Line 5 Wisconsin Segment Relocation Project

Wisconsin Department of Natural Resources

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Enbridge Reponses to DNR Information Request Dated March 10, 2023

Attachment 10

Surface Water Sampling Quality Assurance Project Plan

SURFACE WATER SAMPLING QUALITY ASSURANCE PROJECT PLAN

Line 5 Wisconsin Segment Relocation Project

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1.0 INTRODUCTION

This Quality Assurance Project Plan ("QAPP") outlines the quality assurance ("QA") measures that will be implemented to determine the background concentrations of analytes upstream and downstream of the Enbridge Energy Line 5 Wisconsin Segment Relocation Project ("Project"), which crosses the following Wisconsin counties: Douglas, Bayfield, Ashland, and Iron. This QAPP has been prepared based on USEPA Region 5's March 2001 guidance for QA project plans, which addresses four major QA/quality control ("QC") elements as follows:

- Project Management
- Data Generation and Acquisition
- Assessment/Oversight
- Data Validation and Usability

This QAPP defines the general approach to program and data quality management based on the four elements described above.

The remainder of the QAPP is organized as follows:

- Section 2.0 describes project management, project background, and describes data quality and data management objectives.
- Section 3.0 describes sampling and decontamination procedures, including sample preparation and preservation.
- Section 4.0 describes sample custody procedures.
- Section 5.0 describes the procedures and frequency requirements for calibration of both laboratory and field equipment.
- Section 6.0 describes the analytical methods and requirements.
- Section 7.0 describes the data reporting procedures, validation as well as the documentation requirements.
- Section 8.0 describes the laboratory and field QC checks including the use of QC samples.
- Section 9.0 describes the preventative maintenance procedures.
- Section 10.0 presents the data validation procedures.
- Section 11.0 describes the procedures for implementing corrective measures and the parties to be notified in the event corrective action is necessary; and
- Section 12.0 identifies Wisconsin Department of Natural Resources ("WDNR") representatives to which relevant information will be submitted.

2.0 PROJECT MANAGEMENT

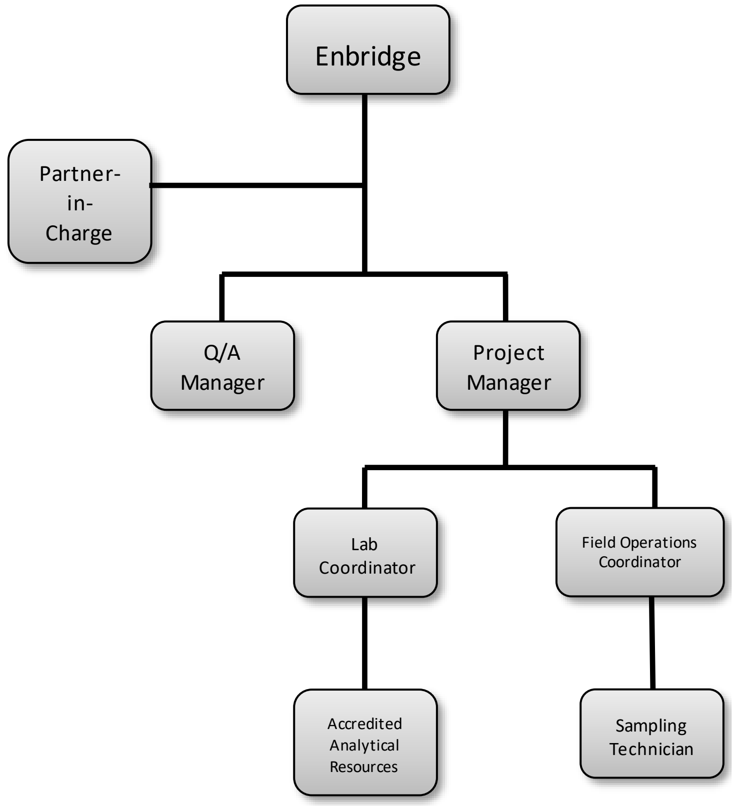
This section outlines the fundamental framework for conducting the sampling activities, ensuring that proper QA measures are implemented throughout the process. By defining the project organization, including the roles and responsibilities of team members involved in the sampling efforts, and providing a comprehensive project description, this chapter establishes a solid foundation for the successful execution of the water quality sampling program. A clear understanding of the project organization and a detailed project description are essential for ensuring the accuracy, reliability, and consistency of the data collected, thus enabling informed decision-making and effective management of tasks and resources. Additionally, the data quality objectives ("DQOs") and criteria ensure that the data collected throughout the project meet the required standards of accuracy, precision, representativeness, completeness, and comparability. Lastly, the data management objectives guide the systematic and organized handling, storage, analysis, and dissemination of the collected data.

