

DRAFT INTERIM QUALITY ASSURANCE PROJECT PLAN

GREAT LAKES SURVEY STUDIES OF LAKES MICHIGAN
HURON, ERIE, ONTARIO, AND SUPERIOR
APRIL 1992 THROUGH FEBRUARY 1993

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Great Lakes National Program Office
Great Lakes Studies
Survey Plan
Lakes Michigan, Huron, Erie, Ontario, and Superior

| | |
|-------------------|---|
| Limnology Program | April 1992-February 1992 |
| Survey | Dates April, August |
| Region | Lakes Michigan, Huron, Erie, Ontario and Superior |
| Vessel | <u>R/V Lake Guardian</u> |
| Master | Captain R. Ingram |
| Agency | United States Environmental Protection Agency |
| Chief Scientist | Dr. G.J. Warren |
| Chief Chemist | Mr. M.F. Palmer |
| Chief Biologist | Dr. P.E. Bertram |
| Date of Issue | March |

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1.0 PROJECT DESCRIPTION

1.1 Relevance of Water Quality Monitoring Program

Great Lakes water quality monitoring is needed to measure and evaluate indicators of Great Lakes Ecosystem Health. Monitoring surveys are conducted to sample biological, chemical and physical parameters which lead to an understanding of the current state of the ecosystem. As an integral part of Great Lakes EMAP, data from the water quality surveys will contribute to the evaluation of the state of the environment on a regional and national basis. The long-term data record compiled by GLNPO from past surveys allows an evaluation of the degree of success of past regulatory actions. In a historical context, the water quality surveys provide data to evaluate the degree to which the objectives of the Canada - U.S. 1978 Great Lakes Water Quality Agreement are being achieved, particularly relating to phosphorus. This program will conduct limited surveillance of Lakes Michigan, Huron, Erie, Ontario, and Superior.

1.2 Purpose

The purpose of this surveillance program is to collect biological, chemical and physical water quality data for use in evaluating the ecosystem health of the Great Lakes, and to establish a long term information data base on water quality changes in the Lakes.

1.3 Survey Outline

Limnology Program Cruise Outline

Survey Approximate Date

| | |
|---------------------|--|
| 1 April | Spring conditions - pre stratification |
| 2 August(tentative) | Stratified period |

The spring survey is important in assessing the initial conditions in nutrient levels and their annual variance from year to year. A summer survey will measure conditions during a biologically active period under thermally stratified conditions.

1.4. Project Schedule

The R/V Lake Guardian is scheduled for approximately 35 days of 24-hour operations. Expected sampling time, running time between stations, waste disposal and reprovisioning the ship with fuel and supplies will vary depending on wind, wave, and availability of services when the ship is in port.

The plan is to complete a transit of the track from Bay City, MI through Lakes Erie and Ontario, returning through Lakes Erie, Huron and Michigan. (Tables 1-1 to 1-4, Figures 1-1 to 1-4). After a delay to accomodate ice dispersal, Lake Superior will be sampled. Expected time to complete the first segment of the sampling is 25 days: Lake Superior expected time, including transit is approximately 14 day. This is based on 11 knots sailing speed, 1 to 4 hour sampling time on station, 24 hours to transit interconnecting channels, 24 hours between lakes to complete analytical work, 12 to 24 hours to refuel and reprovision the R/V Lake Guardian two to three times per survey. Additional days estimated at 25% of sailing days may be needed due to adverse weather conditions.

1.5. Vessel

The R/V Lake Guardian is a former offshore oil field supply vessel built by Halter Marine, Moss Point, MS, in 1981. The ship's dimensions are: length - 180', beam - 40', draft - 11', displaced tonnage - 850 tons. Propulsion is twin screws enclosed in Kort nozzles and driven by 1200 hp Caterpillar diesel engines. Cruising speed is 11 knots, range is 6000 miles.

