## North Dakota Water Resources Research Institute Annual Technical Report FY 2001

## Introduction

This report describes the activities of the North Dakota Water Resources Research Institute (ND WRRI) during the period March 2001 to February 2002. The ND WRRI is one of 54 entities known collectively as the National Institutes for Water Resources. The Institutes were established by Congress (Water Resources Research Acts of 1964,1972, 1984 and 1990) at the Land Grant University in each state, the District of Columbia, the Virgin Islands, Puerto Rico, and Guam/Federated States of Micronesia, and are administered by the United States Geological Survey. The bulk of the ND Institute's resources are allocated to the research and education functions through the mechanism of Graduate Research Fellowships. Information transfer is done through an annual newsletter initiated in 1992, a website initiated in 1999, and presentations and publications by grant and fellowship recipients. The ND WRRI has its offices at North Dakota's land grant institution, North Dakota State University (NDSU). The current director who is also the Chair of the Department of Civil Engineering and Construction, NDSU assumed charges effective October 1, 2001. The Institute's administrative office has been moved since then to the Department of Civil Engineering and Construction. Graduate Students are supported by Federal 104b funds at both NDSU and the state's other research university, the University of North Dakota (UND).During FY 2001, the Institute operated with a Federal allotment of \$75,320 administered through the United States Geological Survey, plus co-funding from the two universities, regional water resources agencies and facilities, and a Minnesota mining operation. The State Advisory Committee has participated in the formulation of water resources research priorities for the Institute and state of North Dakota, and in the evaluation of research proposals and projects. The committee membership consists of:Gregg Wiche, District Chief, U.S. Geological Survey, Water Resources Division, Bismarck, North Dakota; Milton Lindvig, Director, Water Appropriation Division, ND State Water Commission, Bismarck, North Dakota; and Francis J. Schwindt, Chief, Environmental Health Section, ND State Health Department, Bismarck, North Dakota.William Schuh of the ND State Water Commission and Mike T. Sauer of the ND State Health Department, and Jimmie L. Richardson of the NDSU Soil Science Department participated as additional reviewers of applications to the graduate research fellowship. Dr. G. Padmanabhan, Professor and Chair of the NDSU Department of Civil Engineering and Construction, assumed charges as the Director of the Institute effective October 1, 2001. Various support personnel of the Department assist with Institute functions on a part-time basis. The offices of the Institute are located in Civil and Industrial Engineering Building on the North Dakota State University campus. The director may be reached at ND Water Resources Research Institute, CIE 201 A, North Dakota State University, Fargo, ND 58105; phone: (701) 231-7043, fax: (701) 231-6185; Internet: G.Padmanabhan@ndsu.nodak.edu.

## **Research Program**

For the past six years, the bulk of the Institute's modest Federal funds have been used to support research by a small grants program developed in consultation with the State Advisory Committee and the faculty of both universities. Competitive Graduate Research Fellowships (GRFs) are provided directly to water resources research graduate students. During the year, the 2001 Graduate Research Fellows Eric Dodds

(MS), Anthony Miller (MS), and Kyle Zimmer(Ph.D), graduated. Also graduated during the year are the 2000 Fellows Stuart Hurley (MS), and Paul Skubinna. Eric Dodds now works for a company as a staff-engineer designing water treatment plants. Kyle Zimmer is a Post-doc in University of Minnesota where he continues to study ecological interactions determining water quality in shallow lakes and wetlands. Kyle's ultimate goal is a faculty position where he can teach and conduct research in the field of aquatic ecology. Tony Miller completed his thesis on "Impacts of Logging on Invertebrates in Seasonal Forest Wetlands" in December. Tony is currently working in Dr. Butler's lab on analysis of data from other projects. The theses submitted by NDWRRI Fellows in 2001 are: Eric Dodds, Investigation of Metal Removal by Constructed Wetlands at LTV Steel Mining Company. M.S. Thesis, Department of Civil Engineering, North Dakota State University, Fargo, December 2001; Stuart Hurley, An Investigation of Disinfection By-Product Formation and Removal at The Moorhead Water Treatment Plant, M.S. Thesis, Department of Civil Engineering, North Dakota State University, Fargo, April 2001; Tescher, Melani L., An Analysis of Mercury in Mallards from Kellys Slough National Wildlife Refuge in Grand Forks County, North Dakota, M.S. Thesis, Department of Biology, University of North Dakota, Grand Forks, August 2001; Anthony Miller, Impacts of Logging on Invertebrates in Seasonal Forest Wetlands. M.S. Thesis, Department of Zoology, North Dakota State University, Fargo, December 2001; Paul Skubinna, Modeling the Hydrogeochemistry of Denitrification in In-Situ Mesocosms in the Elk Valley Aquifer, University of North Dakota, Grand Forks, Expected completion In December 2002; and Zimmer, K.D., Effects of Fathead Minnows and Drainage on Wetland Ecosystems, Ph.D. Dissertation, Department of Zoology, North Dakota State University, Fargo, May 2001.

