MINNESOTA POLLUTION CONTROL AGENCY

Sampling and Analytical Methods for Wild Rice Waters

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Environmental Analysis and Outcomes Division

The analytical methods and sampling procedures provided in this document are incorporated by reference in Minn. R. pt. 7050.0224. They apply to the analysis and sampling of sediment and sediment porewater for purposes of implementing the sulfate water quality standard applicable to wild rice waters.

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Sediment sampling procedure for wild rice waters

Background

The Minnesota Pollution Control Agency has developed these procedures to ensure that samples taken for the purposes of establishing the sulfate standard to protect wild rice (Minn. R. 7050.0224) are accurate. The sulfate standard is an equation that calculates a sulfate concentration necessary to maintain a sulfide concentrations in sediment less than or equal to 120 µg/L (0.120 mg/L). The standard uses measured sediment concentrations of total organic carbon (TOC) and total extractable iron (TEFe) in the calculation of the protective sulfate concentration. This procedure establishes the methodology that must be used to collect sediment samples in wild rice waters.

The terms used in this document have the following meanings.

- Wild rice water is the entire WID identified in Minn. R. 7050.0471.
- Wild rice habitat identifier describes the type of information available to identify observed or potential wild rice habitat within a wild rice water.
- Sediment sample area is an identified portion of the wild rice water containing wild rice habitat.
- Transect is a straight line across the sediment sample area along which sediment cores are obtained.
- Core sample site is the location along a transect where an individual sediment core is taken.

1. Identify areas of wild rice habitat

The first step is to identify areas within the wild rice water where wild rice is growing or may grow. The entire wild rice water must be evaluated to determine areas of wild rice habitat.

On a map or aerial photograph of the wild rice water, outline the areas of wild rice habitat and identify them with one of the following wild rice habitat identifiers.

1. Areas where wild rice is observed or where there is evidence of wild rice, such as rooted wild rice plants that have been grazed or wild rice plant residue from previous year's growth.
2. Areas where information accurately identifies the past location of wild rice beds. Examples of acceptable information are plant surveys, sampling events, or historical records where the location of wild rice beds can be accurately determined.
3. Areas with yellow or white waterlilies (*Nuphar variegata* and *Nymphaea odorata*) where the water depth is less than 120 cm*.

* Where a depth defines a habitat, that depth is based on average conditions, i.e., where water is at or below the ordinary high water level, but not at levels typical of flood or drought conditions. If sampling occurs during high or low water conditions, the sampler must determine if the sediment sample area would normally meet the depth criteria.

4. Areas with either floating-leaved plants or emergent plants where water depth is less than 120 cm* (excluding species that form dense monocultures that exclude wild rice, such as cattails (*Typha* species), phragmites *(Phragmites australis*), purple loosestrife (*Lythrum salicaria*), and reed canary grass (*Phalaris arundinacea*)). Examples of the types of floating-leaved or emergent plants that will approximate the conditions for wild rice growth are pondweeds (*Potamogeton* species), watershield (*Brasenia schreberi*), pickerelweed (*Pontederia cordata*), and arrowhead (*Sagittaria latifolia*).
5. Areas where satellite or aerial photographs indicate the past presence of floating-leaved or emergent plants where the water depth is less than 120 cm*.
6. Areas where water depth is between 30 and 120 cm*.

2. Selection of sediment sample areas

The second step is to select sediment sample areas from the areas of wild rice habitat identified in section 1.

Select five representative sediment sample areas based on the following decision framework:

- If the wild rice water contains areas with wild rice habitat identifier #1, all sediment sample areas must be in the #1 areas.
    - If there are at least five separate areas with wild rice habitat identifier #1, five separate areas must be selected.
    - If there are fewer than five separate areas with wild rice habitat identifier #1, the largest areas must be divided to establish five sediment sample areas.
    - If the areas of wild rice habitat #1 are very small or of a very limited number, (e.g. one small bed) all sediment sample areas must be selected in those areas unless it is not possible to obtain the required sediment cores from those areas. In those cases, if there is documentation that wild rice was present in other areas (wild rice habitat identifier #2) those areas may be sampled to provide a total of five sediment sample areas.
- If the wild rice water does not have any areas with wild rice habitat identifier #1, all sediment sample areas must be selected based on the next highest level of wild rice habitat identifier (#s 2, 3, 4, 5, or 6).
    - If there are at least five separate areas with the highest level of wild rice habitat, those areas must be selected as sediment sample areas.
    - If there are fewer than five separate areas with the highest level of wild rice habitat identifier, the largest areas must be divided to establish five separate sample areas with the highest priority wild rice habitat identifier.
    - If the areas of the highest wild rice habitat are very small or of a very limited number, so that it is not possible to obtain the required sediment cores from those areas, additional sediment sample areas can be established in areas with the next highest priority wild rice habitat identifier.

