Report for 2001ND2721B: Graduate Research Fellowships

- Conference Proceedings:
  - 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.
  - 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.
  - Anthony Miller, Seasonal Forested Wetlands: Factors Influencing Aquatic Invertebrate Communities. Presented at the 2001 North American Benthological Society Conference in Lacrosse, WI.
  - 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.
- Articles in Refereed Scientific Journals:
  - 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.
  - 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.
- Dissertations:
  - 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.
  - Anthony Miller, Impacts of Logging on Invertebrates in Seasonal Forest Wetlands. M.S. Thesis, Department of Zoology, North Dakota State University, Fargo, December 2001.

Report Follows:

GRADUATE RESEARCH FELLOWSHIPS

Project Number: **ND01-01**

Start: 01 March 2001
End: 28 February 2002

Title: **Graduate Research Fellowships**

Coordinator: **Gregory J. McCarthy**, ND WRRI Director, Department of Chemistry, North Dakota State University, Fargo

Focus Category: WATER QUALITY; WETLANDS; 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 ***www.ce.ndsu.nodak.edu/wrri*** 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.

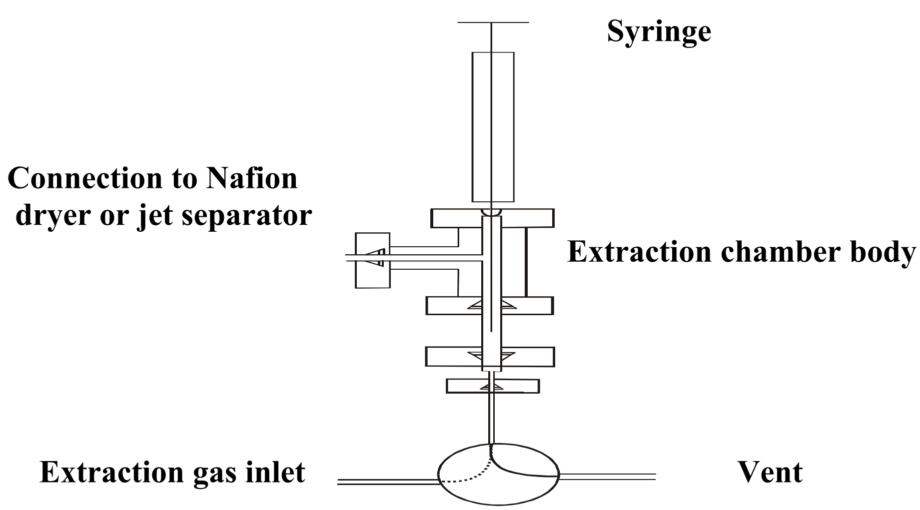

Figure 1 Rapid extraction system

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.

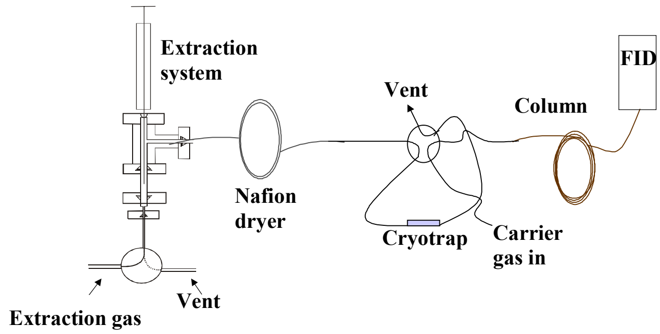

Figure 2 Schematic of the rapid extraction/HSGC system

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).

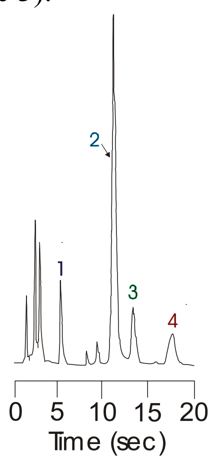

Figure 3. Chromatogram depicting 10 ppb spikes of 1) cyclohexane, 2) toluene, 3) *o*-xylene, and 4) isopropylbenzene into a raw wastewater sample.

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.

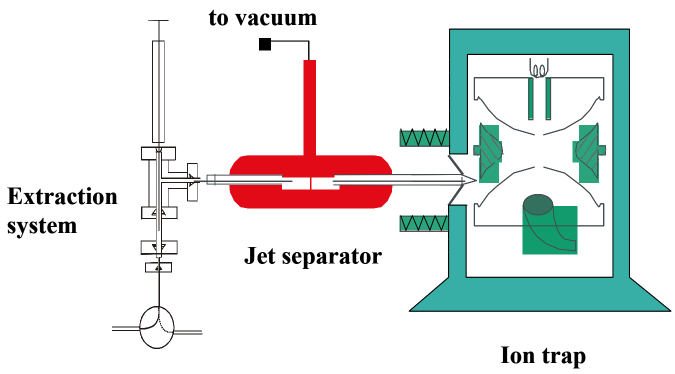

Figure 4 Schematic of the rapid extraction/ITMS system.

Preliminary data for this system indicate a decrease in 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
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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.