2.1 PROJECT ORGANIZATION

While all personnel involved in an investigation and in the generation of data are implicitly a part of the overall project and QA program, certain individuals have specifically delegated responsibilities. Within this project, these individuals are the Partner-in-Charge ("PIC"), Project Manager, Quality Assurance Manager, Laboratory Coordinator, and Sampling Technician. A project organization chart is presented in Figure 2-1. It should be noted that the same individual may serve multiple roles on the project. For example, the Laboratory Coordinator may also be the Sampling Technician.

At this time, a laboratory has not been selected to analyze the surface water samples. However, the selected laboratory will be fully accredited for all necessary analyses required as part of the Project.

Figure 2-1 Project Organization



2.1.1 Partner-in-Charge

The PIC for the Surface Water Sampling Program is an experienced technical professional who provides project oversight and assists in senior oversight and participates in major meetings and regulatory discussions & reporting.

2.1.2 Project Manager

The Project Manager for the Surface Water Sampling Program is an experienced manager and technical professional who provides QA review and assists in the coordination of the sampling program.

2.1.3 *Quality Assurance Manager*

The Quality Assurance Manager's responsibilities include the development, evaluation, and documentation of the QAPP and procedures appropriate to the sampling program. The Quality Assurance Manager is also responsible for all data processing activities, data processing QC and final analytical data quality review.

It is a major responsibility of the Quality Assurance Manager to ensure that all personnel have a good understanding of the project QA plan, an understanding of their respective roles relative to one another, and an appreciation of the importance of the roles to the overall success of the program.

2.1.4 *Laboratory Coordinator*

The primary responsibilities of the Laboratory Coordinator are to coordinate the communication between the project team and the contracted laboratory. The Laboratory Coordinator’s duties will include scheduling analytical services and informing the laboratory of sample shipment and expected receipt dates; managing chain-of-custody report forms; tracking, logging, and filing documentation returned from the laboratory.

2.1.5 *Field Operations Coordinator*

The Field Operations Coordinator will be responsible for all sampling activities and for all field QA. Further responsibilities include the verification for accuracy of field notebooks, chain-of-custody records, sample labels, and all other field related documentation.

2.1.6 *Sampling Technicians*

All sampling required by this investigation will be conducted by trained environmental scientists and technicians. Their responsibilities will include the documentation of the proper sample collection protocols, sample collection and field measurements, equipment decontamination, and chain-of-custody documentation.

2.1.7 *Laboratory Quality Assurance Officers*

The volume of analytical work for a project of this size may necessitate that the analytical laboratory designates a Quality Assurance Officer whose duties will be specific to the project. A Laboratory Quality Assurance Officer would have the responsibility for maintenance of all laboratory QA activities in association with the Project.

2.2 *PROJECT DESCRIPTION*

Enbridge Energy, Limited Partnership ("Enbridge" hereafter) submitted applications requesting permits from the WDNR and the U.S. Army Corps of Engineers ("USACE") to construct its Project in Ashland, Bayfield, Douglas and Iron Counties, Wisconsin. Enbridge's existing Line 5 pipeline, a 645-mile interstate pipeline, became operational in 1953. It originates in Superior, Wisconsin, traverses northern Wisconsin, the Upper and Lower Peninsulas of Michigan, and terminates near Sarnia, Ontario, Canada. The Wisconsin portion of the existing Line 5 pipeline crosses Douglas, Bayfield, Ashland, and Iron Counties. Within Ashland County, the existing Line 5 crosses through approximately twelve miles of the Bad River Reservation ("Reservation") of the Bad River Band of Lake Superior Chippewa Tribe ("Bad River Band").

Enbridge's Project will replace the existing Line 5 pipeline segment that traverses through the Reservation with a new, 30-inch outside diameter pipeline segment to be located entirely outside the Reservation. The new, 30-inch outside diameter pipeline segment will cross approximately 30.6 miles of Ashland County and 10.5 miles of Iron County. The Project would also utilize temporary construction workspace (pipe storage yard) in Douglas County, Wisconsin and would install a new mainline valve on the existing Line 5 pipeline as well as make minor modifications to the existing Ino Pump Station in Bayfield County, Wisconsin. The new pipeline will be constructed of high yield carbon steel pipe and be coated for corrosion resistance.

