
**WORK PLAN TO PERFORM A NITRATE
APPLICATION FIELD TRIAL IN THE HYPOLIMNION
OF ONONDAGA LAKE**

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WT DYE**

LIST OF ACRONYMS

GPS	Global Positioning System
ISUS	<i>in situ</i> ultraviolet spectrophotometry
Metro	Metropolitan Wastewater Treatment Plant (discharge of treated municipal and other pre-treated wastewater into the south (upstream) end of Onondaga Lake)
MSDS	Material Safety Data Sheet
NYSDEC	New York State Department of Environmental Conservation
OCDWEP	Onondaga County Department of Water Environment Protection
ROD	Record of Decision
SMU	Sediment Management Unit
SOP	Standard Operating Procedure
SU	Syracuse University
UFI	Upstate Freshwater Institute (based in Syracuse, NY)
USEPA	United States Environmental Protection Agency
YSI	Yellow Springs Instruments

GLOSSARY OF TERMS

Epilimnion – During summer stratification, the upper portion of the water column located between the 0 and 30-ft (0 and 9-meter) water depth in Onondaga Lake. The epilimnion is warm and well-mixed by wind and waves.

Hypolimnion - The lower portion of the profundal zone water column during summer stratification where water temperatures are cooler than upper waters (typically below the 30-ft water depth in Onondaga Lake). The hypolimnion is not well-mixed by winds or inflows to the lake.

Methylmercury - An organic form of mercury, which can be created from metallic or elemental mercury by bacteria in sediments and water.

Profundal Zone – The portion of a water body where water depths are greater than the depth to which sunlight penetration can support aquatic plants, in contrast with the littoral zone closer to shore.

Thermocline - During summer stratification, a layer of water at approximately mid depth shows temperature changes with depth from the epilimnion temperature at the top to the hypolimnion temperature at the bottom. This mid-depth layer where water temperatures changes significantly with depth is referred to as the thermocline.

**WORK PLAN TO PERFORM
A NITRATE APPLICATION FIELD TRIAL IN THE
HYPOLIMNION OF ONONDAGA LAKE****EXECUTIVE SUMMARY**

A nitrate application field trial will be conducted by Honeywell during 2009 as part of the design effort for the profundal (*i.e.*, deep water) zone of Onondaga Lake and as a follow up to dye tracer tests conducted during 2008. This field trial is preceding a nitrate pilot test being planned for 2010. The two objectives of the nitrate application field trial are to demonstrate an electron acceptor (*i.e.*, a widely-available nitrate solution) can be added effectively to the hypolimnion of Onondaga Lake and to provide additional measurements of horizontal dispersion in the hypolimnion.

The field trial includes two barge-based applications to be conducted during the July-August 2009 timeframe. Each application will include simultaneous application of a diluted calcium nitrate solution and Rhodamine-WT dye. The first application is being planned for the North Basin, and the second application is being planned for the South Basin. The two applications will be conducted at times when public events on the lake are not scheduled. A barge equipped with a crane along with a tug boat will be used to conduct both applications. Nitrate and dye will be applied over approximately six to eight hours during each application. Following both applications, monitoring will be conducted for several days. Results will be reported to the agencies by late September 2009 in accordance with the schedule outlined in the Remedial Design Work Plan for this site (Parsons, 2009).

1.0 INTRODUCTION

This work plan describes how a nitrate application field trial will be performed during the summer of 2009. The field trial will be performed for Honeywell by Parsons and monitored by Upstate Freshwater Institute (UFI) to demonstrate an electron acceptor can be added effectively to thermally-stratified bottom waters of Onondaga Lake and to provide additional measurements of horizontal dispersion.

The remedy for the lake is described in a 2005 Record of Decision (ROD) prepared by the New York State Department of Environmental Conservation (NYSDEC) and the United States Environmental Protection Agency (USEPA). The remedy for the lake includes a pilot study to evaluate methods to reduce the accumulation of methylmercury in the deep water areas of the lake, called Sediment Management Unit (SMU) 8. Before an effective pilot study can be conducted, and as outlined in the Remedial Design Work Plan (Parsons, 2009), a field trial will be conducted in accordance with the Statement of Work attached to the Consent Decree between NYSDEC and Honeywell. The purpose of the field trial is to demonstrate that an electron acceptor (in this case, a widely-available calcium nitrate solution) can be effectively added and mixed with lake bottom waters in a manner that retains the electron acceptor within the lake

bottom waters to counteract nitrate depletion below critical levels which has occurred prior to 2007 in late summer when the lake is stratified. The field trial will also provide additional information about horizontal dispersion of the electron acceptor as a follow-up to the 2008 dye tracer tests (UFI, 2008).

When Onondaga Lake waters are thermally stratified (typically each year between late May and late October), oxygen and nitrate concentrations gradually decline over time in the hypolimnion and, as a result, sediments can release methylmercury to the water column. During 2007 and 2008, releases of methylmercury to the hypolimnion were found to be substantially lower than in previous years due primarily to wastewater treatment process now online at the Onondaga County Metropolitan Wastewater Treatment Plant (hereafter called Metro). In 2004, Onondaga County activated a biologically active filter system at Metro which converts ammonia to nitrate which roughly doubled the available nitrate pool in the hypolimnion at the start of summer stratification in the lake. In 2005, Onondaga County activated a phosphorous-removal system resulting in decreased algal growth in the upper waters and reduced demand for electron acceptors in the hypolimnion. As a consequence of these wastewater treatment systems, nitrate levels persisted in the hypolimnion for a significantly greater duration during the summers of 2007 and 2008, which inhibited the release of methylmercury.

In light of these recent water quality improvements, the benefit of adding an electron acceptor such as nitrate or oxygen to hypolimnion waters of Onondaga Lake has declined substantially compared to 2005 when the ROD was issued for the lake bottom. Nonetheless, future addition of an electron acceptor in the lower waters of the lake's hypolimnion through the use of an engineered system may be required to maintain sufficient quantity of one or more electron acceptors to further reduce methylmercury accumulation. Mechanical equipment and field procedures for adding nitrate to the lake hypolimnion need to be tested in a manner that mimics maximum anticipated rates for applying nitrate. In order to mimic maximum anticipated nitrate application rates, the field trial will be conducted by placing a maximum nitrate application rate at a single location within the SMU 8 hypolimnion.