1.6. Station Selection

The locations of the stations in the four lakes (Tables 1-1 to 1-5 and Figures 1-1 to 1-5) are selected from sites within homogeneous areas of the lakes. These sites are also part of the Great Lakes International Surveillance Program. Additional stations in Lake Michigan, and the stations to be sampled in Lake Superior are those from the EMAP base grid. EMAP stations will be the permanent stations for Lake Superior. Determination of future (post 1992) stations for the lower four lakes is dependent on the evaluation of GLNPO/EMAP grid comparison.

Ref Experience on Lake Michigan, Lake Erie, Lake Huron and Lake Ontario shows that spatial variation in open lake waters, (beyond 13 KM from shore, and in deep water > 30M in depth) is not great compared to nearshore spatial variation.

Core stations have been selected in each major lake basin: Southern Lake Michigan station 18, mid-Lake Michigan station

27, Northern Lake Michigan station 41, Northern Lake Huron stations 43 and 45, Southern Lake Huron stations 15 and 93, Western Lake Erie station 91, Central Lake Erie station 78, Eastern Lake Erie station 15, Western Lake Ontario station 33, and Eastern Lake Ontario station 55.

The core stations represent the deepest points within the basin amongst the selected stations. At regular depths, the thermal and chemical structure will be monitored in detail to better characterize the vertical conditions during the survey.

1.7 Dry Run & Shakedown Cruise

A dry run of the ship laboratory will be performed prior to the ship leaving port. At this time the scientific crew will install the analytical equipment. Contract personnel will demonstrate QC proficiency by analyzing check standards after calibrating the analytical instruments using set standards and demonstrating each analytical system is in control (for out of control situations see section 13). A series of stations from Saginaw Bay (Table 1-6 - Figure 1-6) will be used for shakedown purposes. Water samples will be taken at these stations, and the water analyzed for all usual water quality parameters.

1.8 Site & Depth Selection

Loran C will be used for navigation in locating the stations and in recording drift of the ship while nominally "on station." Radar will be used as the primary system for determining position. In the event that the Loran C and Radar indicate different positions, the Radar will be used to position the vessel and readings from the Loran C will be recorded until the discrepancy can be corrected.

Tables 1-6A through 1-11A give approximate depths for chemical sampling during unstratified (isothermal conditions) and Tables 1-6B through 1-11B give approximate depths for chemical sampling during stratified conditions for Lake Michigan, Lake Huron, Lake Erie, Lake Ontario, and Saginaw Bay, respectively.

For Lakes Michigan, Huron, Ontario, and Superior, unstratified or isothermal sampling depths for normal stations are surface, (1M) mid-depth, and 2 meters from the bottom (B-2). Unstratified sampling depths for Lake Erie are surface (1M), mid-depth, and 1 meter from the bottom (B-1). Samples at core stations will be more frequent through the water column.

During stratified conditions, sampling depths for normal stations in Lakes Michigan, Huron, Ontario, and Superior are surface (1M), lower epilimnion 1 meter above the knee (LE), thermocline (T), upper hypolimnion 1M below the knee (UH), B-10, and B-2. Where water depth is sufficient, samples will

also be taken at 100M and 200M. For Lake Erie, sampling depths during stratified conditions are surface (1M), mid-epilimnion (ME), lower epilimnion 1M above the knee (LE), thermocline (T), upper hypolimnion 1M below the knee (UH), mid-hypolimnion (MH), and 1 meter from bottom (B-1).

Phytoplankton will be from a composite of equal volumes from depths of 1, 5, 10, and 20 meters hereafter referred to as the "integrated sample" for all stations. (See discussion on phytoplankton for more details.) When regular sampling depths do not fall within 3 meters of integrated sample depths, samples will be collected at the appropriate depths for use in the composite or "integrated" samples only.

Zooplankton sampling shall be vertical tows from B-2 to the surface, and from 20M to the surface.