The Project will require installation of the pipeline segment across numerous waterbodies, including perennial, intermittent, and ephemeral waterbodies. Most of the Project impacts because of construction activities will be temporary and short-term in nature, including a short-term increase in suspended sediments during instream construction activities.

2.3 DATA QUALITY OBJECTIVES AND CRITERIA

2.3.1 Overall Project Objectives

DQOs are quantitative and qualitative statements specifying the quality of the environmental data required to support the decision-making process. DQOs define the total uncertainty in the data that is acceptable for each specific activity during the investigation. This uncertainty includes both sampling error and analytical error. Ideally, zero uncertainty is the intent; however, the variables inherently associated with the process (field and laboratory) contribute to uncertainty in the data. It is the overall Project objective to keep the total uncertainty within an acceptable range that will not hinder the intended use of the data. To achieve this objective, data quality requirements such as quantitation limits, criteria for accuracy and precision, sample representativeness, data comparability, and data completeness have been specified. The overall DQOs and requirements will be established such that there is a high degree of confidence in measurements performed during the Project.

Data collection requirements for sampling analytes in surface water are included in this QAPP. DQOs for this activity are:

- The parameters that will be used to specify data quality requirements and to evaluate the analytical system performance are Precision, Accuracy, Representativeness, Completeness, and Comparability ("PARCC"). Table 2-1 presents definitions for these parameters.

Surface water samples will be collected to evaluate the levels of several parameters upstream and downstream of pipeline construction areas prior to construction, during construction, and after construction work is completed. The specific parameters and associated methodologies can be found detailed in Appendix A.

Table 2-1 - Definitions of Data Quality Parameters

Precision	A measure of the reproducibility of measurements under a given set of conditions.
Accuracy	A measure of the bias that exists in a measurement system.
Representativeness	The degree to which sample data accurately and precisely represent selected characteristics.
Completeness	A measure of the amount of valid data obtained from the measurement system compared to the amount that is required.
Comparability	A measure of confidence with which one data set can be compared with another.

2.3.2 Criteria Objectives

The quantitative objectives ("criteria") that ERM will require for laboratory accuracy and precision are summarized in Table 2-2.

2.3.3 Laboratory Data Quality Objectives

The laboratory will demonstrate analytical precision and accuracy by the analysis of laboratory duplicates and matrix spike duplicates. Precision (as well as instrument stability) will also be demonstrated by comparison of response factors for calibration standards. Laboratory accuracy will be demonstrated by the addition of surrogate and matrix spike compounds. Accuracy will be presented as percent recovery ("R"). Precision will be presented as relative percent differences ("RPD"), relative standard deviation ("RSD"), or percent difference ("PD"), whichever is applicable to the type of QC samples involved. Laboratory method blanks will also demonstrate accuracy with respect to the analyses. The frequencies of laboratory duplicates and matrix spikes are specified in Appendix A.

The laboratory will be expected (as an ideal objective) to report the contract required quantitation/detection limits ("QL/CRDL") for all samples in the appropriate statistical reporting units for all analyses, as described in Section 6.0. However, it should be noted that actual quantitation limits are sample specific and depend on variables such as dilution factors, sample matrices, percent moisture, and the specific analyte. The data reported at or near the QL/CRDL will be handled cautiously since the stated DQOs for accuracy and precision may not "translate" well in some situations (i.e., accuracy and precision suffer for results near the QL/CRDL).

The analytical laboratory will be expected to process (purge, extract, or digest) an aliquot of sample such that the analytical results will provide a high degree of representation with respect to the sampling point. In addition, the analytical laboratory will be expected to document all analytical problems encountered during the investigation. Communication will be maintained with the laboratory so that analytical problems encountered with any sample will allow these samples to be re-collected, if necessary. Data Management Objectives

It is a data management objective that all aspects of the investigation from sample design, collection, shipment, analysis use/decisions, etc. be performed in conjunction with rigorous QA/QC documentation. The specific details of this QA/QC reporting can be found throughout this document.

It is expected that by the design of separate data quality requirements for field sampling and laboratory analysis, clear distinctions can be made such that any problems found in the system can be isolated with respect to the cause. Conversely, the data quality requirements are also designed to provide an indication of the variability inherent to the overall system.

- The overall data management objective is to provide a complete data set of baseline surface water concentrations and to assess potential water quality impacts post-construction for the parameters specified in Table 2-2.

Samples of select parameters will also be collected and analyzed during active construction.

3.0 SAMPLING PROCEDURES

Surface water grab samples will be collected from 204 waterbodies that intersect Enbridge's Line 5 construction areas and activities. The tabulated list of all 204 waterbodies can be found attached in Appendix D.