Title:	Effects of Fathead Minnows and Drainage on Wetland Ecosystems
Project Number:	2001ND461B
Start Date:	3/1/2001
End Date:	2/28/2002
Research Category:	
Focus Category:	Ecology, Wetlands, Water Quality
Descriptors:	fish, wetlands
Principal Investigators:	Malcolm George Butler

- 1. Zimmer, K.D., Effects of Fathead Minnows and Drainage on Wetland Ecosystems, Ph.D. Dissertation, Department of Zoology, North Dakota State University, Fargo, May 2001.
- 2. Zimmer, K.D., M.A. Hanson, M.G. Butler, and W.G. Duffy, 2001, Influences of fathead minnows and aquatic macrophytes on nutrient partitioning and ecosystem structure in two prairie wetlands, Archiv für Hydrobiologie, 15, 411-433.
- 3. Zimmer, K.D., M.A. Hanson, M.G. Butler, and W.G. Duffy, Size distributions of aquatic invertebrates in two prairie wetlands, with and without fish, with implications for community production, Freshwater Biology, in press.
- 4. Muscha, M.J., K.D. Zimmer, M.G. Butler, and M.A. Hanson, A comparison of horizontally and vertically deployed aquatic invertebrate activity traps, Wetlands, in press.
- 5. Zimmer, K.D., M.A. Hanson, and M.G. Butler, Effects of fathead minnow colonization and removal on a prairie wetland ecosystem, Ecosystems, in press.
- 6. Melaas, C.L., K.D. Zimmer, M.G. Butler, and M.A. Hanson, Effects of rotenone on aquatic invertebrate communities in prairie wetlands, Hydrobiologia, in press.

#### Effects of Fathead Minnows and Drainage History on Prairie Wetland Ecosystems

Kyle Zimmer (Graduate Research Fellow) Malcolm Butler (Advisor) Professor of Biological Sciences Department Biological Sciences North Dakota State University Fargo ND 58105

Many studies have shown that fish can influence the structure and processes of aquatic ecosystems, but studies with replication at the ecosystem level are rare, as are studies involving wetlands. Some wetlands of the Prairie Pothole Region of North America support fish communities dominated by fathead minnows while others are fishless, providing an opportunity to assess the influence of these fish on wetland ecosystems. Additionally, extensive drainage of prairie wetlands has led to restoration of thousands of basins, but the success of these efforts is poorly known. I assessed the effects of fathead minnows and prior drainage on characteristics of prairie wetlands by studying 20 semipermanent wetlands in Minnesota from 1996-1999. I used a 2x2 factorial design to examine the effects of minnows (presence/absence) and drainage (restored/nondrained)on the abundances of aquatic invertebrates, aquatic macrophytes, and amphibians, as well as water-column levels of chlorophyll a, total phosphorus, total nitrogen, and turbidity. Results showed that presence/absence of fathead minnows is an important determinant of many biotic and abiotic characteristics of prairie wetlands. Wetlands with minnows had significantly fewer aquatic insects, large and small-bodied cladocerans, calanoid copepods, ostracods, and larval tiger salamanders, as well as a higher abundance of corixids and higher levels of turbidity and chlorophyll a. In contrast, higher concentrations of phosphorus in restored basins was the only consistent history effect, and no consistent fish-x-history interactions were detected. Additional research showed that the ecological characteristics of prairie wetlands can change rapidly in response to both minnow colonization and elimination. Thus, temporal variability in minnow presence/absence may be a source of temporal variability in other ecosystem components. Abiotic variables influence prairie wetlands, but this research indicates that these ecosystems may also be strongly influenced by the presence/absence of minnows. Inter-basin and inter-annual variability in minnow presence may be important for maintaining diverse assemblages of species at the landscape level, with fishless basins favoring certain assemblages of organisms and basins with minnows favoring others. From a management perspective, these effects should be considered prior to landscape manipulations that alter the regional proportion of basins supporting fathead minnow populations.