Table 1-1
Lake Michigan Plan

| Station | Latitude/Longitude | Approx. Depth (m) | Est. No. of Samples Unstratified/Stratified | Distance Between Sites (KM) |
|---------|--------------------|----------------------|--|-----------------------------------|
|---------|--------------------|----------------------|--|-----------------------------------|

Straits of Mackinac to Milwaukee

| | | | | | | | |
|----|-----|----------|----------|-------|----|-----|----|
| 1 | 47 | 45 10 42 | 86 22 30 | 186 | 4 | 11 | |
| 2 | 41C | 44 44 12 | 86 43 18 | 250 | 13 | 13 | 55 |
| 3 | 40 | 44 45 36 | 86 58 00 | 160 | 4 | 11 | 19 |
| 4 | 32 | 44 08 24 | 87 14 00 | 159 | 4 | 11 | 70 |
| 5 | 34 | 44 05 24 | 86 46 00 | 160 | 4 | 11 | 38 |
| 6 | 27C | 43 36 00 | 86 55 00 | 112 | 11 | 11 | 60 |
| 7 | 23 | 43 08 00 | 87 00 00 | 88 | 4 | 11 | 52 |
| 8 | 19 | 42 44 00 | 86 35 00 | 92 | 4 | 10 | 58 |
| 9 | 18C | 42 44 00 | 87 00 00 | 161 | 12 | 12 | 37 |
| 10 | 17 | 42 44 00 | 87 25 00 | 100 | 4 | 10 | 42 |
| 11 | 11 | 42 23 00 | 87 00 00 | 128 | 4 | 11 | 62 |
| | | | | Total | 68 | 122 | |

EMAP Stations

| | | | | | | |
|----|--------|----------|----------|-------|----|--|
| 1 | 780400 | 45 35 44 | 86 03 55 | 101 | 4 | |
| 2 | 781000 | 44 11 37 | 86 29 31 | 110 | 4 | |
| 3 | 781200 | 43 43 31 | 86 41 57 | 92 | 4 | |
| 4 | 781400 | 43 14 24 | 86 53 11 | 110 | 4 | |
| 5 | 781600 | 42 46 15 | 87 05 11 | 156 | 4 | |
| 6 | 781800 | 42 18 04 | 87 17 58 | 97 | 4 | |
| 7 | 812300 | 45 29 33 | 86 31 00 | 92 | 4 | |
| 8 | 812500 | 45 00 27 | 86 44 48 | 190 | 4 | |
| 9 | 812700 | 44 32 20 | 86 56 22 | 180 | 4 | |
| 10 | 812900 | 44 04 11 | 87 09 42 | 135 | 4 | |
| 11 | 813100 | 43 36 01 | 87 21 48 | 135 | 4 | |
| 12 | 813300 | 43 08 48 | 87 33 41 | 135 | 4 | |
| | | | | Total | 48 | |

C designates core stations

Table 1-2
Lake Huron Plan

| Station No. | Latitude/Longitude | | Approx. Depth (m) | Est. No. of Samples Unstratified/Stratified | | Distance Between Sites (KM) |
|-----------------------------------|--------------------|----------|----------------------|--|-----|-----------------------------------|
| Port Huron to Straits of Mackinac | | | | | | |
| 61 | 45 45 00 | 83 55 00 | 120 | 4 | 10 | |
| 54 | 45 31 00 | 83 25 00 | 91 | 4 | 10 | 47 |
| 53 | 45 27 00 | 82 54 54 | 119 | 4 | 10 | 41 |
| 48 | 45 16 42 | 82 27 06 | 115 | 4 | 10 | 31 |
| 45C | 45 08 12 | 82 59 00 | 110 | 11 | 11 | 53 |
| 37 | 44 45 42 | 82 47 00 | 73 | 4 | 10 | 45 |
| 38 | 44 44 24 | 82 03 36 | 137 | 4 | 10 | 27 |
| 32 | 44 27 12 | 82 20 30 | 73 | 4 | 10 | 39 |
| 27 | 44 11 54 | 82 30 12 | 50 | 4 | 10 | 31 |
| 93C | 44 06 00 | 82 07 00 | 91 | 11 | 11 | 31 |
| 15C | 44 00 00 | 82 21 00 | 68 | 11 | 11 | 25 |
| 12 | 43 53 24 | 82 03 24 | 86 | 4 | 10 | 27 |
| 9 | 43 38 00 | 82 13 00 | 57 | 4 | 10 | 32 |
| 6 | 43 28 00 | 82 00 00 | 46 | 4 | 10 | 26 |
| Total | | | | 77 | 102 | |