Grab samples will be collected during three surveys corresponding to pre-determined project phases: pre-construction, active construction, and post-construction. Pre-construction samples will be collected from each designated waterbody at an upstream and downstream location approximately one hundred feet from related construction work areas. The pre-construction grab samples will be used to determine the chemical baseline of each waterbody.

Post-construction samples will be collected following the same standard procedures as the pre-construction samples and will be collected approximately 1 year after the final construction has finished. The post-construction grab samples will be used to establish that the chemical baselines of the 204 designated waterbodies have been maintained.

During the active phase of construction, grab samples will be collected from upstream, midstream, and downstream locations of the designated waterbodies to monitor field parameters described in detail in Appendix A.

Immediately after collection, water samples will be transferred to new properly labeled sample containers (see Section 4.0 of this QAPP) with all necessary preservatives added (see Appendix A). Samples will be immediately transferred to coolers packed with ice or ice packs. Proper chain-of-custody documentation will be maintained as discussed in Section 4.0 of this QAPP.

4.0 SAMPLE CUSTODY

The primary objective of sample custody procedures is to create an accurate written record which can be used to trace the possession and handling of all samples from the moment of their collection, through analysis, until their final disposition. Custody for samples collected during this investigation will be maintained by the Field Operations Coordinator or the field personnel collecting the samples. The Field Operations Coordinator or the field personnel will be responsible for documenting each sample transfer and maintaining custody of all samples until they are shipped to the laboratory.

Analyte collection/sample bottles will be supplied by the selected analytical laboratory. All necessary chemical preservatives will be added to the bottles by the laboratory prior to the sampling event, where appropriate. Preservative type and source will be documented. The Field Operations Coordinator will maintain custody of the sample bottles. Sample bottles needed for a specific sampling task will then be relinquished by the Field Operations Coordinator to the sampling team after the Field Operations Coordinator has verified the integrity of the bottles and ensured that the proper bottles have been assigned to the task to be conducted.

A self-adhesive sample label will be affixed to each container before sample collection. At a minimum, the sample label will contain the following information.

- Client and Project Name
- Sample identification - place of sampling
- Date and time collected.
- Sampler's initials
- Testing required.
- Preservatives added.

After sample collection, each sample bottle will be sealed in an individual plastic bag. Samples will then be placed into an insulated cooler for shipment to the laboratory. Field Chain-of-Custody records completed at the time of sample collection will accompany the samples inside the cooler for shipment to the laboratory. The samples will be properly relinquished on the field Chain-of-Custody record by the sampling team. These record forms will be sealed in a Ziploc plastic bag to protect them against moisture.

Each cooler will contain sufficient ice and/or ice packs to ensure that proper temperature is maintained and will be packed in a manner to prevent damage to sample containers. The Field Operations Coordinator or the laboratory's authorized designee will then initial and seal each sample cooler with a Custody Seal. All coolers will be shipped by an overnight or laboratory courier according to current US DOT regulations or dropped off at the selected laboratory receiving facilities. Upon receiving the samples, the Field Operations Coordinator or the laboratory's authorized designee will inspect the condition of the samples, compare the information on the sample labels against the field Chain-of-Custody record, assign a control identification number, and log the control number into the computer sample inventory system.

The preparation of all sample bottles (preservative added, etc.) will be documented. When samples requiring preservation by either acid or base are received at the laboratory, the pH will be measured and documented. The Field Operations Coordinator or the laboratory's authorized designee will then then store the sample in a secure sample storage cooler maintained at 4°C and maintain custody until the sample is assigned to an analyst for analysis. Custody will be maintained until disposal of the analyzed samples.

The Field Operations Coordinator or the laboratory's authorized designee will note any damaged sample containers or discrepancies between the sample label and information on the field Chain-of-Custody record logging the sample and will note any discrepancies. This information will be communicated to the Field Operations Coordinator or field personnel so that proper action can be taken. The Chain-of-Custody form will be signed by both the relinquishing and receiving parties each time the sample changes hands, and the reason for transfer indicated.

5.0 CALIBRATION PROCEDURES AND FREQUENCY

Field equipment will be used during the collection of active construction phase grab samples to measure several specified field parameters (Appendix A). The calibration and frequency of the required field equipment can be found detailed in Appendix B.

6.0 ANALYTICAL PROCEDURES

All analytical parameters, methodologies and procedural information can be found referenced in Appendix A.