-----

Kyle's work demonstrated that the presence of fathead minnows is an important determinant of ecosystem structure in prairie wetlands. Restored wetlands are very similar to non-drained analogs. Not only were these patterns consistent in five years of data collected from over 20 wetlands, but Kyle was able to demonstrate unequivocally that minnows actually cause observed differences between minnow-supporting and fishfree wetlands such as higher turbidity and lower invertebrate diversity and abundance.

Title:	Physical and environmental factors influencing the periphyton communities of the Sheyenne River, North Dakota
Project Number:	2001ND681B
Start Date:	3/1/2001
End Date:	2/28/2002
Research Category:	
Focus Category:	Water Quality, Ecology, None
Descriptors:	algae, diatoms, River Periphyton
Principal Investigators:	Marvin W. Fawley, Karen Anne Phillips

## **Publication**

 Jaskowiak, M. A., Phillips, K. A. and Fawley, M. W. 2001. Three possible new species of Nitzschia (Hassall) from the Sheyenne River, ND. Poster presentation at the Phycological Society of America Meeting.

#### The Periphyton in the Sheyenne River, North Dakota

Megan Jeskowiak (Graduate Research Fellow) Marvin Fawley (Advisor) Professor of Biological Sciences Department of Biological Sciences North Dakota State University Fargo ND 58105

Devils Lake in Northeastern North Dakota is presently a closed basin, but rising, lake. Its size has been increasing for more than a decade, and if the rise continues there will be an uncontrolled flow into the Sheyenne River at some time in the future. An engineered outlet is being considered in order to provide a more controlled flow and reduce physical damage and water quality degradation that would come from an uncontrolled flow. This research began as part of the environmental impact statement for the Army Corps of Engineers Devils Lake outlet project. In the first part of this study, periphytic algae were collected using artificial substrates at several sites along the Sheyenne River. The major goal of this study was to relate the periphyton communities to environmental factors that could potentially be affected by a Devils Lake outlet. The relative abundance data for species of periphytic algae and environmental data were used for the assessment. This analysis was completed using canonical correspondence analysis (CCA). The environmental variables which explained the most variance in the periphyton communities were pH, orthophosphate, hardness, arsenic, sulfate and nitrite+nitrate. This analysis included all species identified. An analysis was repeated after the species which are considered to be phytoplanktonic were removed. This evaluation showed different environmental variables which explained the most variance. These environmental variables were percent sodium, calcium, pH, arsenic, and sulfate. This analysis proved to be more statistically significant. The phytoplankton species are not really part of the periphyton community and therefore, the variation seen in these species is coincidental. Therefore, the removal of these species makes the analysis more precise. The research that has been completed also includes a comparison of the natural substrates and artificial substrates and a comparison of the use of presence/absence data versus relative abundance data in CCA. Natural substrate communities appear to be quite different than the artificial substrate communities. These differences include several species, which were not found at all on the artificial substrates. An example of these additional species is the diatom, *Navicula mutica*. For the past three years the periphyton communities in the Sheyenne river have been studied. This research not only provides baseline data for the Devils Lake outlet project, but also provides an opportunity to examine the ecology of algal communities in a river that has yet to be examined. The knowledge gained from this ecological research will contribute to both regional water quality studies and diatom ecology overall. The research provides information on several levels. First, if Lake Ashtabula produces a significant effect on the periphyton communities. Second, the new species that I am finding from the Sheyenne basin indicate that the algal communities in North Dakota are diverse and not well documented. These results will contribute to a better understanding of the algal communities and the environmental factors that affect them. This study will help guide water quality management decisions in North Dakota.