C designates Core Stations

Table 1-3
Lake Erie Plan

| Station # | Latitude/Longitude | Approx. Depth (m) | Est. No. of Samples Unstratified/Stratified | |
|-------------------------|--------------------|----------------------|--|-----|
| Detroit to Port Colburn | | | | |
| 1 61 | 41 56 48 83 02 42 | 10 | 4 | 11 |
| 2 60 | 41 53 30 83 11 48 | 9.5 | 4 | 11 |
| 3 59 | 41 43 36 83 09 00 | 10 | 4 | 11 |
| 4 58 | 41 41 06 82 56 00 | 11.5 | 4 | 11 |
| 5 91C | 41 50 27 82 55 00 | 10.5 | 7 | 11 |
| 6 92 | 41 57 00 82 41 12 | 11 | 4 | 11 |
| 7 43 | 41 47 18 81 56 42 | 23 | 4 | 11 |
| 8 42 | 41 57 54 82 02 30 | 22 | 4 | 11 |
| 9 73 | 41 58 40 81 45 25 | 24 | 4 | 11 |
| 10 36 | 41 56 06 81 28 42 | 23 | 4 | 11 |
| 11 37 | 42 06 36 81 34 30 | 24 | 4 | 11 |
| 12 38 | 42 16 54 81 40 18 | 22 | 4 | 11 |
| 13 78C | 42 07 00 81 15 00 | 23 | 7 | 11 |
| 14 32 | 42 04 54 81 00 42 | 22 | 4 | 11 |
| 15 31 | 42 15 12 81 06 24 | 21 | 4 | 11 |
| 16 30 | 42 25 48 81 12 18 | 21 | 4 | 11 |
| 17 63 | 42 25 00 79 48 00 | 45 | 4 | 11 |
| 18 15C | 42 31 00 79 53 36 | 60 | 12 | 12 |
| 19 10 | 42 40 48 79 41 30 | 32 | 4 | 11 |
| 20 9 | 42 32 18 79 37 00 | 47 | 4 | 11 |
| Total | | | 94 | 221 |

Port Colburn to Detroit
Reverse of above station order

C designates Core Stations

Table 1-4
Lake Ontario Plan

| Station # | | Latitude/Longitude | | Approx. Depth (m) | Est. No. of Samples Unstratified/Stratified | |
|--------------------------|-----|--------------------|----------|----------------------|--|-----------|
| Port Weller to Rochester | | | | | | |
| 1 | 12 | 43 30 12 | 79 21 12 | 98 | 4 | 10 |
| 2 | 25 | 43 31 00 | 79 04 48 | 133 | 4 | 11 |
| 3 | 33C | 43 35 48 | 78 48 06 | 131 | 12 | 12 |
| 4 | 41 | 43 43 00 | 78 01 36 | 122 | 4 | 11 |
| 5 | 49 | 43 46 18 | 77 26 18 | 50 | 4 | 10 |
| 6 | 63 | 43 43 54 | 77 01 00 | 82 | 4 | 10 |
| 7 | 60C | 43 34 48 | 77 12 00 | 133 | 12 | 12 |
| 8 | 55 | 43 26 36 | 77 26 18 | 183 | 4 | 11 |
| | | | | Total | <u>48</u> | <u>97</u> |