7.0 DATA REPORTING, VALIDATION, AND REDUCTION

Data validation practices will be followed to ensure that raw data are not altered and that an audit trail is developed for those data that required reduction. All the field data, such as those generated during field measurements, observations, and field instrument calibrations, will be entered directly into a bound field notebook. Each project team member will handle proofing all data transfers made, and the Field Operations Coordinator will proof at least ten percent of all data transfers.

It is expected that data reduction for this investigation will be minimal and will consist primarily of tabulating the analytical results onto summary tables using computerized spreadsheet software. All analytical data will be provided in the form of electronic data deliverables.

As proper, raw field data will be summarized, reduced, or tabulated. All laboratory analytical data will be summarized and tabulated upon receipt and qualified (see Section 10.0).

A rigorous data control program, which will ensure that all documents for the investigations are accounted for as they are completed, will be needed. Accountable documents include items such as logbooks, field data records, correspondence, chain-of-custody records, analytical reports, data packages, and photographs.

The documentation of sample collection will include the use of bound field logbooks in which all information on sample collection will be entered in indelible ink. Appropriate information will be entered to reconstruct the sampling event, including site/location name (top of each page), sample identification, brief description of sample, date and time of collection, sampling method, field measurements and observations, and sampler's initials (bottom of each page with date).

8.0 INTERNAL QUALITY CONTROL CHECKS

Internal QC checks for the analytical laboratory and the field are presented below.

8.1 LABORATORY INTERNAL QUALITY CONTROL CHECKS

The selected analytical laboratory will follow Internal Quality Control Checks that will be included in Appendix C. These will be a continuation of the Field Internal Quality Control Checks presented below.

8.2 FIELD INTERNAL QUALITY CONTROL CHECKS

Field Internal Quality Control Checks will be used during this investigation by the following:

- <u>Matrix Spike Sample</u> - Matrix spike samples will be prepared and conducted per the selected laboratory's analytical procedures.

9.0 PREVENTIVE MAINTENANCE

9.1 LABORATORY MAINTENANCE

The selected analytical laboratory will be required to provide a copy of its preventive maintenance programs and requirements.

9.2 FIELD MAINTENANCE

Field equipment will be supported using a tracking system incorporating the tagging of each equipment item. This tag will identify its most recent maintenance and condition. When damaged or equipment in need of repair is returned to the equipment supplier, it is appropriately flagged for the required maintenance to be performed. This process ensures that only operable and maintained equipment enters the field. Routine daily maintenance procedures conducted in the field will include the following:

- Removal of surface dirt and debris from exposed surfaces of the sampling equipment and measurement systems.
- Storage of equipment away from the elements.
- Routine inspections of sampling equipment and measurement systems for potential problems.
- Routine calibration using known standards.

Spare and replacement parts stored in the field to minimize downtime may include the following:

- Extra sample containers and preservatives
- Extra samples coolers, packing material, and sample location stakes.
- Additional supply of health and safety equipment (i.e., boots, gloves, etc.).
- Additional equipment as necessary for the field tasks.

10.0 SPECIFIC ROUTINE PROCEDURES USED TO ASSESS DATA PRECISION, ACCURACY, AND COMPLETENESS

10.1 OVERALL PROJECT ASSESSMENT

Overall data quality will be assessed by a thorough understanding of the data quality objectives, which are stated during the design phase of the investigation. Data accuracy, precision, and completeness will be closely monitored by maintaining thorough documentation of all decisions made during each phase of sampling, performing field and laboratory audits, thoroughly reviewing the analytical data as it is generated by the laboratory, and providing appropriate feedback as problems arise in the field or at the laboratory.

10.2 FIELD QUALITY ASSESSMENT

The evaluation (data review) of field QC samples will provide definitive indications of the data quality. If a problem arises that can be isolated, corrective actions can be instituted for future field efforts.

10.3 LABORATORY DATA QUALITY ASSESSMENT

Specific measures that will be taken by the selected analytical laboratory to assess data quality will be updated and included in Appendix A following selection of the laboratory.

10.4 LABORATORY DATA ASSESSMENT

A review will be performed to verify all necessary paperwork (chain-of-custodies, analytical reports, laboratory personnel signatures).

The selected laboratory will perform a detailed QA review to verify the qualitative and quantitative reliability of the data as it is presented.

10.5 DATA MANAGEMENT QUALITY ASSESSMENT

As the analytical data generated from this investigation are evaluated, qualified, and submitted to the Project Manager, the quality of the data will be assessed from an overall management perspective.

11.0 CORRECTIVE ACTION

11.1 THE ANALYTICAL LABORATORY'S CORRECTIVE ACTION

The selected analytical laboratory will provide a Correction Action Plan. This plan will be incorporated into Appendix C. The laboratory will provide documentation as to what, if any, corrective actions were initiated concerning this study and report them to the Quality Assurance Manager.

