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STANDARD OPERATING PROCEDURE
Procedure for Collecting Water Chemistry Samples and Data at the GSI Land-Based RDTE Facility

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BACKGROUND

The Great Ships Initiative (GSI) is a regional effort devoted to ending the problem of ship-mediated invasive species in the Great Lakes-St. Lawrence Seaway System and globally. In support of that goal, the GSI has established superlative freshwater ballast treatment evaluation capabilities at three scales—bench, land-based, and on board ship. Each scale is dedicated to addressing specific evaluation objectives. These include:

GSI Bench-Scale Tests

- Range finding for effective treatment dose against diverse freshwater taxa and water quality conditions;
- Generation of freshwater relevant chemical degradation curves; and
- Estimation of residual toxicity given diverse freshwater taxa and water quality conditions.

GSI Land-Based Tests

- Pre-certification testing, i.e., operational and biological performance (including residual toxicity) status-testing given scale-up and a range of challenge conditions; and
- Certification/verification testing, i.e., formal assessment of performance against international and other discharge standards.

GSI Shipboard Tests

- Confirmation of biological and operational treatment performance as expected in the ship environment;
- U.S. Coast Guard Shipboard Technology Evaluation Program (STEP) testing;
- Shipboard type approval testing;
- Ship discharge monitoring; and
- Methods development.

GSI awards its independent status-testing services to candidate systems only if technical and programmatic criteria are met. Decisions are based on third party technical assessments as well as GSI Advisory Committee programmatic input. Testing services are currently offered at no cost to the developer with the exception of transportation and system installation/removal costs. Instead, tests are supported by general project funds which derive from federal and state agency grants, Great Lakes port contributions, and in-kind contributions by local governments and universities.

GSI has no involvement, intellectual or financial, in the mechanics, design or market success of the actual treatment systems it tests. To ensure GSI remains completely independent and is uncompromised by any real or perceived individual or project bias, GSI subjects itself to rigorous quality management policies and procedures. In addition, GSI test activities are subject to rigorous QAQC procedures and documentation. This attention to quality management and QAQC assures the high quality and credible evaluation of both GSI and its findings.

INTRODUCTION

This GSI Standard Operating Procedure (SOP) describes collection of water chemistry samples and data at the GSI Land-Based Research, Development, Testing, and Evaluation (RDTE) Facility located on the Duluth-Superior Harbor of Lake Superior (Superior, WI). Water chemistry samples are collected in-line as discrete grab samples, most frequently during intake operations, but may also be collected during discharge depending on the Test/Quality Assurance Plan (TQAP) or other test plan. Samples that are not time-sensitive are transported to the Lake Superior Research Institute (LSRI; University of Wisconsin-Superior) chemistry laboratory for analysis. Time-sensitive samples (e.g., total residual chlorine and total residual oxidants) are analyzed immediately at the GSI Land-Based RDTE Facility. Water chemistry parameters analyzed include, but are not limited to: active substance concentration, total suspended solids, non-purgeable organic carbon, dissolved organic carbon, and percent transmittance at 254 nm.

Water chemistry parameters are also quantified continuously during intake (and treatment tank discharge if the system treats on discharge) operations using four in-line sensors that measure the following parameters: chlorophyll *a*, turbidity, dissolved oxygen, and pH/temperature. In addition, parameters are measured from the sample collection tubs during biological sample collection using YSI 6600 V2-4 Multiparameter Water Quality Sondes (YSI Incorporated, Yellow Springs, OH). YSI Sondes are also used to continuously measure water chemistry from the control and treatment retention tanks. Following collection of all samples during and immediately after intake, the YSI Sondes are deployed into the control and retention tanks and used to continuously measure water chemistry during the retention period (see *GSI/SOP/LB/G/C/4 – Procedure for Calibration, Deployment, and Storage of YSI Multiparameter Water Quality Sondes*). The YSI Sondes have several probes that are able to measure the following parameters: dissolved oxygen, specific conductance, salinity (via specific conductance measurement), temperature, pH, turbidity, and total chlorophyll.