C designates Core Stations

Table 1-5
Lake Superior Plan

| Station | Latitude/Longitude | Approx. Depth (m) | Est. No. of Samples Unstratified/Stratified | Distance Between Sites (KM) |
|---------|--------------------|----------------------|--|-----------------------------------|
| | | | | |
| 779800 | 46 59 35 85 09 40 | 130 | 4 | |
| 811500 | 47 21 38 85 37 14 | 185 | 4 | |
| 811700 | 46 53 40 85 51 05 | 160 | 4 | |
| 843800 | 47 15 33 84 20 54 | 185 | 4 | |
| 844000 | 46 46 29 86 33 20 | 130 | 4 | |
| 875900 | 48 33 31 86 22 37 | 165 | 4 | |
| 876100 | 48 04 27 86 35 29 | 185 | 4 | |
| 876300 | 47 36 21 86 49 04 | 284 | 4 | |
| 909000 | 48 26 12 87 05 10 | 175 | 4 | |
| 909400 | 47 30 51 86 32 46 | 130 | 4 | |
| 942500 | 48 20 37 87 49 31 | 230 | 4 | |
| 942700 | 47 51 22 88 02 31 | 250 | 4 | |
| 976400 | 48 13 47 88 32 40 | 150 | 4 | |
| 976600 | 47 44 27 88 44 15 | 210 | 4 | |
| 1010700 | 48 06 41 89 15 37 | 185 | 4 | |
| 1010900 | 47 37 17 89 27 47 | 185 | 4 | |
| 1011100 | 49 09 52 89 39 43 | 205 | 4 | |
| 1045600 | 47 30 52 90 09 07 | 135 | 4 | |
| 1080700 | 47 22 13 90 51 14 | 190 | 4 | |

Table 1-6
Lake Huron
Saginaw Bay Plan

| Station # | Latitude/Longitude | Approx. Depth (m) | Est. No. of Samples Unstratified/Stratified |
|-----------|--------------------|----------------------|--|
| 1 | 43 52 30 83 40 00 | 3 | |
| 2 | 44 07 30 83 20 00 | 3 | |

Any scheduled depth between 5 and 30 meters will be altered to determine conditions during the stratified period if it is within 3 meters of the thermocline depth.

Table 1-6A
Lake Michigan Sampling Depths (Unstratified)
(April, October, February, March)

| Station # | Surface | Estimated Sampling Depths in Meters | | B-10 | B-2 | Maximum Number of Samples+ |
|-----------|---------|--|--|------|-----|-------------------------------|
| | | Mid-depth | | | | |
| 11 | 1 | 64 | | 118 | 126 | 5 |
| 17 | 1 | 50 | | 90 | 98 | 5 |
| 18* | 1 | 5,10,20,30,40,50,100 | | 151 | 159 | 11 |
| 19 | 1 | 46 | | 82 | 90 | 5 |
| 23 | 1 | 64 | | 118 | 126 | 5 |
| 27* | 1 | 5,10,20,30,40,50 | | 102 | 110 | 10 |
| 32 | 1 | 79.5 | | 149 | 157 | 5 |
| 34 | 1 | 80 | | 150 | 158 | 5 |
| 40 | 1 | 80 | | 150 | 158 | 5 |
| 41* | 1 | 5,10,20,30,40,50,100,200 | | 240 | 248 | 12 |
| 47 | 1 | 92.5 | | 175 | 183 | 5 |
| 780400 | 1 | Other Depths To Be Determined | | | | 5 |
| 781000 | 1 | on Station | | | | 5 |
| 781200 | 1 | | | | | 5 |
| 781400 | 1 | | | | | 5 |
| 781600 | 1 | | | | | 5 |
| 781800 | 1 | | | | | 5 |
| 812300 | 1 | | | | | 5 |
| 812500 | 1 | | | | | 5 |
| 812700 | 1 | | | | | 5 |
| 812900 | 1 | | | | | 5 |
| 813100 | 1 | | | | | 5 |
| 813300 | 1 | | | | | 5 |

*Core stations are 18, 27, 41.

+In each basin, a station and depth will be randomly selected for field duplicate sampling (2 Niskin samples taken from the same depth). A second station will be randomly selected for field blank analysis. These field quality control samples will result in three duplicates and three field blanks for analysis. A laboratory split (duplicate) of a sample from a randomly chosen depth will be analyzed at each station. An integrated sample is included in sample total.