Five different dye tracer tests were conducted by UFI for Honeywell between July 22 and October 7, 2008. The work plan and report documenting results from these 2008 dye tracer tests have been provided separately (UFI, 2008 and UFI, 2009). Each of these tests involved placing Rhodamine-WT dye into the SMU 8 hypolimnion at water depths of 14.7 to 16.1 meters (48 to 53 feet) within the North Basin and the South Basin. These tests consisted of placing dye for 20 to 40 minutes at a flow of approximately 20 gallons per minute. In contrast, the 2009 field trial will include placing nitrate and dye over six-hour periods at higher flow rates that are being determined as part of field trial design.

2.0 MATERIALS, METHODS AND PROTOCOLS

Calcium nitrate ($\text{Ca}(\text{NO}_3)_2$), a common agricultural fertilizer, is the source of the electron acceptor that will be applied during the field trial into the lower waters of the Onondaga Lake hypolimnion. The solution of calcium nitrate to be applied is called CN-8 from Yara North

America (www.yara.us) or equivalent. Product information for CN-8 is provided in Appendix A and summarized in Table 1.

Applying the calcium nitrate solution and Rhodamine-WT dye as part of the field trial will not result in any potentially significant effects on biota in the lake or human health. CN-8 (hereafter called the calcium nitrate solution) is most often used as an agricultural fertilizer with no known human health or biota toxicity effects (see Appendix A). There is no statewide water quality standard applicable to Onondaga Lake for either calcium or nitrate. There is a statewide water quality standard of 100 micrograms per liter for nitrite-nitrogen for fish propagation in warm-water fishery waters. Nitrite-nitrogen is not present in CN-8 according to the manufacturer. However, a CN-8 sample will be analyzed by UFI for nitrite-nitrogen using EPA Method 353.2 and also for ammonia-nitrogen and phosphorus. The potential for reduction of nitrate to nitrite within the lake is recognized but is not significant given the short duration of each field trial application and quantity of nitrate to be applied. Furthermore, anoxic conditions in the hypolimnion preclude fish propagation regardless of the nitrite levels. For Rhodamine-WT dye, concentrations known to affect biota are generally much higher than those required for tracer use (Martin and McCutcheon, 1999). A description of properties and a material safety data sheet (MSDS) for Rhodamine-WT dye was provided in the work plan for the 2008 Dye Tracer Tests (UFI, 2008). Properties of Rhodamine-WT are well-suited to most studies and this is the dye most commonly used as a water tracer (Martin and McCutcheon 1999). Additional properties of Rhodamine-WT are presented in Table 1 of the work plan approved for the 2008 Dye Tracer Tests (UFI, 2008).

Selection of a quantity of nitrate to apply during the field trial was based on a highest nitrate application rate that may need to be implemented during full-scale application in the future. This application corresponds to a peak four-week nitrate application rate to satisfy nitrate demand for the entire Onondaga Lake hypolimnion from a single input location. The calcium nitrate solution application rate has been quantified for the field trial based on peak four-week rolling average nitrate uptake rates in the hypolimnion water as measured at the South Deep station by UFI during 2007 and 2008. The peak nitrate uptake rate over a four-week period during 2007 and 2008 was approximately 0.8 metric tons of nitrate per day (or 33 kilograms per hour) for the entire hypolimnion as shown in Figure 1. An application rate of 1.1 gallons per minute of the calcium nitrate solution over six hours is equivalent to applying 0.8 metric tons of nitrate-nitrogen over 24 hours as shown below:

- 0.8 metric tons times 1,000 kilograms per metric ton = 800 kilograms
- 800 kilograms over 24 hours = 200 kilograms over 6 hours

The calcium nitrate solution contains 0.0855 kilograms of nitrate-nitrogen per kilogram of solution (see Table 1).

The specific gravity of the calcium nitrate solution is 1.48 (see Table 1).

200 kilograms over 6 hours = 0.0855 kilograms of nitrate-nitrogen per kilogram of solution times 1.48 kilograms of solution per liter times Q in liters per hour, where Q is the amount of calcium nitrate solution to apply.

$Q = 263$ liters per hour or 1.1 gallons per minute.

Thus, the nitrate release during the field trial will mimic the procedure that could possibly be used in a full-scale, lake-wide, seasonal nitrate application based on: (1) an assumption that a single release point is adequate to effectively apply nitrate to the entire lake, and (2) the application would occur continuously over the period of significant nitrate depletion.

The calcium nitrate solution (with a specific gravity of 1.48 compared to 1.00 for fresh water at 70 degrees Fahrenheit) and Rhodamine-WT dye will need to be diluted with lake water and applied within the lake through an end-of-pipe diffuser at an appropriate density so the calcium nitrate-dye-water mixture remains near the lake bottom and spreads horizontally at measureable concentrations following application. The diffuser will be designed to release the mixture at a prescribed water depth and provide additional dilution beyond the dilution provided by adding lake water to the calcium nitrate and dye. A likely diffuser depth for releasing the mixture is approximately 6 to 7 ft (2 meters) above the lake bottom which is the same depth where dye was released as part of the 2008 dye tracer tests. Diluting the calcium nitrate and Rhodamine-WT dye with water from the epilimnion would result in less dilution needed to achieve the target density compared to diluting with water from the hypolimnion. Appropriate dilution ratios for use during the field trial will be determined by UFI based on the factors described above, based on ambient 2009 densities of lake water for various lake water temperatures and dissolved solids concentrations (UFI and SU, 2007a), and based on the following NYSDEC Division of Water requirements for this discharge:

- Narrative standards for nitrogen contained in Part 703.2 of the DEC's water quality regulations are to be met- "None in amounts that will result in growths of algae....that will impair the waters for their best usage";
- A calcium nitrate solution (CAS# is 10124-37-5, specific gravity=1.48, 8.55 percent nitrate-nitrogen, 12.10 percent calcium, less than or equal to 0.02 percent ammonia-nitrogen) application rate not to exceed 1.1 gallons per minute over a time period no longer than six hours;
- The total discharge rate will not exceed 0.8 metric tons of nitrate-nitrogen per day;
- The calcium nitrate solution will be applied via a diffuser, at a depth of approximately 6 to 7 ft (2 meters) above the lake bottom, in the anoxic, deepwater region of the Lake;
- The water quality standard of 100 micrograms per liter for nitrite-nitrogen (based on fish propagation), is not exceeded; and
- Conduct a detailed monitoring program, as described in this work plan.

Attempts will be made to establish a dye cloud with a significant vertical dimension to enhance monitoring effectiveness. If the results of the monitoring program indicate that there are any violations of water quality standards, NYSDEC will be notified immediately. A description of the diffuser will be provided to NYSDEC prior to mobilization.