DEFINITIONS

Continuous: Measurement is continuous throughout the period of operation at a defined rate (NSF International, 2010). This term is also used to describe the collection of sample water in the tubs, which is continuous during the entire intake or discharge operation.

Discrete Grab: An acquired sample for analysis at a specific place and time (NSF International, 2010). For example, a total suspended solids sample is considered a discrete grab sample.

In-Line: A sample collected from an in-line sample point pitot or in-line tap.

In-Tank: A sample collected from the control or treatment retention tanks, or from the Wastewater Storage Tank.

EQUIPMENT

- 3 Gallon Bucket with Attached 20’ Rope
- Chlorophyll *a* In-Line Sensor

- Cooler
- Dissolved Oxygen In-Line Sensor
- EcoWatch Software for Windows (one copy for each computer that the Sondes may be linked with)
- Four Permanently Installed Field Cables (one to each of four retention tanks), connecting the Sondes to a Computer
- Four Permanently Installed Ropes (one tied to each retention tank ladder)
- Kemmerer Water Sampler
- One Field Cable (to connect Sondes to YSI 650 MDS Logger)
- pH/Temperature In-Line Sensor
- Sample Bottle Crate
- Step ladder
- Turbidity In-Line Sensor
- YSI 650 MDS Display/Logger
- YSI 6600 V2-4 Multiparameter Water Quality Sondes
- YSI Sonde Deployment Cages
- YSI Sonde Long Calibration Cups

SUPPLIES

- 1 L High-Density Polyethylene (HDPE) Sample Bottles
- 125 mL Glass Sample Bottles
- Ice Packs
- Deionized water rinse bottle
- *GSI/FORM/LB/C/3 - In-Line, Discrete Grab Sample Collection Form* (Appendix 1)
- *GSI/FORM/LB/C/4 - Sample Collection Tub Water Chemistry Data Collection Form* (Appendix 2)

PROCEDURE

In-Line, Discrete Grab Water Chemistry Sample Collection

1. Ensure that all sample bottles have been cleaned according to the appropriate SOP:
    a. *GSI/SOP/LB/G/O/4 – Procedure for Cleaning Sampling Equipment at the GSI Land-Based RDTE Facility* for HDPE sample bottle cleaning.
    b. *GSI/SOP/BS/RA/C/3 – Procedures for Measuring Organic Carbon in Aqueous Samples* for additional cleaning of 125-mL glass sample bottles for organic carbon analyses.

2. Ensure that sample bottles are properly labeled according to *GSI/SOP/G/RA/SC/3 – Procedure for Labeling Samples Collected at the GSI Land-Based RDTE Facility*, and have been transported to the GSI Land-Based RDTE Facility.

3. Prepare the appropriate datasheet (*GSI/FORM/LB/C/3 - In-Line, Discrete Grab Sample Collection Form;* Appendix 1).

4. Collect the number and type of water chemistry samples required by the TQAP or other test plan using the following procedure:

    a. Open the appropriate valve (to achieve a moderate flow of water) located at the sample point pitot or tap, and let the sample water flow for at least 30 seconds.
    b. Partially fill the labeled sample bottle with water, cap loosely, invert bottle several times to rinse, and discard rinse water.
    c. Fill the rinsed sample bottle with sample water and allow to overflow briefly.
    d. Cap the sample bottle and immediately place the sample in a cooler with ice packs.
    e. Complete *GSI/FORM/LB/C/3 – In-Line, Discrete Grab Sample Collection Form* (Appendix 1) as soon as possible after each sample is collected.

5. Repeat Step 4 for all water chemistry samples to be collected, at the appropriate time (i.e., usually collected at the beginning, middle, and end of intake) and location specified in the TQAP or test plan. Place each sample in a cooler with ice packs immediately following collection. Following sample collection activities transport the sample cooler to the LSRI chemistry laboratory for analysis.