Table 1-6B

Lake Michigan Sampling Depths (Stratified)
August

Estimated Sampling Depths in Meters

| | | | | | | Maximum |
|---------------------|---------|---|---------|-----|-------------|---------|
| Number Station # | Surface | Thermocline | B-10 | B-2 | of Samples+ | |
| 11 | 1 | LE,T,UH | 100 | 118 | 126 | 8 |
| 17 | 1 | LE,T,UH | | 90 | 98 | 7 |
| 18* | 1 | 5,(10 or LE),(20 or T),(30 or UH),40,50 | 100 | 151 | 159 | 11 |
| 19 | 1 | LE,T,UH | | 82 | 90 | 7 |
| 23 | 1 | LE,T,UH | 100 | 118 | 126 | 8 |
| 27* | 1 | 5,(10 or LE),(20 or T),(30 or UH),40,50 | | 102 | 110 | 10 |
| 32 | 1 | LE,T,UH | 100 | 149 | 157 | 8 |
| 34 | 1 | LE,T,UH | 100 | 150 | 158 | 8 |
| 40 | 1 | LE,T,UH | 100 | 150 | 158 | 12 |
| 41* | 1 | 5,(10 or LE),(20 or T),(30 or UH),40,50 | 100,200 | 240 | 248 | 13 |
| 47 | 1 | LE,T,UH | 100 | 175 | 183 | 8 |

*Core stations are 18, 27, and 41. Any regularly scheduled depth at a core station closest to a thermocline depth sample will be replaced by the appropriate thermocline depth sample. Any regularly scheduled B-10 depth sample within 3 meters of a thermocline depth sample will be omitted.

++In each basin, a station and depth will be randomly selected for field duplicate sampling (2 Niskin samples taken from the same depth). A second station will be randomly selected for field blank analysis. These field quality control samples will result in three duplicates and three field blanks for analysis. A laboratory split (duplicate) of a sample from a randomly chosen depth will be analyzed at each station. An integrated sample is included in sample total.

Table 1-7A
Lake Huron Sampling Depths (Unstratified)
(April, October, February, March)

| Station # | Surface | Mid-depth | B-10 | B-2 | Maximum Number of Samples+ |
|-----------|---------|------------------|------|-----|-------------------------------|
| 6 | 1 | 23 | 36 | 44 | 5 |
| 9 | 1 | 28.5 | 47 | 55 | 5 |
| 12 | 1 | 43 | 78 | 84 | 5 |
| 15* | 1 | 5,10,20,30,40,50 | 58 | 66 | 10 |
| 27 | 1 | 25 | 40 | 48 | 5 |
| 32 | 1 | 36.5 | 63 | 71 | 5 |
| 37 | 1 | 36.5 | 63 | 71 | 5 |
| 38 | 1 | 68.5 | 127 | 135 | 5 |
| 45* | 1 | 5,10,20,30,40,50 | 100 | 108 | 10 |
| 48 | 1 | 57.5 | 105 | 113 | 5 |
| 53 | 1 | 45.5 | 109 | 117 | 5 |
| 54 | 1 | 59.5 | 81 | 89 | 5 |
| 61 | 1 | 21 | 110 | 118 | 5 |
| 93* | 1 | 45 | 81 | 89 | 5 |

*Core stations are 15, 45 and 93.

++In each basin, a station and depth will be randomly selected for field duplicate sampling (2 Niskin samples taken from the same depth). A second station will be randomly selected for field blank analysis. These field quality control samples will result in three duplicates and three field blanks for analysis. A laboratory split (duplicate) of a sample from a randomly chosen depth will be analyzed at each station. An integrated sample is included in sample total.

Table 1-7B
Lake Huron Sampling Depths (Stratified)
August

| Station # | Surface | Thermocline | B-10 | B-2 | Maximum Number of Samples* |
|-----------|---------|--------------------------------|------|-----|-------------------------------|
| 6 | 1 | LE,T,UH | 36 | 44 | 10 |
| 9 | 1 | LE,T,UH | 47 | 55 | 10 |
| 12 | 1 | LE,T,UH | 78 | 84 | 10 |
| 15* | 1 | 5,(10,LE),(20,T),(30,UH) 40,50 | 58 | 66 | 11 |
| 27 | 1 | LE,T,UH | 40 | 48 | 10 |
| 32 | 1 | LE,T,UH | 63 | 71 | 10 |
| 37 | 1 | LE,T,UH | 63 | 71 | 10 |
| 38 | 1 | LE,T,UH | 127 | 135 | 10 |
| 45* | 1 | 5,(10,LE),(20,T),(30,UH) 40,50 | 100 | 108 | 11 |
| 48 | 1 | LE,T,UH | 105 | 113 | 10 |
| 53 | 1 | LE,T,UH | 109 | 117 | 10 |
| 54 | 1 | LE,T,UH | 81 | 89 | 10 |
| 61 | 1 | LE,T,UH | 110 | 118 | 10 |
| 93* | 1 | 5,(10,LE),(20,T),(30,UH) 40,50 | 81 | 89 | 11 |