Based on an anticipated dilution ratio of 300 from a prior UFI analysis (UFI and SU, 2007a), the concentration of nitrate-nitrogen following initial mixing of 1.1 gallons per minute of CN-8 with lake water would be approximately 420 milligrams per liter. A typical solubility for nitrate-nitrogen in water is 120 grams per 100 grams of water or 1.2 million milligrams per liter. So, the mixed calcium nitrate solution is expected to become soluble easily when mixed with lake water.

Temporary piping will be provided from the barge and used to withdraw lake water to mix with the calcium nitrate solution and Rhodamine-WT dye and also to deliver the nitrate-dye-water mixture to the hypolimnion.

Two different applications of the calcium nitrate solution and Rhodamine-WT dye will be conducted. The first application will be conducted in the North Basin near North Deep, and the second application will be conducted in the South Basin near South Deep. Monitoring of the discharged nitrate and dye will be conducted during both applications by UFI using a fluorometer to measure Rhodamine dye and an *in situ* ultraviolet spectrophotometer (ISUS) device which UFI has used for many years in Onondaga Lake to provide real time measurements of nitrate and other parameters (see UFI and SU, 2008 and also Johnson and Coletti, 2002). The overall profiling package that contains ISUS will also be capable of measuring specific conductance, optical backscatter, water temperature, and water depth. These monitoring instruments together will be able to provide high spatial resolution over short time intervals (e.g., three-dimensional resolution available within several hours). Sampling devices will be integrated with a GPS sensor to track and record the position of the measurements.

The field trial will be conducted in accordance with the application rates of calcium nitrate specified in this work plan, and every reasonable effort will be made to avoid a violation of New York State water quality standards during the field trial. Because this work is required under a Consent Order through NYSDEC, no additional permit from NYSDEC will be required.

3.0 FIELD TRIAL MOBILIZATION

The first week of field effort will involve mobilization of the barge and installation of pumps, controls and the on-board storage tanks. Mobilization will take place near the shoreline on Honeywell property northwest of Settling Basin B. A second week will be allotted to fill the barge tanks, move out into the lake and test the pumps, controls, and diffuser. Another two weeks will be allotted for the two applications and follow up monitoring, based on one week of monitoring following each application. A final week for demobilization brings the duration of the on-lake field trial activities to five weeks. The goal is to conduct two successful applications during the June-July 2009 timeframe.

To prepare for the nitrate application field trial, the following mobilization activities will take place:

- A temporary onshore preparation area approximately 1,000 square feet in size will be prepared on Honeywell property if needed in an area north-northwest of Settling Basin B adjacent to the shoreline barrier wall. This area will be used for equipment and material transfer from land to the barge. If needed to hold the calcium nitrate solution and/or the Rhodamine-WT dye onshore, the preparation area will also include one or two temporary storage tanks with secondary containment.
- A barge with a crane on board and an accompanying tug boat will be brought to the site via the NY State Canal system. The barge will be fitted with temporary storage tanks provided with secondary containment along with mixing equipment, temporary piping, and other equipment and supplies needed to conduct the field trial. The barge will have ample usable deck space in addition to the working space of the crane. During mobilization and for nights and standby time during the field trial and between applications, the barge and tug boat will be secured near the lake shoreline adjacent to the temporary on-shore preparation area and 10 to 12 ft offshore from the barrier wall.
- Field trial equipment will be mobilized including pumps, storage tanks, meters, suction piping, and piping to transmit the nitrate-dye-water mixture to hypolimnion waters.
- Monitoring equipment will be tested including a global positioning system (GPS) sensor; a Yellow Springs Instruments (YSI) 6130 Rhodamine-WT fluorometer (or equivalent) connected to an YSI multiprobe for measurement of dye concentration, temperature, and water depth; the ISUS equipment; and a portable computer. Specifications for the YSI 6130 are provided in the work plan for the 2008 Dye Tracer Tests (UFI, 2008). A standard operating procedure (SOP) for field trial monitoring is provided in Appendix B.
- Software will be checked and modified as needed to allow reliable recording and display of field measurements on the on-board computer to be used by UFI. Because the nitrate-dye-water mixture will not be visible from the monitoring boat, the ability to compare the current position of the boat relative to the position of the dye cloud as identified from earlier measurements will be invaluable.

A brief pre-trial test will be conducted in Onondaga Lake following the onset of summer stratification and before the first application is conducted. A small amount of the calcium nitrate solution and Rhodamine-WT dye (approximately a few liters) will be mixed with lake water and then applied and tracked. This pre-test will allow testing of the individual sensors (GPS, nitrate, fluorescence, water depth, and temperature), the recording of measurements on the on-board computer, and the software to be used to display these measurements. During pre-testing, zero background dye concentrations in the hypolimnion will be confirmed as well.

4.0 FIELD TRIAL IMPLEMENTATION

It is anticipated that both applications will be initiated on a Tuesday or a Wednesday, thus providing at least five to six days of dilution prior to the baseline water column and zooplankton sampling that is scheduled to be conducted on Monday June 22, Monday July 6, and Monday

July 20, 2009. The nitrate and dye will preferably be applied during morning timeframes to allow as much time as possible for tracking over the course of the first day. The first application will be conducted in the North Basin, and the second application will be conducted in the South Basin.

To begin each application, the barge and tug boat will be moved to the application location. Inflow piping and outflow piping with an end-of-pipe diffuser will be positioned in the lake water column. Nitrate and dye will then be mixed on the barge with lake water and applied to the hypolimnion. The end-of-pipe diffuser will be pointed away from the lake bottom so as to avoid disturbing SMU 8 sediment. The accompanying tug boat and the barge anchor will be used as needed to hold the barge in place while the calcium nitrate solution and Rhodamine-WT dye are being applied. The duration for a single application of the calcium nitrate solution and Rhodamine-WT dye is estimated to be six hours.

After allowing time for some initial spreading, the nitrate and dye will begin to be monitored by UFI using at least one monitoring boat (see the SOP presented as Appendix B). While monitoring, the position of the monitoring boat and output from the monitoring sensors will be recorded at regular intervals by an on-board computer. The approach to monitoring is anticipated at this time to be the same as for the 2008 dye tracer tests, which will be to “sweep” across the nitrate and dye cloud in both longitudinal and lateral directions, where each sweep will begin outside the detectable limit of the nitrate and dye cloud, continue through the nitrate and dye cloud, and end on the opposite side where the detectable limits will be identified. The depth of the monitoring sensors will also be adjusted occasionally to identify the extent of nitrate and dye movement in the vertical direction. The goal is to provide a picture of the extent of dye movement (and nitrate movement as practicable) twice daily during the monitoring period.