Title:	Graduate Research Fellowships	
Project Number:	2001ND2721B	
Start Date:	3/1/2001	
End Date:	2/28/2002	
Research Category:		
Focus Category:	Water Quality, Wetlands, Methods	
Descriptors:	prairie potholes , minnows, VOCs, aromatic hydrocarbons, chromatography, wetlands,graduate fellowships	
Principal Investigators:	Gregory J. McCarthy	

- 1. Eric Dodds and Wei Lin. Investigation of Metal Removal by Constructed Wetlands, Presented at the North Dakota Water and Pollution Control Conference, Fargo, ND. October 24, 2001.
- Eric Dodds, Investigation of Metal Removal by Constructed Wetlands at LTV Steel Mining Company. M.S. Thesis, Department of Civil Engineering, North Dakota State University, Fargo, December 2001.
- 3. Anthony Miller, Impacts of Logging on Invertebrates in Seasonal Forest Wetlands. M.S. Thesis, Department of Zoology, North Dakota State University, Fargo, December 2001.
- 4. Anthony Miller, Influence of Hydroperiod and Environmental Variables on Aquatic Invertebrates in Seasonal Forested Wetlands. Presented at the 2001 Midwest Fish and Wildlife Conference in Minneapolis, MN.
- 5. Anthony Miller, Seasonal Forested Wetlands: Factors Influencing Aquatic Invertebrate Communities. Presented at the 2001 North American Benthological Society Conference in Lacrosse, WI.
- 6. Meyer, M. J., Borgerding, A. J. "Analysis of Aqueous VOCs using Rapid Extraction with High Speed Gas Chromatography or Ion Trap Mass Spectrometry", Federation of Analytical Chemistry and Spectroscopy Societies (FACSS) Conference, Detroit, MI 2001.
- 7. Current, R.W.; Meyer, M. J.; Borgerding, A. J. "Rapid Aqueous Sample Extraction of VOCs: Effect of Physical Parameters" Talanta 2001, 55 (3), 519-529.
- 8. Meyer, M. J.; Gress, M. F.; Borgerding, A. J. "Rapid Aqueous Sample Extraction of VOCs: Effect of Sample Matrix and Analyte Properties" Talanta 2001, 55 (4), 755-764.

#### **GRADUATE RESEARCH FELLOWSHIPS**

Project Number:	ND01-01	Start: 01 March 2001		
		End: 28 February 2002		
Title:	Graduate Research Fellowships			
Coordinator:	<b>Gregory J. McCarthy</b> , ND WRRI D North Dakota State University, Fargo	· 1 · · · · · · · · · · · · · · · · · ·		
Focus Category:	WATER QUALITY; WETLANDS; I	ECOLOGY		
Descriptors:	bioindicators, ecosystems, fish ecology, heavy metals, organic			
	compounds, phosphorus, pollutants, rivers, suspended sediments, trace			
	elements water quality, water treatment, wetlands			

One objective of the Section 104b Program is to ensure the future availability of water resources research professionals. Graduate education/training is currently the major activity of the ND WRRI through a competitive Graduate Research Fellowships (GRF) awarded to students in a degree program on a topic directly related to water resources. Each fellowship is a research project and will result in a thesis or dissertation and a new water resources research professional.

The research advisor is responsible for support of his/her own time on the project and for operating funds. For faculty with established and externally funded research programs, this fellowship allows the advisor to add another graduate student to the research group. With more junior faculty, NDSU and UND administrative offices provide faculty summer salary, and/or small matching grants to the advisor or student to cover operating costs.

Applications were solicited from both the University of North Dakota and North Dakota State University. Those applications were reviewed by State and Federal government water resources professionals. A panel consisting of the Institute Director, three members of the State Advisory Committee selected the fellows. For FY 2001, six applications were reviewed. Three were renewals and three were new. The panel judged that the renewal applications were meritorious, and the new applications were highly worthy of funding. The FY 2001 Graduate Research Fellows and their project titles and faculty advisors follow.

#### ND WRRI FY 2001 Graduate Research Fellows

Six graduate research fellowships were approved by the State Advisory Committee in December. Three doctoral candidates, Andrea Arruda (Chemistry), Megan Jaskowiak (Botany), and Kyle Zimmer (Zoology) had their fellowships renewed. Three new fellowships were awarded.