*Core stations are 15, 45, and 93. Any regularly scheduled depth at a core station closes to a thermocline depth sample will be replaced by the appropriate thermocline depth sample. Any regularly scheduled B-10 depth sample within 3 meters of a thermocline depth sample will be omitted. Total number of samples between 1M and 100M will be six samples.

+At random stations a depth will be randomly selected for quality control work consisting of a duplicate Niskin bottle sampling, and a field blank. An integrated sample is included in sample total. At each station a lab split of a randomly chosen depth will be done. Total number of field duplicates and field blanks will result in two analysis each run in Lake Huron. Over the entire survey the total number of field duplicates and field blanks will result in four analysis for each in Lake Huron. There will be at least one field duplicate and one field blank per run in each basin.

Table 1-8A
Lake Erie Sampling Depths (Unstratified)
April, October, February, March)

Estimated Sampling Depths in Meters

| Station # | Surface | Mid-depth | B-10 | B-1 | Maximum Number of Samples+ |
|-----------|---------|-------------------|------|------|-------------------------------|
| 09 | 1 | 20 | 38 | 46 | 5 |
| 10 | 1 | 20 | | 31 | 5 |
| 15* | 1 | 5, 10, 20, 30, 40 | 51 | 59 | 9 |
| 30 | 1 | 10.5 | | 20 | 5 |
| 31 | 1 | 10.5 | | 20 | 5 |
| 32 | 1 | 11 | | 21 | 5 |
| 36 | 1 | 11.5 | | 22 | 5 |
| 37 | 1 | 12 | | 23 | 5 |
| 38 | 1 | 11 | | 21 | 5 |
| 42 | 1 | 11 | | 21 | 5 |
| 43 | 1 | 11.5 | | 22 | 5 |
| 58 | 1 | 5.5 | | 10.5 | 5 |
| 59 | 1 | 4.5 | | 9 | 5 |
| 60 | 1 | 5 | | 8.5 | 5 |
| 61 | 1 | 5 | | 9 | 5 |
| 63 | 1 | 20 | 36 | 44 | 5 |
| 73 | 1 | 12 | | 23 | 5 |
| 78* | 1 | 5, 10 | | 22 | 6 |
| 91* | 1 | 5 | | 9.5 | 5 |
| 92 | 1 | 5 | | 10 | 5 |

*Core stations are 15, 91, and 78

++In each basin, a station and depth will be randomly selected for field duplicate sampling (2 Niskin samples taken from the same depth). A second station will be randomly selected for field blank analysis. These field quality control samples will result in three duplicates and three field blanks for analysis for each run (a total of six each for the entire survey). A laboratory split (duplicate) of a sample from a randomly chosen depth will be analyzed at each station. An integrated sample is included in sample total.

Table 1-8B
Lake Erie Sampling Depths (Stratified)
(August)