11.2 PROJECT CORRECTIVE ACTION

Field QA activities will be reported topically to the Project Manager. Problems affecting QA that are encountered during the study will be reported to the Project Manager. The Project Manager will be responsible for initiating the corrective actions and for ensuring that the actions are taken in a timely manner and that the desired results are produced.

12.0 DATA REPORTING

The data generated from this sampling program will be submitted to the applicable agencies.

Appendix A
WNDR Data Request Sample Procedures Table

Chemical	WDNR: Test Methods	Enbridge Test Methods	Parameter function	Parameter assistance in water quality evaluation
Total Phosphorus	**Digestion:** 4500-P B (5)-1999 (Standard Method), 973.55 (USGS/AOAC/Other) **Colorimetric, Manual ascorbic acid:** 365.3 (EPA), 4500-P E (Standard Method), D515-88 (ASTM) **Colorimetric, Automated ascorbic acid reduction:** 365.1 (EPA), 4500-P, F, G, H (Standard Method), 973.56 (USGS/AOAC/Other) **Colorimetric, Semi−automated block digestor (TKP digestion):** 365.4 (EPA), D515-88 (ASTM), I-4610-91 (USGS/AOAC/Other)	Standard Method 4500-P F (Pace Analytical)	Phosphorus is an essential nutrient for the plants and animals that make up the aquatic food web. Phosphorus in aquatic systems occurs as organic phosphate and inorganic phosphate. Inorganic phosphorus is the form required by plants. Animals can use either organic or inorganic phosphate (5.6 Phosphorus | Monitoring & Assessment | US EPA).	Although phosphorus is an essential element for plant life, when there is too much of it in water, it can speed up eutrophication of rivers and lakes (Phosphorus and Water | U.S. Geological Survey (usgs.gov)). Even a modest increase in phosphorus can, under the right conditions, set off a whole chain of undesirable events in a stream including accelerated plant growth, algae blooms, low dissolved oxygen, and the death of certain fish, invertebrates, and other aquatic animals (5.6 Phosphorus | Monitoring & Assessment | US EPA).
Nitrogen – Total Kjeldahl	**Manual digestion 20 and distillation or gas diffusion:** 4500−Norg-B or C and 4500-NH3B (Standard Method), D3590-02(06) (ASTM), I-4515-91 (USGS/AOAC/Other) **Titration:** 4500-NH3C (Standard Method), 973.48 (USGS/AOAC/Other) **Electrode:** 4500-NH3C (Standard Method), 973.48 (USGS/AOAC/Other) **Semi-automated phenate**: 350.1, Revision 2.0 (EPA), 4500-NH3 G, 4500-NH3 H (Standard Method)	EPA 351.2, Revision 2.0 (Pace Analytical)	Kjeldahl method turns organic substances in the water into ammonium sulfate.	Nitrogen – Total Kieddahl is an important measure in environmental monitoring because excess nitrogen in water bodies can lead to harmful algal blooms and other negative impacts on aquatic ecosystems. When measured, the higher the total kjeldahl nitrogen value, the more algae blooms, the less water is clear, and the less oxygen there will be (Total Kjeldahl Nitrogen - Water Rangers).

Chemical	WDNR: Test Methods	Enbridge Test Methods	Parameter function	Parameter assistance in water quality evaluation
	Manual phenate, salicylate, or other substituted phenols in Berthelot reaction based methods: 4500-NH3F (Standard Method)			
Nitrate + Nitrite	**Cadmium reduction, Manual**: 4500-NO3-E (Standard Method), D3867-04 (ASTM) **Cadmium reduction, Automated:** 353.2, Rev. 2.0 (EPA), 4500−NO3 −F (Standard Method), D3867−04 (ASTM), I−2545−90 (USGS/AOAC/Other) **Automated hydrazine:** 4500−NO3 −H (Standard Method) **Ion Chromatography:** 300.0, Rev 2.1 and 300.1−1, Rev 1.0 (EPA), 4110 B−2000 or C−2000 (Standard Method), D4327−03 (ASTM), 993.30 (USGS/AOAC/Other **Capillary ion electrophoresis (CIE/ UV):** 4140-B (Standard Method), D6508−00(05) (ASTM), D6508, Rev. 2 (USGS/AOAC/Other)	EPA 353.2 (Pace Analytical)	Nitrates are essential plant nutrients.	Although Nitrates are necessary for plants, in excess amounts they can cause significant water quality problems. Excess nitrates can cause hypoxia and can become toxic to warm-blooded animals at higher concentrations under certain conditions (EPA).
Ammonia	**Manual distillation or gas diffusion (pH > 11):** 350.1, Rev. 2.0 (EPA), 4500−NH3B (Standard Method), 973.49 (USGS/AOAC/Other) **Titration:** 4500−NH3C (Standard Method)	EPA 350.1 (Pace Analytical)	Ammonia causes direct toxic effects on aquatic life	When ammonia is present in water at high enough levels, it is difficult for aquatic organisms to sufficiently excrete the toxicant, leading to toxic buildup in internal tissues and blood, and potentially death. Environmental factors, such as pH and temperature,