#### **Renewed Fellowships**

#### Andrea F. Arruda, M.S.

Ph.D. Program, Department of Chemistry, NDSU New Methods to Detect Chlorinated Organic Pollutants in Water Advisor: Dr. Andres D. Campiglia

#### Megan A. Jaskowiak

Ph.D. Program, Department of Botany, NDSU An Assessment of the Periphyton Communities in the Sheyenne River, ND Advisor: Dr. Marvin Fawley

#### Kyle D. Zimmer, M.A.

Ph.D., Department of Zoology, NDSU Effects of Fathead Minnows and Drainage History on Prairie Wetland Ecosystems Advisor: Dr. Malcolm Butler

#### New Fellowships

#### Eric Dodds

M.S. program, Environmental Engineering, NDSU Evaluation of Peat Uptake Capacity for Copper and Nickel in Constructed Wetlands of the LTV Mining Company Advisor: Wei Lin

#### **Melissa** Meyer

Ph.D. program, Chemistry, UND Rapid Spray Extraction and Analysis of Organic Compounds from Water Advisor: Anthony Borgerding

#### Anthony T. Miller

M.S. program, Zoology, NDSU Northern Forested Wetlands: Characteristics and Influences of Upland Tree Harvest Advisor: Malcolm Butler In four of the six fellowship projects, Federal and Sate Agencies, and a Mining company provided co-funding or in-kind services such as water analyses:

• **LTV Mining Company, Minnesota:** Dodds/Lin, Evaluation of Peat Uptake Capacity for Copper and Nickel in Constructed Wetlands of the LTV Mining Company

• ND Department of Health: Jaskowiak/Fawley, Sheyenne River Periphyton Study.

• Minnesota Department of Natural Resources: Zimmer/Butler, *Effects of Fathead Minnows on Wetlands Ecosystems* 

Summaries of the research objectives and progress from each of the FY 2001 fellows follow.

Periodic updates of research progress are made to the web page of each GRF. See the Institute's website at <u>www.ce.ndsu.nodak.edu/wrri</u> and select the 2001 Fellows link.

#### **Evaluation of Peat Uptake Capacity for Copper and Nickel in Constructed Wetlands of the LTV Mining Company**

Eric Dodds (Graduate Research Fellow) Wei Lin (Advisor)

Assistant Professor of Civil Engineering Department of Civil Engineering and Construction North Dakota State University Fargo, ND 58105-5285

Release of heavy metals from mining products and processes can create significant environmental damages to receiving water bodies. The heavy metals can accumulate in sediments and biological tissue. Removing of these metals from seepage or runoff water through the use of constructed wetlands can eliminate these potential problems. This study provided necessary information for estimating the effective life of peat in constructed wetlands at LTV Steel Mining Company's (LTVSMC's) Dunka Mine in Northeastern Minnesota. Batch removal experiments were conducted using peat to remove metals from synthetic single and mixed copper (Cu) and nickel (Ni) solutions and from mine runoff samples. Relationships between removal capacity from single metal solutions, mixed metal solutions, and mine runoff samples were developed. The impacts of pH and temperature on Cu and Ni removal were studied. The results of batch removal experiments with peat and Cu and Ni indicate that metal removal increases with pH, but temperature was determined to be insignificant for Cu and Ni removal from single metal solutions. Metal removal at higher pH was influenced by metal insolubility. Results observed during the study indicate that competition effects lower Cu and Ni removal from mixed metal solutions and that low metal concentrations and high ionic strengths affected metal removal from mine runoff.

The primary objective of this research was to determine the effective treatment life of the constructed wetlands at LTV Steel Mining Company (LTVSMC). Several batch sorption experiments were performed with single metal and mixed metal solutions at pH 4, 6, and 8 and also at 5°C, 10°C and 20°C to determine the importance of pH and temperature on metal removal by peat. Mixed metal solutions were used to determine the competitive nature of Cu and Ni removal. Actual mine water from the mine seeps was also studied for metal removal by peat. The results lead to the following conclusions:

- 1. pH had a definite impact on metal removal. Metal removal increased with increasing pH. At high pH, pH 8, metal removal seemed to be controlled by precipitation of metals. The peat may provide an initial site for crystals to form. Copper was more affected by insolubility than nickel.
- 2. Temperature was insignificant for Cu and Ni removal from single metal solutions at any pH. This result contrasts other research and commonly accepted thought that sorption processes are exothermic and increased sorption occurs at low temperatures.

