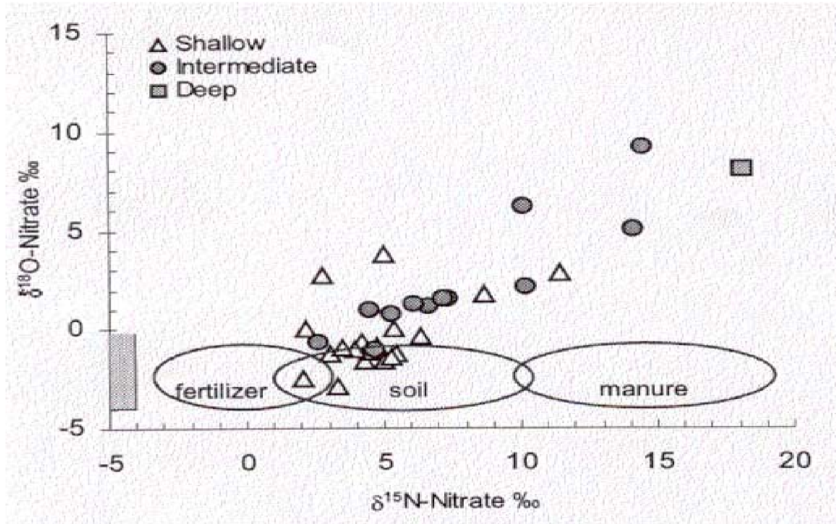

Figure 3. Plot of $\delta^{18}O$-nitrate versus $\delta^{15}N$-nitrate showing an enrichment trend attributed to denitrification. The shaded box on the y-axis is the expected range of $\delta^{18}O$ from the oxidation of N with local groundwater. The approximate range of $\delta^{18}O$ and $\delta^{15}N$ derived from ammonia fertilizer, manure, and soil organic matter is outlined (Phipps and Betcher, 2003).

METHODS, PROCEDURES, AND FACILITIES

The North Dakota State Water Commission (NDSWC) provided us with well data on nitrate concentrations from the Karlsruhe aquifer. These include nitrate (NO_3^-) concentrations from the fall of 2002 and the spring and summer of 2003 from twelve wells owned and operated by the NDSWC. Data from each well consists of concentrations at various depths ranging from five to forty feet below the ground surface. It is from these wells that we will be drawing multiple samples from various levels. Currently it is planned that sampling trips will be conducted this fall (2003), winter (2004), and spring (2004). This schedule is subject to change depending on weather conditions (time of spring thaw) and results from the first two sampling events.

Water from each sample will be tested for nitrate, chloride, and isotope concentrations. The University of North Dakota Environmental Analytical Research Laboratory (EARL) will be used to measure nitrate and chloride levels while isotope analysis will be conducted by the University of Waterloo Stable Isotope Laboratory. Our denitrification research team has used this lab for over six years and has been satisfied with the quality of service and results. Chloride (Cl^-) will be used as a natural tracer to be compared with nitrate levels. This anion is relatively inert in groundwater and does not participate in denitrification reactions. Simple dilution by foreign groundwater should be the only means for chloride levels to fluctuate. Thus if nitrate levels decrease at an accelerated rate compared to chloride, it is likely that nitrate has been eliminated by some process other than dilution, such as denitrification.

Isotopic analysis of $\delta^{15}N$ and $\delta^{18}O$ will be conducted once the sampling portion of the project is complete. Evidence of denitrification will be directly dependent on the relationship between nitrate and isotope fractionation as shown in Figure 3. This coupled with chloride levels will be the basis for determining the process leading to reduction of nitrate in the Karlsruhe Aquifer.

PROGRESS TO DATE

Our first sampling trip was conducted on October 21, 2003. A total of thirty-one samples were taken from the five different wells with multi-level sampling ports and transported back to the UND EARL for immediate analysis. Once the results were produced and approved by Dr. Korom, the remaining groundwater samples were treated with mercuric chloride to kill bacteria and prevent further denitrification. Samples were then refrigerated and will remain there until isotopic analysis will be conducted at a later date in the project. Up to two additional sampling trips will be conducted before the end of the project in the summer of 2004. Below is a table showing results from one of the wells in the sample set. It is apparent at the deepest level that the nitrate concentration has decreased much more than the chloride concentration. This is evidence that the groundwater at this site has been denitrified. Isotope data should help us confirm this hypothesis.

Well #15407731DDD

Depth Below Surface (ft)	NO_3^--N (mg/l)	Cl^- (mg/L)
10.1	17.92	10.20
12.1	26.56	14.93
14.1	30.26	16.75
16.1	32.81	19.12
18.1	32.52	20.56
23.1	26.58	19.46
28.1	1.46	10.52

ANTICIPATED RESULTS AND DELIVERABLES

It is believed by those associated with this project, that the $\delta^{18}O$ and $\delta^{15}N$ data will verify that denitrification is occurring in the Karlsruhe aquifer. Also it is felt that nitrate concentrations will decrease over the winter months at an accelerated rate compared to chloride. Ultimately these factors will provide supporting evidence to the opinion that the lowering of NO_3^- concentrations within the Karlsruhe aquifer is the direct result of natural denitrification.

LITERATURE CITED

Korom, S.F., A.J. Schlag, W.M. Schuh, and A.K. Schlag. In situ mesocosms: Denitrification in the Elk Valley aquifer. In review with Ground Water Monitoring and Remediation.

Phipps, G. C., and Betcher, R.N., 2003. The source and fate of groundwater nitrate beneath a field fertilized with hog manure: Assiniboine Delta aquifer, Manitoba, Canada. 4th Joint IAH-CNC/CGS Conference, Winnipeg.

Schlag, A.J., 1999. In-situ measurement of denitrification in the Elk Valley aquifer, Masters Thesis, Department of Geology and Geological Engineering, University of North Dakota.

Information Transfer Program

Information dissemination is done through an annual newsletter initiated in 1992, a website initiated in 1999, and presentations and publications by grant and fellowship recipients. The institutes website address is http://www.ce.ndsu.nodak.edu/wrri. This year, the Institute also has been working on up grading its web page. The efforts included changing the address from current www.ce.ndsu.nodak.edu/wrri/ to www.ndsu.edu/wrri/ to make the search and access of the website easier, and adding more functions to make the website more users friendly. The newsletter is usually issued in the month of December of each year. Copies of past newsletters can be obtained writing to the director.

NDWRRI continued its sponsorship of the Biotic Resources Seminar Series at North Dakota State University. Since 1987 it has brought about 70 biology-oriented speakers to the campus. Under this multi disciplinary program, visiting scientists are hosted by the faculty and graduate students from several departments in the College of Science and Mathematics, and College of Agriculture, Food Systems and Natural Resources. Seminar topics range widely, with the common thread being organismal/environmental biologies in the broadest sense.

NDWRRI sponsored the Second International Water Conference titled Research Education in an International Watershed: Implications for Decision Making. The conference organized by the Red River Basin Institute brought administrators, researchers, professionals and educators to Winnipeg, Manitoba Canada to discuss water resources, flood control and water quality management issues related to the Red River of the North.

Student Support

None

Notable Awards and Achievements

Publications from Prior Projects