Identify the each sample area as (A) through (E) and record the wild rice habitat number that most closely corresponds to each sampling area.

3. Identify Sampling Transects

The third step is to establish one sampling transect within each of the five identified sediment sample areas. The transect must be

- A straight line across the sediment sample area; and
- Perpendicular to the shore, unless the area is an island of habitat that is far from any shore;

Identify the approximate location of each transect within each sediment sample area on the map or aerial photograph of the wild rice water.

4. Sediment Sample Collection and Processing

The fourth step is to collect the sediment samples. Within each transect, five sediment cores must be collected and composited for analysis.

Collect and composite the sediment samples from each of the five transects using the following procedures:

1. Collect five sediment cores within each transect. To the extent possible, cores must be equally spaced across the entire transect. However, transects that cross areas that do not meet the habitat description (e.g., an area of a #1 sediment sample area where there is no wild rice or evidence of wild rice, or an area of a #3 sediment sample area that is more than 120 cm deep) should apportion the 5 sediment coring sites to the areas that correspond to the habitat description.
2. Record the latitude and longitude coordinates for the first and last core site of each transect. If the coring sites are more than 100 feet apart, record the latitude and longitude at each coring site. Record the coordinates in the format of Sediment sample area, core number (e.g., A1, A2, A3, A4, A5, B1, B2, etc.).
3. Collect each sediment core from the top 10 centimeters of the sediment. Use the same diameter core tube for all cores collected.
4. Place the 10-cm long core into a clean container.
5. Repeat for each of the five cores collected from the transect.
6. Thoroughly mix all five sediment cores together. Discard any large plant or rock material.
7. After mixing, remove a sample of approximately 0.2 L and place into an appropriately labelled sample container.

5. Data Reporting

In the report of the sample data, include:

1. The map or aerial photograph of the wild rice water, marked with the areas of wild rice habitat (required in Step 1), location of the sample areas (required in Step 2) and transects (required in Step 3);
2. The latitude and longitude of the ends of each transect, or the core site if the core sites are more than 100 feet apart; and
3. The wild rice habitat number that most closely corresponds to each sediment sample area.

Example Data Report of sediment samples

Wild Rice Water: Sediment samples and analysis

Sediment sampling date:

Field crew names:

Name of Wild Rice Water:

State of Minnesota ID for the waterbody:

Sediment Sample Area (A-E)	Wild Rice Habitat Identifier (1-6)	Location of transect ends, or each core site (if > 100 feet apart)			Sediment sample analytical results	
		Core Identifier	Latitude	Longitude	TOC	TEFe
A	#	A1				
		A2				
		A3				
		A4				
		A5				
B	#	B1				
		B2				
		B3				
		B4				
		B5				
C	#	C1				
		C2				
		C3				
		C4				
		C5				
D	#	D1				
		D2				
		D3				
		D4				
		D5				

Sediment Sample Area (A-E)	Wild Rice Habitat Identifier (1-6)	Location of transect ends, or each core site (if > 100 feet apart)			Sediment sample analytical results	
		Core Identifier	Latitude	Longitude	TOC	TEFe
E	#	E1				
		E2				
		E3				
		E4				
		E5				

Analytical method for the determination of total extractable iron in sediment

This document describes the methods for the preparation and analysis of sediment samples for total extractable iron (TEFe) for analysis by Inductively Coupled Plasma-Atomic Emission Spectrometry Spectroscopy.