- 3. Ni removal from solutions with Cu was lower than Ni removal from single metal solutions. Competition effects from Cu in solution lowered Ni removal.
- 4. Cu removal rates from the equally concentrated mixed metal solution were higher than Ni removal rates. The removal differences may be due to the lower solubility of Cu.
- 5. Metal removal from the actual mine water was not as high as that from the synthetic metal solutions. The high hardness, salt, and other ion concentrations may interfere with metal removal.
- 6. Treatable influent volumes per gram of peat were determined using the Freundlich model constants to meet the permitted effluent total toxicity requirements for each wetland. The treatable volumes (Liters of average influent per gram of peat) were determined to be 1.75 for 043 and 2.5 for 044. No treatment is needed for the 041 seep water because the water has been satisfying the total toxicity permit without any treatment. The effective treatment life of each wetland can be determined from the treatable influent volumes per gram of peat in each wetland.

#### **Rapid Spray Extraction and Analysis of Organic Compounds from Water**

Melissa Meyer (Graduate Research Fellow) Anthony Borgerding (Advisor)

Assistant Professor of Chemistry Department of Chemistry University of North Dakota Fargo, ND 58202

Typically, when new methods for water analysis are being developed, a large portion of the time is spent perfecting analysis time and detection limits. In this development process, analyte extraction from water is often neglected. It is important to be able to extract the analyte in an efficient and reproducible manner. Therefore, a focus of this research will be the extraction of analytes from water using a rapid extraction system. In our rapid extraction system, the speed of the extraction is dependent upon the interaction of aqueous and gaseous layers. The aqueous sample is introduced into an extraction chamber via a syringe and the organic compounds are removed using an extraction gas, which flows counter-current to the liquid sample. Previous studies have characterized this rapid extraction system. The conclusions drawn from them demonstrate that the rapid extraction system is capable of removing organic compounds from aqueous samples in 5-20 seconds. Building on this knowledge of rapid extraction, it is possible to think about the other steps of the analysis (separation, and detection). Rapid analysis techniques, such as high speed gas chromatography (HSGC) and ion trap mass spectrometry (ITMS), make it possible to separate or detect components of a sample in a matter of seconds. Consequently, the next step was to couple the rapid extraction system with HSGC or ITMS to further test its abilities. The extraction system, shown in Figure 1, is composed of commercially available stainless steel parts, which may easily be reconfigured as needed.

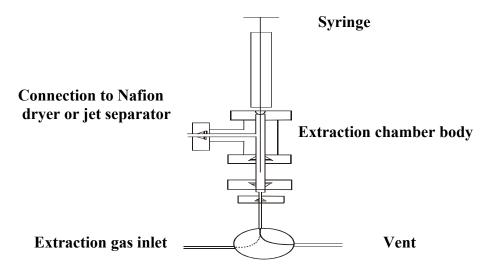


Figure 1 Rapid extraction system

Coupling the rapid extraction system to a HSGC, as shown in Figure 2, involved the use of a cryotrap to focus the analytes into a very narrow band before they were injected onto the column for subsequent fast separation.

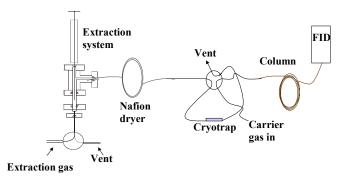
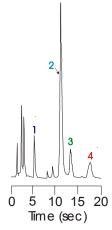
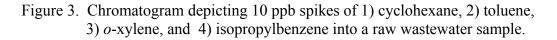


Figure 2 Schematic of the rapid extraction/HSGC system

One advantage of this system was that it was capable of extracting, separating and detecting low parts per billion concentrations of organic compounds from aqueous samples. It is also possible to analyze samples with complex matrices. This is important because typical water samples will not be pristine and may contain salts or suspended solids. A raw wastewater sample was spiked with 10 ppb of cyclohexane, toluene, *o*-xylene, and isopropylbenzene (Figure 3).





This sample was injected, extracted, separated and detected in less than 45 seconds using the rapid extraction/HSGC configuration. A disadvantage of this particular configuration involving a cryotrap was that a Nafion dryer was needed to remove water vapor from the system prior to the trap. Unfortunately, it also removed polar analytes that were present in the sample. In order to overcome this disadvantage the rapid extraction system was connected to an ITMS. This configuration, which is shown in

Figure 4, did not contain a Nafion dryer, cryotrap, or column. The ITMS is a more selective detector, which is capable of separating analytes to a certain degree. Since the Nafion dryer was not present it was possible to detect polar analytes in aqueous samples.