In-Line, Continuous Measurement of Water Chemistry Parameters

1. Ensure that the in-line sensors have been calibrated according to the following GSI SOPs prior to each ballast water treatment system evaluation trial:
    a. *GSI/SOP/LB/G/C/7 – Calibration of the In-Line pH/Temperature Sensor at the GSI Land-Based RDTE Facility*
    b. *GSI/SOP/LB/G/C/8 – Calibration of the In-Line Chlorophyll a Sensor at the GSI Land-Based RDTE Facility*
    c. *GSI/SOP/LB/G/C/9 – Calibration of the In-Line Turbidity Sensor at the GSI Land-Based RDTE Facility*
    d. *GSI/SOP/LB/G/C/10 – Calibration of the In-Line Dissolved Oxygen Sensor at the Land-Based RDTE Facility*

2. Ensure that the Human-Machine Interface (HMI) is properly set up to measure and log temperature/pH (measured using one sensor), turbidity, dissolved oxygen, and chlorophyll *a* continuously in the pre-treatment, intake line (and treatment discharge line if the treatment system treats on discharge).

3. Water chemistry data are logged, stored, and retrieved using the following process:

    a. Water chemistry measurements collected by the HMI are transferred to a separate "Data Logging" computer connected to the HMI.
    b. This second computer uses FactoryTalk© Historian software (Rockwell Automation, Inc.; Milwaukee, WI) to log and store the water chemistry data into a database. The water chemistry data cannot be edited once in the database.

c. The water chemistry data are retrieved using the PI System (OSIsoft, LLC; San Leandro, CA), which is an extension of FactoryTalk© that runs inside of Microsoft Excel©.
d. The water chemistry data are transferred into MS Excel© as a time-stamped collection of data.

Discrete Measurement of Water Chemistry Parameters from Sample Collection Tubs

1. Ensure that the YSI Sonde to be used is calibrated according to *GSI/SOP/LB/G/C/4 - Procedure for Calibration, Deployment, and Storage of YSI Multiparameter Water Quality Sondes.*

2. Prepare the *GSI/FORM/LB/C/4 - Sample Collection Tub Water Chemistry Data Collection Form* (Appendix 2).

3. Connect the YSI Sonde to the YSI 650 MDS Display/Logger using the field cable; turn on the logger.

4. Immediately following the intake, treatment discharge, and control discharge operations, carry the YSI Sonde to the upper sample collection platform. Rinse the YSI Sonde with deionized water prior to placing in the tub.

5. Lower the YSI Sonde one to two feet (0.3 to 0.6 m) into the sample collection tub to be measured.

6. Ensure that the YSI Sonde is not cleaning the optical probes, and that the measurements have stabilized.

7. Record the data for each parameter measured on the *GSI/FORM/LB/C/4 - Sample Collection Tub Water Chemistry Data Collection Form* (Appendix 2).

8. Repeat Steps 5 to 7 above for each sample collection tub to be measured. Rinse the YSI Sonde in between each measurement using deionized water.

Continuous Measurement of Water Chemistry Parameters from Retention Tanks

1. Ensure that each of the two YSI Sondes to be used is calibrated according to *GSI/SOP/LB/G/C/4 - Procedure for Calibration, Deployment, and Storage of YSI Multiparameter Water Quality Sondes.*

2. Follow the procedure for unattended data logging and YSI Sonde deployment and retrieval as outlined in *GSI/SOP/LB/G/C/4 - Procedure for Calibration, Deployment, and Storage of YSI Multiparameter Water Quality Sondes*.

3. Download the YSI Sonde data files from the YSI Sondes to a computer and upload the water chemistry data to the GSI SharePoint Website following the procedure outlined in

GSI/SOP/LB/G/C/4 - Procedure for Calibration, Deployment, and Storage of YSI Multiparameter Water Quality Sondes.

Discrete Grab Water Chemistry Sample Collection from Retention Tanks

1. Wear appropriate safety equipment to handle treated sample water. Consult the MSDS for the specific active substance(s)/treatment system and follow recommended sample water handling procedures.

2. Follow other appropriate health and safety regulations as required, including requirements for climbing, standing and disembarking from retention tanks. See *GSI/LB/QAQC/EHSP/1 - Great Ships Initiative Environmental, Health and Safety Plan* and *GSI/SOP/LB/G/S/1 - Procedure for Ensuring Worker Health and Safety at the GSI Land-Based RDTE Facility*.

