Title: Wild Rice-Sulfate 2011 Preliminary Field Study

Research Team:

Principal Investigator:

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Key Personnel:

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Overview:

The University of Minnesota Limnological Research Center, hereafter referred to as the "contractor" or "university" agrees to (1) plan and execute a sampling program for water and sediments to help evaluate potential environmental factors important in the distribution and abundance of wild rice (*Zizania* spp.) in Minnesota Lakes, and (2) evaluate methods for effective sampling and analysis of sediment porewaters for chemical constituents important to wild rice distribution and abundance. The data and information gained from this study will aid in the development of a protocol for subsequent studies that will inform further evaluation of the Minnesota sulfate water quality standard for the protection of wild rice.

The objectives of this preliminary field study are to:

1. Better understand and document the range of water column and sediment chemistries at sites with robust, declining, and absent wild rice stands – data that will inform the selection of sites and/or sediment for more detailed study under the protocol through, for example, seasonal sampling or experimentation;
2. Gather ambient (*in situ*) data on sulfate and related parameters to supplement the field study anticipated to occur under the protocol; and
3. Test and perfect the method(s) for sampling sediment porewater in lakes and streams.

Overall Field Study Approach:

During the summer of 2011 the university will sample a minimum of 50 shallow-water ecosystems so that the range of sulfate concentrations and other factors in the water column and sediment that might correlate with the presence or absence of wild rice can be better understood.

Site Selection:

Study sites will be selected to represent various categories in an effort to characterize the range of wild rice habitats in Minnesota (Table 1), including sites that are known to be productive wild rice habitats, apparently good wild rice habitats that nevertheless do not support wild rice (if they can be identified), wild rice sites that John Moyle sampled 50 to 70 years ago, low-sulfate sites, sites naturally high in sulfate, sites enriched with sulfate due to human activity, and paddies used for the commercial production of wild rice. If any of these classes cannot be sampled for logistical reasons, the sampling effort will be redirected to the general goal of understanding the range of sediment and water conditions in which wild rice can successfully grow. The MPCA will prepare a list of potential sample sites based on consultation with the contractor, DNR staff, tribal representatives, paddy growers, and other parties. Using the list of potential sites, the contractor will meet with MPCA staff to finalize a prioritized list within each site class listed in Table 1, identifying at least five backup sites for each class, so that identifying sites to be sampled is not an impediment to meeting the goal of sampling a minimum of 50 sites within this project. Backup sites may be sampled by the contractor when primary sites turn out to be physically or legally

inaccessible or inappropriate from an environmental point of view—for instance, having been drained of all surface water. Sampling crews shall obtain surface water samples from sites at which they cannot identify a wild rice stand in which to sample the sediments. In cases where locations of past wild rice stands are known, but at which they cannot identify a living wild rice stand, field crews may collect core samples in that general location.

Table 1. Classes of sites to be sampled in 2011 to characterize the variability of wild rice habitats in Minnesota.

Site Class	Approximate Number of sites	Information Sources
Productive wild rice sites (in naturally low- and high-sulfate areas)	10 to 20	DNR, MPCA, Tribes, John Moyle reports
Historically productive wild rice sites, but little wild rice recently.	5 to 10	John Moyle reports, Tribes
Sites receiving elevated sulfate loading from human activity	5 to 10	MPCA, DNR
Apparently good wild rice habitat, but without wild rice	5 to 10	DNR, MPCA, Tribes
Commercial wild rice paddies	5 to 10	Commercial Growers

Field Work:

A two-person field crew will travel to designated sites and will use a canoe or other small boat to carry out their tasks (Table 2). Locations will be recorded on maps and by GPS. Dominant aquatic plants will be identified, coverage estimated using methods compatible with those used by Minnesota Tribes, and representative digital photographs taken. One grab sample of water will be obtained from below the surface, but taking care to minimize suspended sediment and dislodged periphyton. Sediment samples will be taken from three locations, composited in a mixing container, and subsampled into a number of different sample jars for the various analyses. In a subset of locations, five subsamples will be preserved separately in order to perform separate analyses, in an effort to understand variability in the sediment matrix. Two separate cores will be taken for extraction of porewater from the top 10 cm, after which pH will be measured in one of the cores. One porewater sample will be preserved for sulfide analysis and anions, and one will be preserved for a suite of parameters (Table 3c).