1. Prior to analysis, store the samples at ≤ 6° C to minimize biological activity. Samples must be analyzed within 180 days of collection date.
2. Dry and prepare the sample using either procedure 2a or 2b:
    - 2a.
        - Manually remove large materials such as rocks, shells, and sticks
        - Dry the sample in an oven at 50° C until constant weight is achieved.
        - Manually break the dried sample into pieces.
        - Pulverize the dry sample using a mill.
    - 2b.
        - Freeze-dry the sample.
        - Homogenize the sample using a stainless steel spatula.
        - Remove remaining large materials such as rocks, shells, and sticks.
3. After the sample has been prepared, digest a small aliquot of the sample (0.25 +/- 0.02 grams) and all necessary QC samples by adding 25 mL of 0.5 N hydrochloric acid to all digestion tubes. Digest samples (and all necessary QC samples) on a hot block at 80-85° C or in a water bath at 80-85° C. Once samples reach 80° C, digest samples for 30 additional minutes. After 30 minutes, remove samples immediately and cool to room temperature, and bring to a constant volume. Immediately either centrifuge the tubes at 1000 rpm for 10 minutes or filter using a 0.45 µm PES-type filter. Remove an aliquot and dilute with reagent water to known volume for iron analysis. Determine iron in the diluted aliquot using Inductively Coupled Plasma-Atomic Emission Spectrometry. Report the results in mg/kg (dry weight).
4. Acceptable performance must be demonstrated on an ongoing basis. With every digestion batch, the laboratory must perform the following:
    - Low Background: At the beginning of each batch, analyze a blank (BLK) to determine reagent or laboratory contamination. The background level of the BLK must be below the report level before samples are analyzed.
    - Accuracy: With every batch of 20 samples processed as a group, analyze a Laboratory Control Sample (LCS). The LCS should be prepared at concentrations similar to those expected in the field samples and ideally at the same concentration used to prepare the matrix spike (MS). The acceptance criteria for recovery of the analyte in the LCS is 80 – 120%.
    - A MS must be prepared and analyzed with each batch of 20 samples processed as a group, or a minimum of 10% of the field samples analyzed, whichever is greater. The same solution used to

fortify the LCS is used to fortify the MS. The acceptance criteria for recovery of the analyte in the MS is 80 – 120%.

- Precision: Analyze a Laboratory Duplicate (DUP) with each batch of field samples processed as a group, or 10% of the field samples analyzed, whichever is greater. The acceptance criteria for the relative percent difference is ≤ 20%.

Analytical method for the determination of total organic carbon in sediment

This document describes the methods for the preparation and analysis of sediment samples for the analysis of Total Organic Carbon (TOC) by Non-Dispersive Infrared Detection.

1. Prior to analysis, store the samples at ≤ 6° C to minimize biological activity. Samples must be analyzed within 28 days of collection date.
2. Dry and prepare the sample using either procedure 2a or 2b:
    - 2a. Manually remove large materials such as rocks, shells, and sticks.
        - Dry the sediment sample in an oven at 50° C until sample is completely dried.
        - Manually break the dried sample into pieces.
        - Pulverize the remaining dry sediment using a mill.
    - 2b. Freeze-dry the sample.
        - Homogenize the material using a stainless steel spatula,
        - Remove remaining large materials such as rocks, shells and sticks.
3. After the sample has been prepared:
    - Treat an aliquot of the homogenized sample with a 5% solution of H_3PO_4 to remove any inorganic carbon.
    - Either air-dry or oven-dry (at 105°C) the sample until constant weight is achieved.
    - Analyze the sample (and all necessary QC samples) for Total Organic Carbon content using a Standard Operating Procedure based on EPA Method 9060A.
    - Analyze all environmental samples in duplicate.
    - Report the results in mg C/kg dry sediment, and as percent C in dry sediment.
4. Acceptable performance must be determined for every digestion batch by performing the following activities:
    - Low Background: At the beginning of each batch, analyze a blank (BLK) to determine reagent or laboratory contamination. The background level of the BLK must be below the report level before analyzing samples.
    - Accuracy: With every batch of 20 samples processed, analyze a Laboratory Control Sample (LCS). The LCS must prepared at the same concentrations as the field samples and at the same concentration used to prepare the matrix spike (MS). The acceptance criteria for recovery of the analyte in the LCS is 70 – 130%.

      Prepare and analyze a MS with every 20 samples processed as a group, or a minimum of 10% of the field samples analyzed, whichever is greater. The same solution used to fortify the LCS is used to fortify the MS. The acceptance criteria for recovery of the analyte in the MS is 70 – 130%.

- Precision: Analyze a Laboratory Duplicate or a MS duplicate with every 20 samples processed as a group, or 10% of the field samples analyzed, whichever is greater. The acceptance criteria for the relative percent difference (RPD) is ≤ 30%.
- Analyze every sample in duplicate. The RPD between duplicates must be ≤ 30%.