The water monitoring sensors will induce some mixing of the dye and nitrate as the sensors are towed through the dye cloud. However, this mixing will be: (a) weak because towing of the monitoring sensors will be conducted as slowly as reasonably possible (boat speed of approximately two knots or two to three miles per hour); (b) small scale because the fluorometer probe that will be towed is approximately 12 inches (30 centimeters) in size; and (c) sustained for only approximately 10 to 20 seconds at any position as the monitoring sensors are towed. The field objective is consistent with the objective of the 2008 dye tracer tests conducted for Honeywell which is to measure sustained, large-scale mixing over tens to hundreds of meters, which will not be affected in any significant manner by the towing of instruments. The sampling approach also provides flexibility to measure various dye shapes in an implementable manner.

This field trial is based on the nitrate-dye-water mixture being applied and remaining at a significant water depth, so visual identification of the dye from the boat will not be possible. Software will display the following graphical information on the on-board computer screen: (1) a map of the lake; (2) current position of the boat (from the GPS sensor); and (3) the location of and nitrate concentrations/dye fluorescence as determined from measurements collected until that time. The monitoring sensors will have a weighted, protective guard intended to keep the sensors vertical, and additional weight will be able to be added if needed. It will be important to keep the monitoring sensors nearly vertical so that the GPS coordinates are representative of the

actual location of the sensor. An additional sampling boat will be used if it is found that two boats are required to track the dye as it expands over time.

Tracking of the dye (and nitrate as practicable) will be conducted during daylight hours for at least three days or until dye is no longer detected. The amount of calcium nitrate-dye-water mixture to be applied will be identified using results from the 2008 dye tracer tests with the intent of providing concentrations of the Rhodamine-WT dye that remain detectable in the hypolimnion for a few days following an application. The time period over which detectable concentrations will persist will also be identified using results from the 2008 dye tracer tests and will be strongly dependent on the magnitude of mixing that occurs.

Unanticipated or unforeseen circumstances or conditions may occur. As a result, this protocol may be modified during the field trial. Any significant modifications of field trial procedures presented in this work plan will be reviewed with the agencies before being fully implemented. Within a few days after completing the first application, Parsons/Honeywell will brief the agencies on field trial progress, discuss any problems that occurred, and present recommendations as to how the second application could be modified to maximize effectiveness.

5.0 HEALTH AND SAFETY

The safety of field team members and the general public is the highest Honeywell priority. The Project Safety Plan for Parsons field efforts (Parsons, 2008) and the UFI Safety Plan (Appendix C of UFI and SU, 2007b) prepared for previous Onondaga Lake field activities will be used for this investigation and will be strictly followed by all personnel. Any task outside of the current scope defined in the relevant safety plans will have new job safety analyses completed as warranted before the task begins. Copies of these Parsons and UFI safety plans will be maintained at the support zone and on the boat.

Various project-specific safety elements will be emphasized during the field trial. For example, personal flotation devices will be worn at all times by anyone on the team that is on a boat or barge. Slip-resistant surfaces and electrical protection around water will be emphasized. Suitable hand and eye protection will be instituted as appropriate when working with the nitrate and Rhodamine-WT dye. Hot work procedures will be approved by the project safety officer prior to conducting any welding or other hot-work activity. Appropriate safeguards will be employed at the chemical storage units.

6.0 SCHEDULE CONSIDERATIONS

A summer time period where calm winds have persisted and are predicted to continue will be preferred for both applications. The goal for the days when the calcium nitrate solution and Rhodamine-WT dye will be applied is to have low sustained wind speeds and no significant storm event within two days prior or forecasted by the National Weather Service for the near future. In addition, major public events occurring on the lake will be avoided to the extent practicable. "Blackout" dates will be established during the summer of 2009 for public events on the lake such as free fishing held during late June 2008, the Hydrofest held during mid-July 2008, and a fishing tournament held during late July 2008.

The two applications that make up the field trial will be separated by at least one week, so that any lingering amounts of nitrate or dye that remain in the lake from the first field trial effort in the North Basin will be dispersed or otherwise not detectable when the second field trial effort is initiated in the South Basin. To confirm this, on the day before the second field trial is to begin, dye concentrations will be measured over the basin where the application is to be conducted. If measurable dye levels are found, the application would be delayed. Book 1 baseline monitoring work in SMU 8 is conducted on Mondays, while the nitrate application field trial work will be conducted beginning most likely on a Tuesday or Wednesday.

7.0 NOTIFICATIONS AND OTHER COMMUNICATIONS WITH OUTSIDE PARTIES

The following protocol has been established by Honeywell for notifying NYSDEC, USEPA, and Onondaga County consistent with the notification protocol successfully implemented during the 2008 dye tracer tests.

- Items to be included in notifications:
 - Scope and purpose of work - Apply the CN-8 calcium nitrate solution and Rhodamine-WT dye to bottom waters to measure natural dispersion within the deepest portions of the lake in the South and North Basins.
 - Lake activity – A barge, tug boat, and one or two boats will be moving slowly in a portion of either the South Basin or the North Basin for a few days.
 - Schedule - Specific timeframes for the two applications have not yet been determined. Follow up notifications will be provided once the additional field trial timeframes are established.
 - Effects of the calcium nitrate solution and Rhodamine-WT dye – The calcium nitrate solution and Rhodamine-WT dye will not be visible given it is being applied into deep, stratified lake waters. Calcium nitrate is commonly used as agricultural fertilizer. The Rhodamine-WT dye is commonly used for tracing work in sewers and has no effects on human health or the environment particularly at the low concentrations being applied. Use of both the calcium nitrate solution and Rhodamine-WT dye is acceptable to NYSDEC who has reviewed the work scope.
- Contacts to be notified by Parsons/Honeywell:
 - Joe Mastriano (OCDWEP), and Bob Geraci (Onondaga County Parks)
 - Tim Larson (NYSDEC project manager) and Tara Blum (NYSDEC Region 7 rep) who in turn can notify others at NYSDEC and at other state agencies as warranted.
 - Bob Nunes (USEPA Region 2 project manager) who can notify other federal contacts as warranted.
 - Honeywell field team leaders including Neil Ringer at the State University of New York College of Environmental and Forestry.

Every reasonable effort will be made to give agencies at least one week of notice prior to each application. Every reasonable effort will also be made to notify NYSDEC in a timely manner of any changes to the schedule and also to confirm field trial start dates once they are identified. In order to mobilize equipment and supplies, and to provide reasonable notification, the decision about a date during which to conduct each application will be made by Honeywell in conjunction with NYSDEC at least a few days in advance. This decision will be based primarily on weather and lake conditions and on the weather forecast.

8.0 QUALITY ASSURANCE

The onshore support zone and facilities established by Honeywell for their design-related field efforts will be used as needed for the nitrate application field trial work described herein. Work efforts not specifically described in this work plan, such as decontamination and waste management activities, will be conducted in accordance with procedures documented in the Phase I Pre-Design Investigation Work Plan (Parsons, 2005). Laboratory procedures will be conducted in accordance with the SOP included in Book 1 Work Plan for Baseline Monitoring (UFI and SU, 2008).

Confirmation of ISUS nitrate concentrations with lab measurements will be done routinely as part of the Book 1 2009 baseline monitoring work.

9.0 DATA MANAGEMENT AND REPORTING

Processing of the field measurements will lead to quantifying the dispersion coefficient over the course of each test.

A detailed analysis of the data from each of the field trials will be provided in a report to Honeywell and discussed with the SMU 8 Technical Work Group as input to the design of the nitrate pilot test planned for 2010. Output from the 2009 nitrate application field trial will also be applied to the comparison of boat-based and pipe-based delivery of nitrate and/or oxygen to the lake's hypolimnion. As indicated in the Remedial Design Work Plan (Parsons, 2009), the draft nitrate application field trial report is due to the agencies by September 25, 2009.

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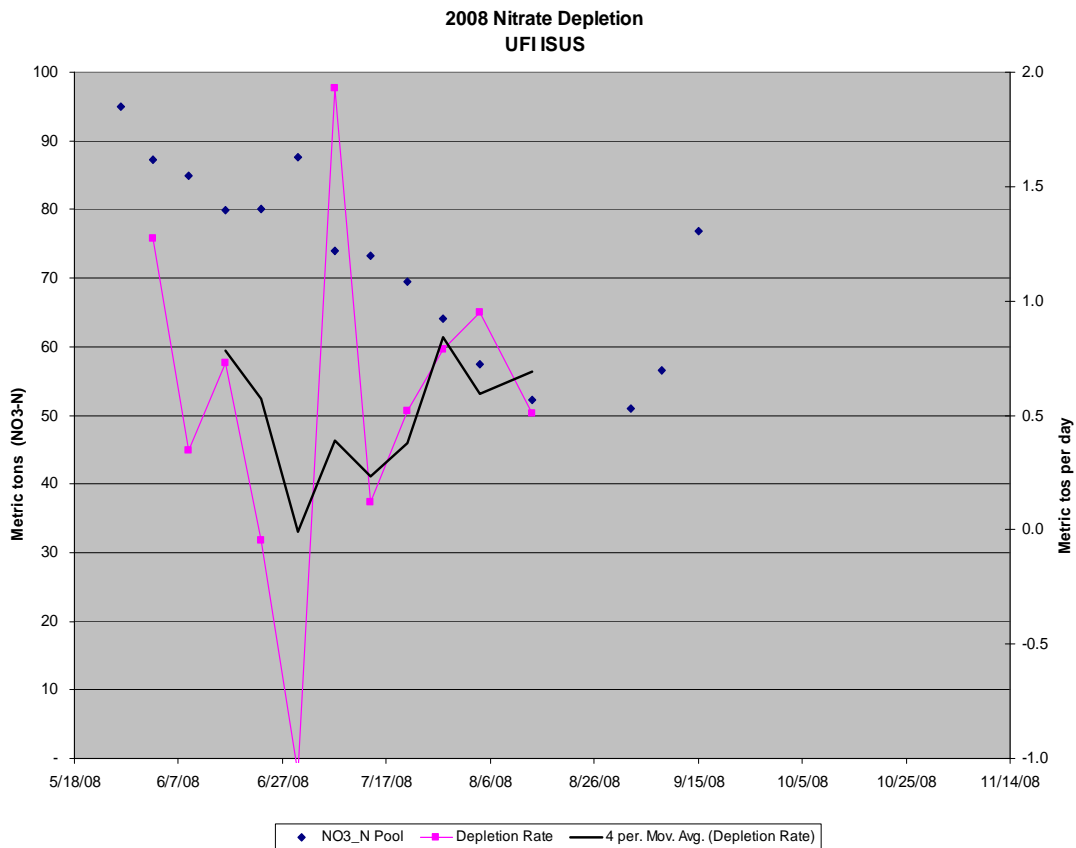
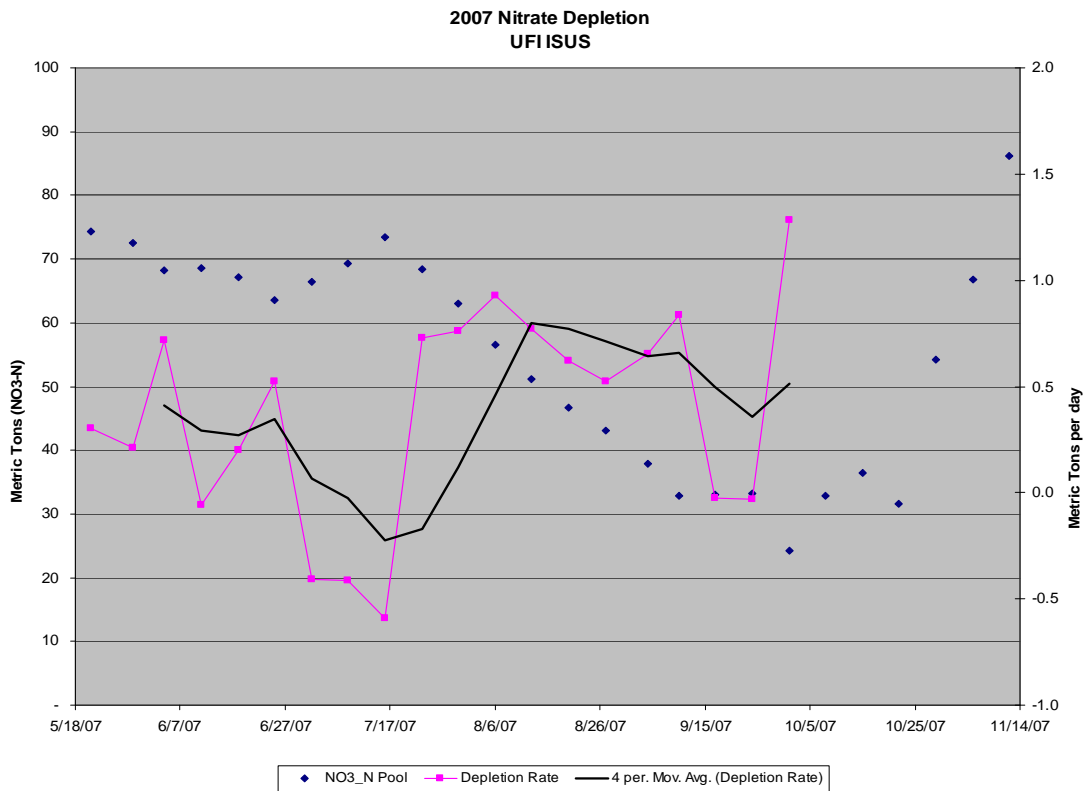
TABLE 1
PROPERTIES OF THE CALCIUM NITRATE SOLUTION
(from www.yara.us)

Property	Description
Preferred available form	CN-8 a 49.8 percent calcium nitrate (Ca(NO ₃) ₂) solution by weight including 8.55% nitrate-nitrogen
Other constituents	Common fertilizer ingredients: 0.02% ammonia nitrogen by weight
Specific gravity	1.48
Weight per gallon, pounds	12.3
Salt out temperature, degrees Fahrenheit	35
pH	5.0 to 7.0
Description	Clear, odorless liquid
Storage and handling	Plastic, fiberglass, or stainless steel
Instructions (for avoiding formation of insoluble precipitates)	Do not mix with phosphate or sulfate-containing materials
Trace contaminant concentrations ⁽¹⁾	Arsenic: less than 0.25 ppm Cadmium: less than 2.0 ppm Cobalt: less than 5.0 ppm Lead: less than 10.0 ppm Mercury: less than 0.02 ppm Molybdenum: less than 2.5 ppm Nickel: less than 5.0 ppm Selenium: less than 0.5 ppm Zinc: less than 3.0 ppm

(1) Concentrations are in parts per million (ppm) as obtained from Yara North America, Inc.

Figure 1

Nitrate Availability and Depletion in Onondaga Lake Hypolimnion Waters During Summer 2007 and Summer 2008



APPENDIX A

PRODUCT INFORMATION SHEET FOR THE CALCIUM NITRATE SOLUTION

(FROM WWW.YARA.US)

(referred to herein as YaraLiva™ CN-8)



Product Information Sheet

YaraLiva™ CN-8

NOTE: THIS IS NOT A MATERIAL SAFETY DATA SHEET SINCE NONE IS REQUIRED FOR THIS PRODUCT. IT IS PROVIDED FOR EMPLOYEE INFORMATION ONLY.

Section 1. Chemical product and company identification

Trade name : YaraLiva™ CN-8
Manufacturer : Yara North America, Inc
100 North Tampa Street
Suite 3200
P.O. Box 24926
Tampa, FL 33623
USA
Tel: +1 813 222 5700
Fax: +1 813 875 5735

Validation date : **2008-04-04.**
Print date : 2008-04-04.
Responsible name : Bill Easterwood
In case of emergency : Additional Product Information: 813-222-5700
or Chemtrec 24-hours Emergency Resonse: 1-800-424-9300

Section 2. Composition, information on ingredients

<u>Name</u>	<u>CAS number</u>	<u>% by weight</u>
No hazardous ingredients.		

Additional information

Contains Water

Section 3. Hazards identification

Physical state : Liquid. [Clear.]
Emergency overview : CAUTION!
MAY BE HARMFUL IF SWALLOWED. MAY CAUSE RESPIRATORY TRACT, EYE AND SKIN IRRITATION.
Do not ingest. Wash thoroughly after handling.

Potential acute health effects

Eyes : Slightly irritating to the eyes.
Skin : Slightly irritating to the skin.
Inhalation : Slightly irritating to the respiratory system. Exposure to decomposition products may cause a health hazard. Serious effects may be delayed following exposure.
Ingestion : Harmful if swallowed.
Carcinogenic effects : No known significant effects or critical hazards.
Mutagenic effects : No known significant effects or critical hazards.
Reproduction toxicity : No known significant effects or critical hazards.

See toxicological Information (section 11)

Section 4. First aid measures

- Eye contact** : Check for and remove any contact lenses. Immediately flush eyes with plenty of water for at least 15 minutes, occasionally lifting the upper and lower eyelids. Get medical attention immediately.
- Skin contact** : In case of contact, immediately flush skin with plenty of water for at least 15 minutes while removing contaminated clothing and shoes. Wash clothing before reuse. Clean shoes thoroughly before reuse. Get medical attention immediately.
- Inhalation** : Move exposed person to fresh air. If not breathing, if breathing is irregular or if respiratory arrest occurs, provide artificial respiration or oxygen by trained personnel. Loosen tight clothing such as a collar, tie, belt or waistband. Get medical attention immediately.
- Ingestion** : Wash out mouth with water. Do not induce vomiting unless directed to do so by medical personnel. Never give anything by mouth to an unconscious person. Get medical attention immediately.

Section 5. Fire fighting measures

- Flammability of the product** : Non-flammable.
- Products of combustion** : These products are
nitrogen oxides
metal oxide/oxides
- Fire-fighting media and instructions** : Use an extinguishing agent suitable for the surrounding fire.
- Promptly isolate the scene by removing all persons from the vicinity of the incident if there is a fire. No action shall be taken involving any personal risk or without suitable training.
- Special protective equipment for fire-fighters** : Fire-fighters should wear appropriate protective equipment and self-contained breathing apparatus (SCBA) with a full face-piece operated in positive pressure mode.

Section 6. Accidental release measures

- Personal precautions** : No action shall be taken involving any personal risk or without suitable training. Evacuate surrounding areas. Keep unnecessary and unprotected personnel from entering. Do not touch or walk through spilled material. Avoid breathing vapor or mist. Provide adequate ventilation. Wear appropriate respirator when ventilation is inadequate. Put on appropriate personal protective equipment (see section 8).
- Environmental precautions** : Avoid dispersal of spilled material and runoff and contact with soil, waterways, drains and sewers. Inform the relevant authorities if the product has caused environmental pollution (sewers, waterways, soil or air).
- Methods for cleaning up** : Stop leak if without risk. Move containers from spill area. Approach release from upwind. Prevent entry into sewers, water courses, basements or confined areas. Wash spillages into an effluent treatment plant or proceed as follows. Contain and collect spillage with non-combustible, absorbent material e.g. sand, earth, vermiculite or diatomaceous earth and place in container for disposal according to local regulations (see section 13). Dispose of via a licensed waste disposal contractor. Contaminated absorbent material may pose the same hazard as the spilled product. Note: see section 1 for emergency contact information and section 13 for waste disposal.

Section 7. Handling and storage

- Handling** : Avoid contact with eyes, skin and clothing. Avoid breathing vapors, spray or mists.
- Storage** : Keep container tightly closed. Keep container in a cool, well-ventilated area. Keep away from heat and direct sunlight.

Section 8. Exposure controls/personal protection

Engineering controls : Use only with adequate ventilation. If user operations generate dust, fumes, gas, vapor or mist, use process enclosures, local exhaust ventilation or other engineering controls to keep worker exposure to airborne contaminants below any recommended or statutory limits.

Personal protection

Eyes : Safety eyewear complying with an approved standard should be used when a risk assessment indicates this is necessary to avoid exposure to liquid splashes, mists, gases or dusts.
Recommended: splash goggles .

Skin : Personal protective equipment for the body should be selected based on the task being performed and the risks involved.

Respiratory : Use a properly fitted, air-purifying or air-fed respirator complying with an approved standard if a risk assessment indicates this is necessary. Respirator selection must be based on known or anticipated exposure levels, the hazards of the product and the safe working limits of the selected respirator.

Hands : Chemical-resistant, impervious gloves complying with an approved standard should be worn at all times when handling chemical products if a risk assessment indicates this is necessary.
>8 hours (breakthrough time): butyl rubber , natural rubber (latex) , nitrile rubber .

Personal protective equipment (Pictograms) :



Personal protection in case of a large spill : Splash goggles. Full suit. Boots. Gloves. Suggested protective clothing might not be adequate. Consult a specialist before handling this product.

Consult local authorities for acceptable exposure limits.

Section 9. Physical and chemical properties

Physical state : Liquid. [Clear.]

Color : Colorless.

Odor : Odorless.

pH : 5 to 7

Boiling/condensation point : 104,44°C (220°F)

Specific gravity : 1,48

Density (lbs/gal) : 12.3 (20°C/68°F)

Section 10. Stability and reactivity

Stability and reactivity : Stable under recommended storage and handling conditions (see section 7).

Incompatibility with various substances : Reactive or incompatible with the following materials: combustible materials, acids and alkalis.

Hazardous decomposition products : Under normal conditions of storage and use, hazardous decomposition products should not be produced.

Hazardous polymerization : Under normal conditions of storage and use, hazardous polymerization will not occur.

Section 11. Toxicological information

Other toxic effects on humans : No specific information is available in our database regarding the other toxic effects of this material to humans.

Section 12. Ecological information

<u>Ingredient name</u>	<u>Species</u>	<u>Period</u>	<u>Result</u>
YaraLiva™ CN-8	Fish (LC50)	96 hour(s)	>100 mg/l

Toxicity of the products of biodegradation : The product itself and its products of degradation are not toxic.

Special remarks on the products of biodegradation : The product does not show any bioaccumulation phenomena.

Section 13. Disposal considerations

Waste disposal : The generation of waste should be avoided or minimized wherever possible. Empty containers or liners may retain some product residues. This material and its container must be disposed of in a safe way. Dispose of surplus and non-recyclable products via a licensed waste disposal contractor. Disposal of this product, solutions and any by-products should at all times comply with the requirements of environmental protection and waste disposal legislation and any regional local authority requirements. Avoid dispersal of spilled material and runoff and contact with soil, waterways, drains and sewers.

Consult your local or regional authorities.

Section 14. Transport information

<u>Regulatory information</u>	<u>UN number</u>	<u>Proper shipping name</u>	<u>Class</u>	<u>Packing group</u>	<u>Label</u>	<u>Additional information</u>
DOT Classification	Not regulated.	-	-	-		-
TDG Classification	Not regulated.	-	-	-		-

Section 15. Regulatory information

HCS Classification : Not regulated.

U.S. Federal regulations : **United States inventory (TSCA 8b)**: All components are listed or exempted.

SARA 302/304/311/312 extremely hazardous substances: No products were found.

SARA 302/304 emergency planning and notification: No products were found.

SARA 302/304/311/312 hazardous chemicals: Calcium Nitrate

SARA 311/312 MSDS distribution - chemical inventory - hazard identification:

Calcium Nitrate: Fire hazard

Clean Water Act (CWA) 307: No products were found.

Clean Water Act (CWA) 311: No products were found.

Clean Air Act (CAA) 112 accidental release prevention: No products were found.

Clean Air Act (CAA) 112 regulated flammable substances: No products were found.

Clean Air Act (CAA) 112 regulated toxic substances: No products were found.

SARA 313

	<u>Product name</u>	<u>CAS number</u>	<u>Concentration</u>
Form R - Reporting requirements	: Calcium Nitrate	10124-37-5	49.8
Supplier notification	: Calcium Nitrate	10124-37-5	49.8

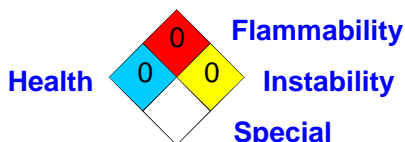
SARA 313 notifications must not be detached from the MSDS and any copying and redistribution of the MSDS shall include copying and redistribution of the notice attached to copies of the MSDS subsequently redistributed.

State regulations

- Connecticut Carcinogen Reporting:** None of the components are listed.
- Connecticut Hazardous Material Survey:** None of the components are listed.
- Florida substances:** None of the components are listed.
- Illinois Chemical Safety Act:** None of the components are listed.
- Illinois Toxic Substances Disclosure to Employee Act:** None of the components are listed.
- Louisiana Reporting:** None of the components are listed.
- Louisiana Spill:** None of the components are listed.
- Massachusetts Spill:** None of the components are listed.
- Massachusetts Substances:** None of the components are listed.
- Michigan Critical Material:** None of the components are listed.
- Minnesota Hazardous Substances:** None of the components are listed.
- New Jersey Hazardous Substances:** The following components are listed: Calcium Nitrate
- New Jersey Spill:** None of the components are listed.
- New Jersey Toxic Catastrophe Prevention Act:** None of the components are listed.
- New York Acutely Hazardous Substances:** None of the components are listed.
- New York Toxic Chemical Release Reporting:** None of the components are listed.
- Pennsylvania RTK Hazardous Substances:** None of the components are listed.
- Rhode Island Hazardous Substances:** None of the components are listed.

Section 16. Other information

National Fire Protection Association (U.S.A.) :



Date of issue : 2008-04-04.

Date of previous issue : 2007-10-11.

Version : 3

📌 Indicates information that has changed from previously issued version.

Notice to reader

To the best of our knowledge, the information provided in this Safety Data Sheet is accurate as at the date of its issue. The information it contains is being given for safety guidance purposes and relates only to the specific material and uses described in it. This information does not necessarily apply to that material when combined with other material(s) or when used otherwise than as described herein. Final determination of the suitability of any material is the sole responsibility of the user. All materials may represent unknown hazards and should be used with caution. Yara International ASA disclaims any liability for loss or damage resulting from the use of any data, information or recommendations set out in this Safety Data Sheet.

APPENDIX B

STANDARD OPERATING PROCEDURES FOR *IN SITU* WATER MONITORING OF NITRATE AND RHODAMINE-WT DYE

EDITED BY: DAM Date: 05/06/08	UPSTATE FRESHWATER INSTITUTE STANDARD OPERATING PROCEDURE	Procedure No. SOP
Revision No: 1	<u>Rhodamine-WT Sensor – YSI 6130</u> <i>In situ</i> Water Tracing	Effective Date: <u>05/06/08</u>

1) Test method:

Rhodamine-WT Sensor – In-Situ Water Tracing

- 2) **Applicable matrix or matrices:** fresh, brackish, and sea waters with less than 61 meter depth
- 3) **Detection limit:** 0.5 micrograms per liter ($\mu\text{g/L}$).
- 4) **Scope and application:** *In situ* measurement of Rhodamine-WT dye for water and pollutant tracing. This procedure is used for time of travel, dispersion, and mixing studies in surface waters.
- 5) **Summary of test method:** The YSI 6130 is an optical sensor that can be used in conjunction with YSI 6-Series sondes and handheld display-loggers. This arrangement allows for manual or automatic collection of Rhodamine-WT dye concentration and various other parameters (e.g., temperature, dissolved oxygen, specific conductance, pH, turbidity, depth, GPS location). Dyes such as Rhodamine-WT mimic the movement of water molecules. The concentration of a dye is directly proportional to its fluorescence. Therefore, the spread of a dye over time is a measure of transport of water or a waterborne substance under the conditions in which the study was performed.
- 6) **Definitions:** none
- 7) **Interferences:** The following substances share excitation or emission spectra with Rhodamine-WT and can cause interference: algae; certain salt compounds; naturally occurring colored organic compounds; and manmade organic pollutants (i.e., dyes, petroleum distillates, detergents). Turbidity can be a significant source of physical interference through inhibition of transmitted and emitted light. Chlorine is a quenching agent of Rhodamine-WT. Photochemical decay is a major loss process for Rhodamine-WT. Rhodamine-WT can also be lost through sorption processes. Dye losses by sorption, photochemical decay, and quenching are rarely large enough to impact time of travel, or dispersion measurements (YSI Environmental 2001).
- 8) **Safety:** Standard field safety procedures should be applied. Keep work area clean and clutter free. The submersible cable should be stowed in an organized fashion and not left in a location where it could become a tripping hazard.
- 9) **Equipment and supplies:** Rhodamine-WT dye (20 percent), appropriate field sheets, GPS, connection cables, and YSI handheld display-logger.
- 10) **Reagents and standards:** Rhodamine-WT dye (20 percent).
- 11) **Reference Solution:** Rhodamine-WT dye (20 percent).
- 12) **Sample collection, preservation, shipment and storage:** No water samples collected.
- 13) **Quality Control:** Inspect sensor for fouling.

PARSONS

EDITED BY: DAM Date: 05/06/08	UPSTATE FRESHWATER INSTITUTE STANDARD OPERATING PROCEDURE	Procedure No. SOP
Revision No: 1	<u>Rhodamine-WT Sensor – YSI 6130</u> <i>In situ</i> Water Tracing	Effective Date: <u>05/06/08</u>

- 14) Calibration and standardization:** The YSI 6130 Rhodamine-WT sensor should be calibrated within 24 hours prior to use. The calibration should include at least 3 standards that span the range of dye concentrations expected to be encountered in the study. The standards should be prepared from the same batch of Rhodamine-WT dye that will be used. In this case,

Rhodamine-WT Liquid
Aniline Corp.
Specific gravity: 1.15 gm/mL
Active ingredient 20% by weight

The steps below describe the preparation of standards for a 3-point calibration (1, 50, 100 µg/L).

1. dilute 4.3 milliliter (mL) of Rhodamine-WT dye to 1 liter
 $4.3 \text{ mL Rhodamine dye} \times 1.15 \text{ grams/mL} = 4.945 \text{ gm dye}$
 $4.945 \text{ gm dye} \times 20 \text{ percent by weight} = 0.989 \text{ active dye}$
 $0.989 \text{ gm dye} \times 1,000,000 \text{ µg/gm} = 989,000 \text{ µg/L solution}$
2. 10 mL of 989,000 µg/L solution diluted to 1 L = 9890 µg/L solution
3. 10 mL of 9890 µg/L solution diluted to 1 L = 98.9 µg/L solution (used as 100 µg/L standard)
4. dilute 500 mL of the 98.9 µg/L solution to 1 L – 49.5 µg/L solution (used as 50 µg/L standard)
5. dilute 20 mL of the 49.5 µg/L solution to 1 L = 0.99 µg/L (used as 1 µg/L standard)

- 15) Data assessment and acceptance criteria for quality control measures:** Assessment of results is done at UFI facilities (post collection). Acceptance criteria for quality control include consideration of field notation concerning interferences and presence of data points outside parameter detection range values.
- 16) Corrective actions for out-of-control or unacceptable data:** Identify data that fail quality assurance/quality control, and record throughout data transfer to client. Analyze cause of unacceptable data (*i.e.*, instrument error or interferences). Return instrument to manufacturer for repair and recalibration if deemed necessary.
- 17) Contingencies for handling out of control or unacceptable data:** Calibration and standardization procedures listed above (#14) ensure that data are within specification.
- 18) Waste management:** This procedure generates no hazardous waste.
- 19) Reference:**

YSI Environmental. 2001. White paper: Water Tracing, *In Situ* Dye Fluorometry and the YSI 6130 Rhodamine-WT Sensor. www.ysi.com.