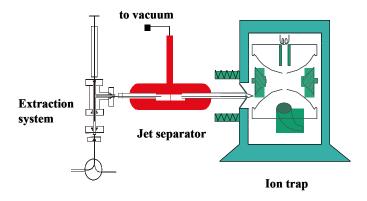


Figure 4 Schematic of the rapid extraction/ITMS system.

Preliminary data for this system indicate a decrease id sensitivity compared to the concentrations detectable using the extraction/HSGC system. This is probably due to non-ideal flow conditions and a large amount of water present in the ion trap. These difficulties are currently being addressed.

In summary, using the extraction/HSGC system extraction, separation, and detection of low ppb concentrations of nonpolar analytes was possible in less than 1 minute. Preliminary results for the extraction/ITMS system suggest that extraction and detection of polar and nonpolar analytes in the low ppm concentration range is possible in 1-2 minutes. Future work on the extraction/ITMS system will involve splitting the extraction gas flow to the ITMS. This will allow higher total flow rates without further taxing the MS, and improve vacuum conditions. Performing chemical ionization using water as the reagent may be attempted. Making these changes should result in sharper pulses and enhanced sensitivity.

# Northern Forested Wetlands: Characteristics and Influences of Upland Tree Harvest

Anthony Miller (Graduate Research Fellow) Malcolm Butler (Advisor)

Professor of Biological Sciences Department of Biological Sciences North Dakota State University Fargo, ND 58105

This research found that canopy reduction around seasonal wetlands in the Chippewa National Forest altered invertebrate food-web dynamics and resulted in the immigration of more predacious invertebrates, resulting in fewer prey invertebrate taxa. Tree reduction also lengthened wetland hydroperiod, and caused earlier spring thawing in these seasonal wetlands.

Using exploratory analysis, the study assessed natural variation and responses to experimental timber harvest by aquatic invertebrate communities in 16 seasonally-flooded wetlands in old-growth (70+ years since harvest) aspen stands in north central Minnesota. In the post-treatment year, the study assessed responses of algae and other wetland physical features to the experimental treatments. Pre-treatment analysis of aquatic invertebrate communities revealed that wetland hydroperiod and organic carbon concentration influenced invertebrate distribution and abundance, although wetland spatial differences between clusters accounted for the greatest variation. Post-treatment analysis also indicated strong influence of hydroperiod, carbon concentration and spatial variation on invertebrate communities. Additionally, wetlands associated with clear-cut treatments had longer hydroperiods, increased primary productivity and both positive and negative invertebrate responses. Algae exhibited no significant response to treatment or measured environmental variables.

#### Summary Findings

- Aquatic invertebrates vary significantly on a relatively small temporal and spatial scale.
- Physical processes such as length of wetland hydroperiod and the abundance or organic carbon govern invertebrate community dynamics.
- Upland tree removal lengthens hydroperiod and increases primary productivity in seasonal forest wetlands.
- Upland tree removal causes alterations in invertebrate community dynamics by making wetlands more visible to colonizing predatory invertebrates, and by lengthening hydroperiods.
- Leaving 50ft. protective buffers around wetlands is sufficient for minimizing anthropogenic disturbance to aquatic plant and invertebrate communities.

These findings will be useful to create ecology-based Best Management Practices (BMP's) implemented by the U.S. Forest Service.

Title:	New Methods to Detect Chlorinated Organic Pollutants in Water
Project Number:	2001ND3021B
Start Date:	3/1/2001
End Date:	2/28/2002
Research Category:	
Focus Category:	Methods, Toxic Substances, Water Quality
Descriptors:	analytical methods, spectroscopy,PCBs
Principal Investigators:	Andres D. Campiglia

- 1. A. F. Arruda, T. L. Martin, A. D. Campiglia. 2001. Phosphorescence Analysis of Organochlorinated Pollutants by Shpol'skii spectroscopy", 28th Annual Conference of Analytical Chemistry and Spectroscopy Societies (FACSS), Detroit, MI, Abstract Book 288, pg. 166.
- 2. A. F. Arruda and A. D. Campiglia. 2001. Time Resolved High-Resolution Phosphorescence Spectroscopy of Organochlorinated Pollutants in Shpol'skii Matrices with Fiber Optic Probes, 3rd biennial Joint EPSCoR Conference, Brookings SD, Abstract Book 27.