3. Ensure that the Kemmerer water sampler has been cleaned before use according to *GSI/SOP/LB/G/O/4 – Procedure for Cleaning Sampling Equipment at the GSI Land-Based RDTE Facility*. If samples are to be collected from multiple tanks, ensure that the Kemmerer water sampler is cleaned between each tank.

4. Ensure that the appropriate number of sample bottles (usually 1-3 bottles per tank) have been cleaned and are clearly and uniquely labeled prior to sample collection. See *GSI/SOP/LB/G/O/4 – Procedure for Cleaning Sampling Equipment at the GSI Land-Based RDTE Facility* and *GSI/SOP/G/RA/SC/3 - Procedure for Labeling Samples Collected at the GSI Land-Based RDTE Facility*. Ensure that sample bottles are made of the appropriate material, i.e., high-density polyethylene (HDPE) for the type of analysis to be conducted. Note: The number of samples collected from each retention tank will be dependent on the TQAP or specific test plan.

5. Place the Kemmerer water sampler and labeled sample bottle(s) into the 3 Gal. bucket. Attach the rope to the bucket.

6. Climb up to the top of the specific retention tank that is to be sampled taking appropriate health and safety precautions. Raise the bucket to the tank roof using the 20’ rope.

7. Open the center vent on the retention tank’s roof or on the wastewater tank use the roof manway.

8. Lower the Kemmerer to the appropriate depth below the water surface (e.g., one sample collected mid-depth; three samples collected from the top, middle, and bottom of the water column; etc.) and collect water by sending the messenger down to the Kemmerer.

9. Retrieve the Kemmerer. Transfer less than 100 mL of sample water from the Kemmerer to the sample bottle. Tighten the lid on the sample bottle, shake the contents of the bottle and then empty contents back into the retention tank. Fill the sample bottle with the remaining water contained in the Kemmerer (approximately 1 L). Repeat steps 8-9 for

each additional replicate sample.

10. Return the sample bottle(s) and Kemmerer to the bucket then lower the bucket to the ground using the attached rope.

QUALITY ASSURANCE/QUALITY CONTROL (QA/QC)

1. Conduct all quality assurance/quality control procedures according to the *GSI/QAQC/QAPP/LB/1 – Quality Assurance Project Plan for Great Ships Initiative (GSI) Land-Based Tests, Revision 2 (2011).*

2. Follow all procedures outlined in this SOP. Any SOP amendments must be approved by the GSI Principal Investigator and communicated to the GSI Senior QAQC Officer. Any deviations made during the experiment must be recorded on *GSI/FORM/QAQC/1 - GSI QAPP, TQAP (Test Plan) and SOP Deviation Form*, approved by the GSI Principal Investigator, and communicated to the GSI Senior QAQC Officer as soon as practicable.

DATA STORAGE AND ARCHIVING

1. Store and archive data according to *GSI/QAQC/QAPP/LB/1 – Quality Assurance Project Plan for Great Ships Initiative (GSI) Land-Based Tests, Revision 2 (2011).*

2. Archive all hard- and electronic-copies of data and records generated for a period of at least seven years. Ensure electronic records are retrievable for the entire length of archival.

REFERENCES AND RELATED DOCUMENTS

GSI/LB/QAQC/EHSP/1 - Great Ships Initiative Environmental, Health and Safety Plan

GSI/QAQC/QAPP/LB/1 – Quality Assurance Project Plan for Great Ships Initiative (GSI) Land-Based Tests, Revision 2 (2011)

GSI/SOP/BS/RA/C/3 – Procedures for Measuring Organic Carbon in Aqueous Samples.

GSI/SOP/G/RA/SC/3 – Procedure for Labeling Samples Collected at the GSI Land-Based RDTE Facility

GSI/SOP/LB/G/C/4 – Procedure for Calibration, Deployment, and Storage of YSI Multiparameter Water Quality Sondes.

GSI/SOP/LB/G/C/7 – Calibration of the In-Line pH/Temperature Sensor at the GSI Land-Based RDTE Facility.

GSI/SOP/LB/G/C/8 – Calibration of the In-Line Chlorophyll a Sensor at the GSI Land-Based RDTE Facility.