Porewater sampling and analytical method for the determination of sulfide

This document describes the methods for the sampling and analysis of sediment porewater samples for total dissolved sulfide in sediment porewater samples for analysis by the automated methylene blue method (Standard Methods 4500-S2 E. Gas Dialysis, Automated Methylene Blue Method).

1. Sample Locations:

Before conducting porewater analysis to determine an alternate sulfate standard, sediment in the water body must have been sampled as described in Sediment Sampling Procedure for Wild Rice Waters. Using the same locational data used for the previous sediment sampling, take ten sediment cores for porewater analysis as close as possible to the sediment sample points within each of the five previously established transects, according to the following table (which was established using a random number generator so that the porewater samples would represent the wild rice water).

Transect (a-e)	Sediment Composite sample #1	Sediment Composite sample #2	Sediment Composite sample #3	Sediment Composite sample #4	Sediment Composite sample #5
a	porewater		porewater		
b		porewater		porewater	
c	porewater			porewater	
d		porewater			porewater
e	porewater		porewater		

2. Sample Collection:

Sediment samples for porewater analysis must be taken from undisturbed sediment, preferably from a boat, with a sediment coring device with a 7 cm diameter core barrel.

- Obtain a 15-50 cm long sediment core with at least 10 cm of overlying water. Insert a piston at the bottom end of each core as it is retrieved.
- Keep the core upright and shaded prior to porewater sampling.
- Immobilize the core tube in a rack while on shore or on a suitable stable surface.

3. Porewater sampling:

- Porewater sampling must begin within 4 hours of collecting the sediment sample.
- Shortly before beginning porewater collection, extrude the overlying water from the top of the core sample.
- Extract porewater using a 10-cm long, 2.5 mm diameter, Rhizon™ filter with a mean pore size of 0.15 µm (Rhizon™ filter is available from Rhizosphere.com, Netherlands). Insert the Rhizon™ filter vertically into the core top and connect with a stainless steel needle and either PVC or

polyethylene tubing to a 125-mL evacuated serum bottle that had been capped with a 20-mm thick butyl rubber septum. Obtain a sample of no less than 15 mL of porewater, although 50 mL is preferable.

Before the needle is inserted into the sulfide sample bottle, using a second evacuated bottle, flush air from the Rhizon-tubing assembly with a small amount of sample porewater. As the porewater sample is collected, keep the top of the Rhizon within the wet sediment as the core subsides. The serum bottle must be preloaded with 0.2 mL of 2.0 N zinc acetate, 0.5 mL of 15 M sodium hydroxide, and a stir bar, flushed with a nitrogen atmosphere, evacuated, and preweighed.

4. Sample Analysis:

- Samples must be analyzed within 14 days of the collection date and must be stored at ≤ 6° C to minimize biological activity. At the laboratory, inject 5-6 mL of alkaline antioxidant reagent into each sample bottle through the septum with a Safety-Lok syringe and stir for at least 1 hour prior to subsampling for analysis.
- Sub-samples for analysis of sulfide should be withdrawn from the serum bottle without removing the septum, which preserves the sample for possible re-analysis. Analyze sulfide colorimetrically using a gas dialysis automated methylene blue method, with in-line acid distillation and NaOH trapping method (Standard Methods 4500-S^{2-} Sulfide).
- Express the results as milligrams sulfide, as sulfur, per liter of porewater (with three significant figures).

5. Acceptable Performance:

Acceptable performance must be demonstrated on an ongoing basis. With every digestion batch, the laboratory must perform the following:

- Demonstration of Low Background: At the beginning of each batch, analyze a blank (BLK) to determine reagent or laboratory contamination. The background level of the BLK must be below the report level; otherwise, investigate and eliminate the source of the contamination before samples are analyzed.
- Accuracy: With every batch of 20 samples processed as a group, analyze a Laboratory Control Sample (LCS). Prepare the LCS at concentrations similar to those expected in the field samples and at the same concentration used to prepare the matrix spike (MS). The acceptance criteria for recovery of the analyte in the LCS is 80 – 120%.
- Prepare a MS is and analyze with each batch of 20 samples processed as a group, or a minimum of 10% of the field samples analyzed, whichever is greater. Use the same solution used to fortify the LCS to fortify the MS. The acceptance criteria for recovery of the analyte in the MS is 80 – 120%.
- Precision: Analyze a Laboratory Duplicate with each batch of field samples processed as a group, or 10% of the field samples analyzed, whichever is greater. The acceptance criteria for the relative percent difference (RPD) is ≤ 20%.