Chemical	WDNR: Test Methods	Enbridge Test Methods	Parameter function	Parameter assistance in water quality evaluation
	Electrode: 4500−NH3D or E (Standard Method), D1426-08 (ASTM) **Manual phenate, salicylate, or other substituted phenols in Berthelot reaction based methods**: 4500−NH3F (Standard Method) **Automated phenate, salicylate, or other substituted phenols in Berthelot reaction based methods:** 350.1, Rev. 2.0 (EPA), 4500−NH3G and 4500−NH3H (Standard Method) **Ion Chromatography:** D6919-09 (ASTM)			can affect ammonia toxicity to aquatic animals (EPA).
Dissolved Oxygen	Not specified in WI NR 219	Standard Methods 4500-AG, EPA 360.1 (Hanna Multiparameter Meter model HI98194)	Dissolved oxygen in surface water is used by all forms of aquatic life, some reliant on it (USGS).	As dissolved oxygen is used by all forms of aquatic life, it constituent typically is measured to assess the "health" of lakes and streams. Excess organic material in lakes and rivers can cause eutrophic conditions, which is an oxygen-deficient situation that can cause a water body to "die" (USGS).
Sulfate		EPA 300.0 and SW-846 Method 9056A (Pace Analytical)		Although sulfate occurs naturally in aquatic environments, when levels are elevated, it can be toxic to aquatic life in freshwater environments (Karjalainen et al., 2021).

Chemical	WDNR: Test Methods	Enbridge Test Methods	Parameter function	Parameter assistance in water quality evaluation
Total Mercury	**Cold vapor, Manual:** 245.1, Rev. 3.0 (EPA), 3112 B (Standard Method), D3223−02 (ASTM), 977.22 and I−3462−85 (USGS/AOAC/Other) **Cold vapor, Automated:** 245.2 (EPA) **Cold vapor atomic fluorescence spectrometry (CVAFS):** 245.7 Rev. 2.0 (EPA), I−4464−01 (USGS/AOAC/Other) **Purge and Trap CVAFS:** 1631E (EPA)	EPA 245.1 (Pace Analytical)	Mercury is one of the most serious contaminants because it is a potent neurological poison in fish, wildlife, and humans (USGS).	Mercury is a concern because it is absorbed easily into the food chain. The harmful methylmercury form of mercury readily crosses biological membranes and can accumulate to harmful concentrations in the exposed organism and become increasingly concentrated up the food chain (USGS).
Conductivity	Not required to be tested by certified laboratory	EPA 120.1 (Hanna Multiparameter Meter model HI98194)	Conductivity is useful as a general measure of water quality (EPA).	Significant changes (usually increases) in conductivity may indicate that a discharge or some other source of disturbance has decreased the relative condition or health of the water body and its associated biota (EPA).
pH	Not required to be tested by certified laboratory	EPA 150.2 (Hanna Multiparameter Meter model HI98194)	pH affects most chemical and biological processes in water. It is one of the most important environmental factors limiting species distributions in aquatic habitats. Different species flourish within different ranges of pH, with the optima for most aquatic organisms falling between pH 6.5-8 (EPA).	Since pH can be affected by chemicals in the water, pH is an important indicator of water that is changing chemically (USGS). U.S. EPA water quality criteria for pH in freshwater suggest a range of 6.5 to 9. Fluctuating pH or sustained pH outside this range physiologically stresses many species and can result in decreased reproduction, decreased growth, disease, or death. This can ultimately lead to reduced biological diversity in streams (EPA).