Table 2. Field data to be collected as part of the 2011 survey.

Analysis	Method	Reference
Site Location	GPS	
Water depth	Sounding line /stage if available	
Water temperature, pH, oxygen, conductivity	Sonde	
Transparency	T-tubes	
Plant species/abundance, including wild rice	Visual	MPCA and DNR guidance
Photo points	4-cardinal directions	

Sediment samples will be collected by gravity corer, or by surface piston corer in cases where macrophyte roots limit gravity-corer penetration. The uppermost 10 cm of sediment will be extruded vertically on site using a precision core-sectioning device and retained for analyses. A detailed protocol for sample collection, handling, and preservation will be developed prior to initiation of field work. As much as possible, given the relatively unique nature of the sediment sampling portion of the field work, field methods will be consistent with established MPCA and Tribal monitoring methods.

Laboratory Analyses:

Analysis of water and sediment samples will follow established laboratory methods as referenced in Table 3. Water samples for all analyses except TP/TN will be filtered in the field, with subsamples for each analysis preserved appropriately and transported in a timely manner to the laboratory. Most sediment analyses will be performed on freeze-dried subsamples. An analytical protocol and quality assurance plan will be developed which will specify details for replicate samples, field blanks, laboratory blanks, and related issues. As much as possible, given the low detection limits required, analytical methods will be consistent with established MPCA and Tribal analytical methods/requirements.

Sample Analyses:

Table 3a. Water chemistry

Analyses	**Analytical**	**Reference**	**Detect. Limits**
Cations/Metals (Na, K, Mg, Ca)	ICP-mass spectrometry (trace metal analyses transferred to new porewater samples, Table 3c)		1 ppb
Anions (SO4, Cl)	Ion chromatography		10 ppb
Alkalinity	Gran titration		1 µeq/L
Total P/Total N	Dual alkaline/persulfate digestion & autoanalyzer	Ameel et al. (1993)	5, 20 ppb
Nitrate/Ammonia	Autoanalyzer		10 ppb
DOC (dissolved organic carbon)	UV/persulfate digestion & carbon analyzer		100 ppb
SUVA (specific UV absorbance)	UV-Vis spectrometer	Weishaar et al. (2003)	n/a

Table 3b. Sediment chemistry

Analyses	Method	Reference	Detect. Limits*
pH of surface sediment (field)	Standard probe	Standard Methods (2005)	N/A
Freeze drying & subsampling	Modulio Bulk Freeze Dryer		n/a
Inorganic grain size	Wet oxidation & Horiba laser-diffraction grain-size analyzer	Horiba Applications Note AN145	n/a
Organic grain size	Wet sieve & combustion weight loss	Modified Quiroga et al. (1996)	n/a
Phytoliths	Light microscopy	*Yost (2006),* Yost & Blinnikov (2011)	n/a
Carbonates	Carbon coulometry	Engleman et al. (1985).	*0.10%*
Total organic carbon	Skalar Primacs carbon analyzer		0.02% (200ppm)
Total nitrogen	LECO nitrogen analyzer		0.02% (200ppm)
Total sulfur	LECO sulfur analyzer		0.05% (500ppm)
Inorganic S (sulfides)	AVS (acid-volatile sulfur)	Hsieh ~~&~~ Shieh (1997); Hsieh et al.~~,~~ (2002)	30 ppb S
Total phosphorus	Wet oxidation/dilute HCl & autoanalzyer	Malo (1977)	65 ppm
P-fractions (NaOH-P, HCl-P, Organic-P)	Selective extraction w/dilute NaOH, HCl & autoanalyzer	Hieltjes and Lijklema (1980)	12 ppm
Extractable metals (Fe, Mn, Ca, K, Mg, Ca, Cu, Zn, Co, Mo)	Dilute HCl-extraction & ICP-MS	Balogh et al. (2010)	0.5 ppm

*Detection limits for sediments reported as concentrations in dry sed (0.1 g sample mass)