#### New Methods to Detect Chlorinated Organic Pollutants in Water

Andrea F. Arruda (Graduate Research Fellow) Andres D. Campiglia (Advisor)

Department of Chemistry North Dakota State University Fargo, ND 58105-5516

Polychlorinated biphenyls (PCB) and polychlorinated dibenzofurans (PCDF) are organic pollutants that can occur in surface, ground and drinking water. The initial objective of this project was to provide a rapid, simple and cost effective screening method for determining total polychlorinated biphenyls (PCB) and polychlorinated dibenzofurans (PCDF) in water samples. The objective was accomplished coupling solid-liquid extraction (SLE) and room temperature phosphorimetry (RTP). The method includes a three-step sample procedure, namely water extraction, application of phosphorescence enhancers to the extraction membrane, and direct RTP detection on the extracting substrate. The water sample (10-100 mL) is processed through an octadecyl extraction membrane with a syringe. The excess of water is removed from the membrane applying positive pressure to the syringe. 5 mL of phosphorescence enhancer is applied to the extracting substrate previous to phosphorescence detection. RTP is performed with a commercial spectrophosphorimeter under a nitrogen flow. Total analysis time varies from 8 to 10 minutes per sample. Limits of detection with 100mL of water sample were estimated at the parts-per-trillion level (10<sup>-12</sup>g.mL<sup>-1</sup>). Lower limits of detection are obtainable with larger water volumes. Environmental pollutants commonly encountered in water samples do not interfere with the screening method. As an alternative to achieve specific compound identification, Laser-Excited Time-Resolved Spectrometry (LETRS) was investigated. The process involves SLE followed by laser spectroscopy measurements in the membrane at low temperature. SLE are performed, as previously described, in water sample spiked with PCB and PCDF. The extraction membrane (5.5mm diameter) is placed in a vial and a fiber optic probe is positioned above the membrane. The sample is then frozen by vial immersion into liquid nitrogen (77K) or liquid helium (4.2K). The spectroscopy is directly performed from the frozen matrix. Analysis at low temperature offered narrow spectral bands, more intense signals and larger difference between the lifetimes compared to room temperature measurements. The total procedure takes 10 minutes per sample and provides excellent reproducibility of measurements (2-5%). For 100mL water sample, limits of detection were at parts-pertrillion level (10<sup>-12</sup>g.mL<sup>-1</sup>). Lifetimes obtained of PCB and PCDF in the membrane showed considerably difference, not only between PCB and PCDF, but also between their congeners. These differences facilitate time resolution of PCB and PCDF congeners.

The support from ND-WRRI permitted the development of a screening method, that can determine total PCB and PCDF in water sample and tell before hand whether the sample merits detailed chromatographic analysis. And also, permitted the investigation of LETRS with fiber optic probes to analyze PCB and PCDF in aqueous samples and overcome the lack of selectivity from the RTP method.

## **Information Transfer Program**

## **Basic Information**

Title:	ND WRRI Information Transfer Program
Start Date:	3/1/2001
End Date:	2/28/2002
Descriptors:	Newsletter, Website
Principal Investigators:	Gregory J. McCarthy, G. Padmanabhan

#### ND WRRI Information Transfer Program

Information transfer is done through an annual newsletter initiated in 1992, a website initiated in 1999, and presentations and publications by grant and fellowship recipients. The newsletter is usually issued in the month of December of each year. Copies of past newsletters can be obtained by writing to the Director. Again this year, the institute continued its modest support of the Biotic Resources Seminar Series at North Dakota State University.

The Institute's website address is www.ce.ndsu.nodak.edu/wrri.

## **Student Support**

Student Support						
Category	Section 104 Base Grant	Section 104 RCGP Award	NIWR-USGS Internship	Supplemental Awards	Total	
Undergraduate	0	0	0	0	0	
Masters	2	0	0	0	2	
Ph.D.	4	0	0	0	4	
Post-Doc.	0	0	0	0	0	
Total	6	0	0	0	6	

## **Notable Awards and Achievements**

None

## **Publications from Prior Projects**