GSI/SOP/LB/G/C/9 – Calibration of the In-Line Turbidity Sensor at the GSI Land-Based RDTE Facility.

GSI/SOP/LB/G/C/10 – Calibration of the In-Line Dissolved Oxygen Sensor at the Land-Based RDTE Facility.

GSI/SOP/LB/G/O/4 – Procedure for Cleaning Sampling Equipment at the GSI Land-Based RDTE Facility.

GSI/SOP/LB/G/S/1 - Procedure for Ensuring Worker Health and Safety at the GSI Land-Based RDTE Facility.

GSI/SOP/LB/RA/SC/3 - Procedure for Algae/Small Protozoa Sample Collection.

GSI/SOP/LB/RA/SC/4 - Procedure for Microbial Sample Collection.

NSF International (2010). Generic Protocol for the Verification of Ballast Water Treatment Technology. Prepared for the U.S. Environmental Protection Agency, Environmental Technology Verification Program in cooperation with the U.S. Coast Guard, Environmental Standards Division, Washington, DC, and the U.S. Naval Research Laboratory, Center for Corrosion Science and Engineering, Washington, DC. Version 5.1., September 2010.

APPENDIX 1

GSI/FORM/LB/C/3: In-Line, Discrete Grab Sample Collection Form

In-Line, Discrete Grab Water Chemistry Sample Collection Form (GSI/FORM/LB/C/3; Page 1 of 2)

Ballast Water Treatment System: _____

Test ID: _____

Date: _____

Challenge (Pre-Treatment Intake) Water – Collected from SP#_____			
Collection Team:			
Sample Type	**Sample Time**		
	Beginning (Rep. 1)	Middle (Rep. 2)	End (Rep. 3)
TSS and Percent Transmittance (1L Total)			
POM and DOM (125 mL Total)			
Other Sample Type: Volume:			

Control Intake Water – Collected from SP#_____			
Collection Team:			
Sample Type	**Sample Time**		
	Beginning (Rep. 1)	Middle (Rep. 2)	End (Rep. 3)
TSS and Percent Transmittance (1L Total)			
POM and DOM (125 mL Total)			
Other Sample Type: Volume:			

Post Treatment Water – Collected from SP#_____			
Collection Team:			
Sample Type	**Sample Time**		
	Beginning (Rep. 1)	Middle (Rep. 2)	End (Rep. 3)
TSS and Percent Transmittance (1L Total)			
POM and DOM (125 mL Total)			
Other Sample Type: Volume:			

In-Line, Discrete Grab Water Chemistry Sample Collection Form (GSI/FORM/LB/C/3; Page 2 of 2)

Treatment Discharge Water – Collected from SP#_____			
Collection Team:			
Sample Type	**Sample Time**		
	Beginning (Rep. 1)	Middle (Rep. 2)	End (Rep. 3)
TSS and Percent Transmittance (1L Total)			
POM and DOM (125 mL Total)			
Other Sample Type: Volume:			

Control Discharge Water – Collected from SP#_____			
Collection Team:			
Sample Type	**Sample Time**		
	Beginning (Rep. 1)	Middle (Rep. 2)	End (Rep. 3)
TSS and Percent Transmittance (1L Total)			
POM and DOM (125 mL Total)			
Other Sample Type: Volume:			

APPENDIX 2

GSI/FORM/LB/C/4 - Sample Collection Tub Water Chemistry Data Collection Form

Sample Collection Tub Water Chemistry Data Collection Form
GSI/FORM/LB/C/4

Date:		**Test ID #**					
Collector(s):							
Sonde Number(s):							
Retention Tanks Filled:		**C1 T1**			**C2 T2**		
Tub #:	**1**	**2**	**3**		**4**	**5**	**6**
Temperature (°C):							
Conductivity (mS/cm):							
Salinity (ppt):							
pH:							
Turbidity (NTU):							
Dissolved Oxygen (mg/L):							
Dissolved Oxygen (% Saturation):							
Total Chlorophyll (μg/L):							
Time Water Chemistry Finished:							

Notes/Observations: