SAMPLING AND ANALYTICAL PROCEDURES FOR GLNPO'S OPEN LAKE WATER QUALITY SURVEY OF THE GREAT LAKES
January 2007
REVISIONS SUMMARY

Chapter 1: Introduction

LG 100 – *Standard Operating Procedure for General Shipboard Scientific Operations*

1) Updated Section 3.1 with italicized words:

   For Lake Erie surveys, sampling locations sometimes should be revisited due to windy conditions that can stir up the lake bottom. The Chief Scientist should review the results of turbidity measures for Lake Erie to determine if another sampling event should be conducted on the return trip through Lake Erie. *If the average turbidity is more than 4 NTU for the Central basin stations on Lake Erie*, the results may be artifacts of the sediment resuspension and may not accurately reflect the conditions of the water column (see Figure 1). In these cases, the Chief Scientist will, if possible, collect additional samples for the full suite of analyses during the return trip through Lake Erie.

Chapter 2: Nutrient Parameters

LG 212 – *Standard Operating Procedure for Nutrient Sample Processing*

1) Updated this entire chapter to include the new filter board which now has 4 filter stations instead of 3.
2) Removed all references of cubitainers and replaced them with "one-half gallon plastic (HPDE) containers.
3) Removed section 3.5 "The labels for nutrient samples are bar-coded so that they can be tracked and loaded into the Lachat Auto-analyzer automatically."
4) Changed Section 4.2 from "5 psi" to "5 inHg (never to exceed 7 inHg) with inline".

Chapter 4: Biological Parameters

LG 401 – *Standard Operating Procedure for Phytoplankton Analysis*

1) Added the following sentence as 6.1:

   6.1 Phytoplankton sample received at the lab shall be logged-in and spiked with 10 ml of Formalin.
2) Re-numbered the rest of section 6 to follow (e.g. 6.2, 6.3 etc.) the new 6.1.

LG 407 – *Benthic Invertebrate Laboratory Procedures*

1) Formatting and editing through out document.
2) Added the following to section 9.2.1

   Samples containing fingernail clams (*Sphaeriidae)* will be given special attention during the training process and the random QA/QC checks. Their small size (some appear as large sand grains) and resistance to stain (some appear translucent) cause them to sometimes be overlooked.

Chapter 5: Board Chemistry Parameters

LG 500 – *Standard Operating Procedure for GLNPO Board Analyses*

1) Updated Sections 6.2 – 6.3.4, "Reagents" Method changes for Conductivity and Turbidity Standards
2) Updated Sections 7.1 Conductivity calibration additional steps were added to properly calibrate the conductivity meter.
3) Corrected 7.2 and 7.3 the pH meter names were switched for pH and alkalinity calibration
4) Updated 7.4 Turbidity calibration for new instrument(HACH Model 2100N Laboratory Turbidimeter)
5) Updated table in section 10.3 "Conductivity" with new values for High and Low check standards and new acceptance criteria.
6) Updated Section 8.2.2 and 8.2.3 to now read as:

   8.2.2 A fresh aliquot is then poured into the conductivity beaker so that the beaker is full to within ¼ inch of the top. The beaker is then placed on the conductivity apparatus and temperature raised to 25.0°C ± 1°C while the stirrer is operating to produce rapid circulation without breaking the surface of the sample.

8.2.3 When the temperature and conductivity readings are stable (this may take some time) at 25.0°C ± 1°C, the conductivity is recorded, and the pH electrode is inserted into the sample. Do not attempt to determine the pH of reagent water (i.e., the field blank).

LG 501 – *Standard Operating Procedure for Dissolved Oxygen Micro Method,Winkler Titration*

1) Updated section 8. "Calibration" with italicized words:

8.2.1 Prepare a saturated (with oxygen) water sample by vigorously shaking (10 - 15 times) a rigid plastic 960- mL bottle half full of reagent water or sample water. Obtain a barometer reading and measure the temperature of the saturated water. The following table can be used to obtain the mg/L DO at 760 mm Hg. *The barometric pressure displayed in the multi purpose wet lab on the Lake Guardian is the true barometric pressure and requires no correction*. The barometer reading in inches of mercury can be converted to millimeters by multiplying by 25.4, from millibars to millimeters of mercury, multiply by 0.75006.

2) Updated first sentence of Section 7.2 from:

Within ten minutes, using the propipetors, add 0.4 mL of the manganous sulfate solution, followed by 0.4 mL of the *alkaline iodide-azide solution (6.2)* allowing the solutions to run down the neck of the bottle.

TO NOW READ AS...

Within ten minutes, using the propipetors, add 0.4 mL of the manganous sulfate solution, followed by 0.4 mL of the *alkaline iodide solution (6.3)* allowing the solutions to run down the neck of the bottle.

3) Removed the following note from the beginning of Section 9:

Note: In 2003, Winkler analyses were performed by two similar procedures, the only difference being that with one procedure the DO reagent #2 contained azide and with the other procedure, reagent #2 did not contain azide. Each sample was processed using both procedures and the results were analyzed to determine the effects of azide versus non-azide in the fixing solution to hold the DO. Upon completion of this study, it was determined that there was no difference in using an azide-containing fixing solution, therefore, DO reagents that do not contain azide will be used hence forth.

Appendix A – Great Lakes Maps

1) Added new maps with fish stations for each lake

Appendix B – *Quality Assurance Project Plan for the Great Lakes Water Quality Surveys*

1) Updated QAPP to reflect all SOP revisions discussed above
2) Updated Attachment A, "Monitoring Stations and Depths," to include fish stations and changed Approximate station depth for SU01 from 130M to 95M.
3) Updated QAPP table 11.3 with new performance criteria for conductivity
4) Updated Section 19.0 "Data Verification and Validation"

Lake Erie

Spring	
Non-Master Station	**Master Station**
SRF	SRF
MID	5M
B10 (only Eastern Basin)	10M
B1	20M (only Eastern Basin)
INT-SPR	30M (only Eastern Basin)
	40M (only Eastern Basin)
	B10 (only Eastern Basin)
	B1
	INT-SPR

Exceptions to this Sampling Scheme:
Exceptions to this sampling scheme may occur depending upon the thermal structure at the time of sampling. These exceptions do not apply to the integrated samples. To eliminate sampling redundancy, the following specifications apply to the sampling regime:

- If an integer meter depth falls within 2 m of B10, then the integer meter depth sample is omitted.
- If B10 falls within 2 m of a stratification depth, the B10 sample is omitted.
- If an integer meter depth falls within 3 m of a stratification depth, the integer meter depth sample is omitted.
- In the summer, if there is a DCL, a sample is taken (at non-master and master stations in the Eastern basin and at non-master stations in the Central and Western basins). If other designated samples are within 3 meters of the DCL, they are not taken.

Integrated Sample Definition:
For an unstratified water column, the integrated sample is prepared by taking equal volumes of water from SRF, 5 m, 10 m and 20 meters unless the depth is less than 20 meters. If the total depth is between 15 and 22 meters, the 20 meter sample is replaced by the bottom sample (B1 or B2). If the total depth is less than 15 meters, equal volumes are taken from surface, mid-depth, and bottom sample (B1 or B2).

Lake Michigan, Lake Huron, Lake Ontario, Lake Superior

Spring	
Non-Master Station	**Master Station**
SRF	SRF
MID	5M
B10	10M
B2	20M
INT-SPR	30M
	40M
	50M
	100
	200
	B10
	B2
	INT-SPR

Exceptions to this Sampling Scheme:
Exceptions to this sampling scheme may occur depending upon the thermal structure at the time of sampling. These exceptions do not apply to the integrated samples. To eliminate sampling redundancy, the following specifications apply to the sampling regime:

- If an integer meter depth falls within 2 m of B10, then the integer meter depth sample is omitted.
- If B10 falls within 2 m of a stratification depth, the B10 sample is omitted.
- If an integer meter depth falls within 3 m of a stratification depth, the integer meter depth sample is omitted.
- In the summer, if there is a DCL, a sample is taken. If other designated samples are within 3 meters of the DCL, they are not taken.
- If the UHY sample is between 37 m and 47 m, the 40 m sample is not taken.

Integrated Sample Definition:
For an unstratified water column, the integrated sample is prepared by taking equal volumes of water from SRF, 5 m, 10 m and 20 meters unless the depth is less than 20 meters. If the total depth is between 15 and 22 meters, the 20 meter sample is replaced by the bottom sample (B1 or B2). If the total depth is less than 15 meters, equal volumes are taken from surface, mid-depth, and bottom sample (B1 or B2).

For a stratified water column, equal volumes are taken from the surface, 5 m, 10 m, and LEP. If the epilimnion is very shallow, equal volumes are taken from a maximum of four sampling depths and a minimum of two sampling depths. The underlying strategy is to collect a representative sample from the epilimnion.

Appendix D – D.O. QAPP

1) Changed "Revision 02, December 2002" to "Revision 03, January 2007"
2) Updated inside cover from "December 2002" to "January 2007"
3) Updated inside cover from "Revision 02" to "Revision 03"
4) Updated the Table of Contents
5) Updated Headers and Footers
6) Deleted the word "be" from the last line in Section A2 on page 1.
7) Updated the dates in the last paragraph in A4 – Project Summary, from "U.S. EPA Great Lakes National Program Office (1991-1993, 1997-1999, 2001-2002)" to "U.S. EPA Great Lakes National Program Office (1991-1993, 1997-1999, 2001-2006)".
8) Updated the last sentence in A4 – Sampling Procedure Summary, from (see Attachment 4, *Standard Operating Procedure for Dissolved Oxygen Micro Method, Winkler Titration*) to (see Attachment 3, *Standard Operating Procedure for Dissolved Oxygen Micro Method, Winkler Titration*).
9) Updated the first paragraph in A4 – Required Records and Reports, from:
   "All data collected in the field will be entered onto a field data sheet (see Attachments 2 and 3) unique to each station visit. Electronic files obtained from the SeaBird instrumentation cluster will be duplicated on site and stored in multiple locations (e.g., hard disk and diskettes). All QA/QC data associated with a station visit will be recorded on the field data sheet or attached to the sheet for convenient audit."
   TO:
   "All data collected in the field will be entered onto a field data sheet (See Attachment 2, *Dissolved Osygen Survey – Lake Erie Central Basin Dissolved Oxygen Data (Winkler)*) unique to each station visit. Electronic files obtained from the SeaBird instrumentation cluster will be duplicated on site and stored in multiple locations (e.g., hard disk and portable memory devices). All QA/QC data associated with a station visit will be recorded on the field data sheet or attached to the sheet for convenient audit."
10) Changed the last sentence of the 2nd paragraph of A5 – Rationale, from:
   "The RPD values are determined from independent measurements taken at or near the surface of the water column and in the hypolimnion 1 meter off the bottom."
   TO:
   "The RPD values for accuracy are determined from independent measurements taken at or near the surface of the water column and in the hypolimnion 1 meter off the bottom. The RPD values for precision are determined from independent SeaBird profiles expressed as an integrated average of hypolimnionic and epilimnionic waters (see B10: Data Management: Calculation of Dissolved Oxygen Depletion Rate)".
11) Changed the reference, "Figure 1" in B1 – Sampling Strategy, to "See Attachment 1, *Dissolved Oxygen survey Stations Lake Erie Basin"*.
12) Updated Station 78's Latitude on Table 1 from "41.97778" to "41.11667" in B1 – Sampling Locations.
13) Changed the last sentence of the 1st paragraph of B1 – Sampling Depths, from:
   "Data from six (6) depths, however, are used in the calculation of dissolved oxygen depletion rate."
   TO:
   "Historically, data from six (6) depths were used in the calculation of the dissolved oxygen depletion rate."
14) Added the following paragraph at the end of B1 – Sampling Depths:
   "An alternate method for calculating the dissolved oxygen depletion rate was introduced in 2005. This technique incorporated the usage of the entire water profile by integrating the continuous temperature and dissolved oxygen profiles."
15) Changed "Attachment 4" in the last sentence of B1 – Water Samples for Winkler Dissolved Oxygen Titrations to "Attachment 3".
16) Changed "0.1°C" in the first sentence of B1 – Surface Temperature to "0.01°C".
17) Changed the first sentence of B2.A – IMB Compatible Computer from:
   "An Intel Pentium-compatible computer is required running MS Windows 95 (or higher version)."
   TO:

"An Intel Pentium-compatible computer is required for running MS Windows operating system."

18) Changed "display and archival of data" in the second sentence of B2.A – IMB Compatible Computer to "display and archiving of data."
19) Changed "Attachment 4" in the last sentence of paragraph 2 in B2.A – Rosette Sampler to "Attachment 3".
20) Changed "Attachment 4" in the first sentence of B2.A – Dissolved Oxygen Sample Bottles and Laboratory Apparatus to "Attachment 3".
21) Added the following paragraph after the first paragraph of B2.C – Deploying the SeaBird 19 or SeaBird 25, Independent of the Rosette Sampler:

    "**Note:** Comparisons of SeaBird 9/11 and SeaBird 25 or SeaBird 19 should be run prior to SeaBird 25 or SeaBird 19 use on an alternate vessel. T-Test statistical comparison ($P \geq 0.05$) should be run for the integrated averages of hypolimnion and epilimnion temperatures and dissolved oxygen values, and hypolimnion thickness (See B10: Data Management: Calculation of Dissolved Oxygen Depletion Rate). If P-values are not statically acceptable alter the SeaBird 25 or SeaBird 19 calibration coefficients such that the temperature and dissolved oxygen profiles are consistent (avoiding the introduction of bias through the use of multiple instruments) and re-run T-test."
22) Split paragraph 7 into 2 paragraphs, the second starting with "Attach the SeaBird".
23) Changed paragraph 16 of B2.C – Deploying the SeaBird 19 or SeaBird 25, Independent of the Rosette Sampler from:

    "Retrieve the SeaBird onto deck. Turn off the switch. Disconnect the safety wire, hydro-wire attachment, and cage extension. Reattach the Tygon tuning to the water inlet for the D.O. sensor and fill it with D.I. water. Bring the SeaBird back into the lab. Position the SeaBird within read of the computer connection cable. Remove the electrical connector's water plug from the SeaBird."

    TO:

    "Retrieve the SeaBird onto deck. <u>Turn off the switch.</u> <u>Reattach the Tygon tubing to the water inlet for the DO sensor and fill it with D.I. water.</u> Position portable notebook computer (computer connector cable) within reach of SeaBird. If portable notebook computer is not available bring the SeaBird back into the lab.

    Remove the electrical connector's water plug from the SeaBird. Attach the computer cable. On the plug and the cable receptacle is a raised dot that marks the location for a larger pin. The raised dot goes to the outside of the cage, parallel to the heavy cross brace."
24) Changed the first sentence of paragraph 1 in B3 – Sample Handling and Custody Requirements from, "All field data forms and computer diskettes will..." to "All field data forms and portable memory devices will..."
25) Changed "Attachment 4" to "Attachment 3" in B4 – Winkler Method for Dissolved Oxygen Concentrations.
26) Changed "Attachment 4" to "Attachment 3" Paragraph 3 of B6 – Instrument / Equipment Testing Inspection and Maintenance Requirements.
27) Changed "See Attachments 2 and 3" in the first sentence of B10 – Data Recording to "See Attachment 2, Dissolved Oxygen Survey – Lake Erie Central Basin Dissolved Oxygen Data (Winkler)".
28) Changed "to diskette" in the second sentence of B10 – Data Recording to "to CD or DVD or memory stick".
29) Changed the 3rd paragraph of B10 – Storing and Backing Up Computer Files from "All SeaBird electronic files will be backed up to 1) to diskette, and 2) to subdirectory on hard disk. All diskettes will be stored in the Offices at GLNPO." To "All SeaBird electronic files will be backed up to 1) CD, DVD and/or memory stick, and 2) subdirectory on hard disk. All portable memory devices will be stored in the Offices at GLNPO."
30) Updated the last two sentences of B10 – Calculation of Dissolved Oxygen Depletion Rate from "the computer program **OXRATES**, written for GLNPO by C. O'Leary (1990), will be used to perform the calculations. Program calculations include:" To "The computer program **OXRATES**, written for GLNPO by C. O'Leary (1990) has been used to perform this calculation. However, beginning in 2005, **LakeErieDOv4.0** (Microsoft Access), written for GLNPO by Computer Sciences Corp, Alexandria, VA was introduced. Annual comparison between these programs will continue through the 2007 sampling season, at which point **LakeErieDOv4.0** (Microsoft Access) will be used exclusively."
31) Added "For **OXRATE**" before "An input" in paragraph 22 of B10 – Calculation of Dissolved Oxygen Depletion Rate.
32) Added the following paragraph to the end of B10 – Calculation of Dissolved Oxygen Depletion Rate:

    "For **LakeErieDOv4.0**, input all data files (.HEX or .DAT) into database, adjusting final upper-hypolimnion if needed. Run "Calculate Oxygen Depletion Rate" function, which integrates the continuous data profile producing a two (2) layer (epilimnion and hypolimnion) temperature and

dissolved oxygen model. See software manual for additional instructions (see Attachment 4, *Lake Erie Dissolved Oxygen Depletion Tool User's Guide*)."

33) Updated the first sentence of C1 – Procedures to be used to Assess Data Precision, Accuracy, and Completeness from "electronically recorded" to "electronically-recorded"
34) Changed "computer hard disk and diskettes" to "computer hard drive and portable memory devices" in C1 – Procedures to be used to Assess Data Precision, Accuracy, and Completeness
35) Changed "Attachment 1" to "Attachment 1 – Dissolved Oxygen Survey Stations - Lake Erie Central Basin".
36) Changed "Attachment 2" to "Attachment 2 – Dissolved Oxygen Survey – Lake Erie Central Basin Dissolved Oxygen Data (Winkler)".
37) Changed "Attachment 3" to "Attachment 3 – Standard Operating Procedure for Dissolved Oxygen Micro Method, Winkler Titration".
38) Changed "alkaline iodide-azide solution (6.2)" in Attachment 3 – 7.2 to "alkaline iodide solution (6.3)".
39) Changed "Attachment A" in Attachment 3 – 8.2.2 to, "Attachment A (Extrapolated Oxygen Sulubility in Water, Increments of 1 and 0.1 Degree Celsius)".
40) Deleted the following note before 9.1 In Attachment 3:

    "**Note:** In 2003, Winkler analyses were performed by two similar procedures, the only difference being that with one procedure the DO reagent #2 contained azide and with the other procedure, reagent #2 did not contain azide. Each sample was processed using both procedures and the results were analyzed to determine the effects of azide versus non-azide in the fixing solution to hold the DO. Upon completion of this study, it was determined that there was no difference in using an azide-containing fixing solution, therefore, DO reagents that do not contain azide will be used hence forth."
41) Deleted Paragraph 10.4 of Attachment 3.
42) Added "Attachment 4 – GLNPO's Open Lake Survey of the Great Lakes – Lake Erie Dissolved Oxygen Depletion Tool User's Guide" after "Attachment 3".
43) Added "Attachment A – Extrapolated Oxygen Solubility in Water, by 1 and 0.1 Degree Celsius" after "Attachment 4".

Appendix H – Field Information Recording Forms

1) Deleted "Calibration Data of Board Chemistry Instruments *Shiftwise Standardization"* Form.
2) On the "Calibration Data of Board Chemistry Instruments" Form, #3 under notes was changed from "Calibration values of pH, Alkalinity & Turbidity meters should be updated w/ Stds. pH 7(pH), pH 4(Alkalinity) & 20 NTU(Turbidity) at the beginning of each shift" to "Calibration values of pH & Alkalinity meters should be updated w/ Stds. pH 7(pH) and pH 4(Alkalinity) at the beginning of each shift".

Appendix L – Chief Scientist Roles and Responsibilities

1) Removed "and turbidity" from the 1st checkbox.