Table 3c. Sediment Porewater Analyses

Analyses	Method	Reference	Detect. Limits*
Sulfide in porewater (sample preservation)	Zinc acetate	Standard Methods (2005) 4500-S2-C	-
Sulfide in porewater (ISE method)	Ion-Selective Electrode	Standard Methods (2005) 4500-S2-G	0.03 mg/L
Sulfide in porewater (Methylene Blue method)	Methylene Blue, by autoanalyzer	Standard Methods (2005) 4500-S2-D; Tucker (2010)	~0.02 mg/L
Cations/Metals (Na, K, Mg, Ca,)	ICP-mass spectrometry		1 ppb
Anions (SO4, Cl)	Ion chromatography		10 ppb
Total P/Total N	Dual alkaline/persulfate digestion & autoanalyzer	Ameel et al. (1993)	5, 20 ppb
Nitrate/Ammonia	Autoanalyzer		10 ppb
DOC (dissolved organic carbon)	UV/persulfate digestion & carbon analyzer		100 ppb

Evaluation of porewater sampling methods:

A small subset of readily accessible sites will be chosen to evaluate and refine method(s) for measuring the chemistry of sediment pore waters, a potentially important link to wild rice survival and growth. This preliminary field study will include a critical review of porewater measurement techniques for characterizing important geochemistry related to the effects of sulfate on wild rice. In light of the challenges associated with sampling in wild rice beds, a thorough review of literature will be conducted and two candidate methods will be chosen to evaluate and refine measurement techniques at 1-2 sites. In addition, the recommended porewater sampling techniques will be tested and evaluated, and recommendations made, in respect to the goal of obtaining an uncontaminated porewater sample for the analysis of total mercury and methyl mercury, in case the MPCA determines that it is desirable to measure these parameters in a future study.

Recommendations for porewater methods will consider:

(1) the effectiveness of methods in quantifying important porewater chemicals (sulfide, iron, sulfate, nitrate, phosphorus, mercury, methyl mercury, trace nutrients and possibly others), and

(2) the ability to characterize both the vertical structure of stratified geochemical zones as well as the lateral variability within a site.

Based on the literature review and preliminary studies, a recommendation will be made to guide more detailed subsequent studies related to the influence of sulfate-related porewater geochemistry on wild rice. This will include both methodological recommendations as well as guidance on sampling design to characterize within-site variability. A report will be submitted to MPCA summarizing the methods review, pros and cons of each technique, preliminary data, and a recommendation for porewater methods.

Data processing and reporting:

Results for field and laboratory analyses will be compiled and stored in spread-sheet format where they will be further summarized and examined for QA review and statistical analysis. Specifically, each dataset will be explored with an unconstrained ordination analysis (such as Principal Components Analysis or Correspondence Analysis). Then a multivariate, unimodal, constrained ordination, such as Canonical Correspondence Analysis, will be used to identify strong correlative relationships between wild

rice abundance – as measured by field observation and phytolith analysis of sediments – and the water and sediment and chemistry of the study sites. The identification of these correlative relationships will allow for the generation of focused hypotheses regarding sediment geochemistry and wild rice growth.

The university will submit a final project report to the MPCA. The final report will contain all field and laboratory results (concentrations), QA data (duplicate analyses, field and lab blanks, CRMs) and assessment of precision and accuracy based on duplicates and CRM recoveries (where appropriate). An interpretive narrative pertinent to the objectives of the study will be included in the final report. A draft report will submitted by February 21, 2012, revised in consultation with MPCA staff, and submitted as a final report by June 30, 2012. Draft and final reports will be provided in electronic and paper formats.

Literature Cited

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Tasks and timeline:

	2011							2012		
Task	June	July	Aug	Sept	Oct	Nov	Dec	Jan	Feb	June
Site Selection & Planning		X	X							
Field Protocol			X							
Lab Protocol & QA Plan			X							
Sample Collection			X	X	X					
Sediment Analysis-Table 3b					X	X				
Water Analysis-Table 3a					X	X				
Porewater analysis-sulfide					X	X				
Porewater analysis-Table 3c					X	X				
Porewater Protocol		X	X	X	X	X	X			
Data Analysis					X	X	X	X		
Draft Report						X	X	X	X	
Final Report										X