Chemical	WDNR: Test Methods	Enbridge Test Methods	Parameter function	Parameter assistance in water quality evaluation
Total Suspended Solids	Not specified in WI NR 219	EPA 160.4 Standard Methods 2540-B, 2540-C, and 2540-D (Pace Analytical)	TSS measures the amount of particulate matter floating in water (which could be organic matter, inorganic substances, and algae).	If TSS values are high, sunlight will not travel well through the water, which in turn makes it difficult for plants and algae to grow. This then reduces productivity and oxygen generation.
Chemical Oxygen Demand (COD)	**Titrimetric:** 410.3 (EPA), 5220 B or C (Standard Method), D1252−06 (ASTM), I−3560−85 and 973.46 (USGS/AOAC/Other) **Spectrophotometric, manual or automatic:** 410.4, Rev. 2.0 (EPA), 5220 D (Standard Method), D1252−06 (ASTM), I−3561−85 (USGS/AOAC/Other)	EPA 410.4 Standard Method 5220D (Pace Analytical)	COD may act as an index for determining overall water quality.	COD measures the amount of oxygen necessary to break down the organic substances that are pollutants in water. With a higher COD value in a sample, it indicates that it contains higher levels of oxidizable material. With higher COD, the water will have reduced dissolved oxygen levels.
Biological Oxygen Demand (BOD)	5210 B−2001 (Standard Method), 973.44, p. 17, 9 I−1578−78 8 Notes 10,63 (Hach Method 10360)	Hach 10360, Revision 1.2 (Pace Analytical)	BOD is a measure of the amount of oxygen required to remove waste organic matter from water in the process of decomposition by aerobic bacteria (EPA).	Determining how organic matter affects the concentration of dissolved oxygen in a stream or lake is integral to water-quality management. The waste organic matter is stabilized or made unobjectionable through its decomposition by living bacterial organisms which need oxygen to do their work (USGS).

Chemical	WDNR: Test Methods	Enbridge Test Methods	Parameter function	Parameter assistance in water quality evaluation
Polycyclic Aromatic Hydrocarbons (PAHs)	Not specified in WI NR 219	EPA SW-846 Methods 8270D SIM and 8270E SIM using Gas Chromatography-Mass Spectrometry (Pace Analytical)	PAHs are organic chemical compounds that naturally occur in the environment (Olayinka et al., 2018).	The presence of PAHs in surface or ground water indicates pollution. The types of PAHs present in water provide information on the derivative sources of organic contaminants (Olayinka et al., 2018).
Perfluoroalkyl and polyfluoroalkyl substances (PFAS)	Not specified in WI NR 219	EPA 537.1 (Pace Analytical)		PFASs are distributed ubiquitously in the aquatic environment. The PFASs are permanently introduced into aquatic ecosystems, which can result in a continuous exposure of those compounds for organisms downstream of the discharges. These insights indicate a long-term (chronic exposure of species in aquatic ecosystems suffering from wastewater discharge and other point and nonpoint sources of PFASs (Ahrens and Bundschuh, 2014).
Total Petroleum Hydrocarbons (TPH)	Not specified in WI NR 219. However, there are many conventional analytical methods available. The most used include infrared spectroscopy (EPA Method 418.1), gravimetry (EPA Method 1664A), gas chromatography with flame ionization detection (EPA Method 8015), gas chromatography with mass spectrometric detection (EPA Methods 8270 and 625), ultraviolet spectrophotometry, immunoassay (EPA Methods 4030 and 4035), Raman spectroscopy, and			When petroleum hydrocarbons (PHs) enter into aquatic ecosystems, they can cause great harm to organisms; they pose acute to chronic toxicity to organisms depending on their metabolism and photooxidation (Ihunwo et al., 2021). Non-bioavailable and/or hydrophobic PHs become bioavailable to several benthic organisms as they get adsorbed onto particulates and sediments. Certain aquatic

Chemical	WDNR: Test Methods	Enbridge Test Methods	Parameter function	Parameter assistance in water quality evaluation
	fluorescence spectroscopy (Adeniji, Okoh, and Okoh, 2017).			invertebrates that ingest suspended oil droplets/oil-bound particulates are highly sensitive to PHs (Kuppusamy et al., 2019).

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Appendix B
Calibration Standard
Operating Procedures

THE CALIBRATION STANDARD OPERATING PROCEDURE (SOP) WILL BE ADDED TO THIS REPORT ONCE THE SUPPLIER AND BRANDS OF THE NECESSARY FIELD EQUIPMENT ARE DETERMINED

Appendix C
Analytical Laboratory Quality Assurance Plan

THE ANALYTICAL LABORATORY QUALITY ASSURANCE PLAN WILL BE ADDED TO THIS REPORT ONCE THE ACCREDITED ANALYTICAL LABORATORY IS SELECTED

Appendix D
Wetland and Waterbody Crossing Table

Provided electronically as an Excel Table