Estimated Sampling Depths in Meters

| Station # | Surface | Thermocline | B-1 | Maximum Number of Samples+ |
|-----------|---------|-------------------|------|-------------------------------|
| 09 | 1 | ME, LE, T, UH, MH | 46 | 8 |
| 10 | 1 | ME, LE, T, UH, MH | 31 | 8 |
| 15* | 1 | 5, 10, 20, 30, 40 | 59 | 9 |
| 30 | 1 | ME, LE, T, UH, MH | 20 | 8 |
| 31 | 1 | ME, LE, T, UH, MH | 20 | 8 |
| 32 | 1 | ME, LE, T, UH, MH | 21 | 8 |
| 36 | 1 | ME, LE, T, UH, MH | 22 | 8 |
| 37 | 1 | ME, LE, T, UH, MH | 23 | 8 |
| 38 | 1 | ME, LE, T, UH, MH | 21 | 8 |
| 42 | 1 | ME, LE, T, UH, MH | 21 | 8 |
| 43 | 1 | ME, LE, T, UH, MH | 22 | 8 |
| 58 | 1 | ME, LE, T, UH, MH | 10.5 | 8 |
| 59 | 1 | ME, LE, T, UH, MH | 9 | 8 |
| 60 | 1 | ME, LE, T, UH, MH | 8.5 | 8 |
| 61 | 1 | ME, LE, T, UH, MH | 9 | 8 |
| 63 | 1 | ME, LE, T, UH, MH | 44 | 8 |
| 73 | 1 | ME, LE, T, UH, MH | 23 | 8 |
| 78* | 1 | 5, 10 | 22 | 5 |
| 91* | 1 | 5 | 9.5 | 4 |
| 92 | 1 | ME, LE, T, UH, MH | 10 | 8 |

*Core stations are 15, 91, and 78. Any regularly scheduled depth at a core station closest to a thermocline depth sample will be replaced by the appropriate thermocline depth sample. If thermal structure is configured such that there is less than 3M between sample depths, keep sample depths at LE, T, UH.

+In each basin, a station and depth will be randomly selected for field duplicate sampling (2 Niskin samples taken from the same depth). A second station will be randomly selected for field blank analysis. These field quality control samples will result in three duplicates and three field blanks for analysis for each run (a total of six each for the entire survey). A laboratory split (duplicate) of a sample from a randomly chosen depth will be analyzed at each station. An integrated sample is included in sample total.

Table 1-9A
Lake Ontario Sampling Depths (Unstratified)
(April, October, February March)

| Station # | Estimated Sampling Depths in Meters | | | | Maximum Number of Samples |
|-----------|-------------------------------------|----------------------|------|-----|------------------------------|
| | Surface | Mid-depth | B-10 | B-2 | |
| 12 | 1 | 49 | 88 | 96 | 5 |
| 25 | 1 | 66 | 123 | 131 | 5 |
| 33* | 1 | 5,10,20,30,40,50,100 | 121 | 129 | 11 |
| 41 | 1 | 61 | 112 | 120 | 5 |
| 49 | 1 | 25 | 40 | 48 | 5 |
| 55* | 1 | 5,10,20,30,40,50,100 | 173 | 181 | 11 |
| 60 | 1 | 66.5 | 123 | 131 | 5 |
| 63 | 1 | 41 | 72 | 80 | 5 |

*Core stations are 33 and 55.

+In each basin, a station and depth will be randomly selected for field duplicate sampling (2 Niskin samples taken from the same depth). A second station will be randomly selected for field blank analysis. These field quality control samples will result in three duplicates and three field blanks for analysis. A laboratory split (duplicate) of a sample from a randomly chosen depth will be analyzed at each station. An integrated sample is included in sample total.

Table 1-98
Lake Ontario Sampling Depths (Stratified)
(August)

| Station # | Estimated Sampling Depths in Meters | | | | Maximum Number of Samples+ |
|-----------|-------------------------------------|-----------------------------------|------|-----|-------------------------------|
| | Surface | Thermocline | B-10 | B-2 | |
| 12 | 1 | LE,T,UH | 88 | 96 | 10 |
| 25 | 1 | LE,T,UH | 123 | 131 | 10 |
| 33* | 1 | 5,(10,LE),(20,T),(30,UH)40,50,100 | 121 | 129 | 12 |
| 41 | 1 | LE,T,UH | 112 | 120 | 10 |
| 49 | 1 | LE,T,UH | 40 | 48 | 10 |
| 55* | 1 | 5,(10,LE),(20,T),(30,UH)40,50,100 | 173 | 181 | 12 |
| 60 | 1 | LE,T,UH | 123 | 131 | 10 |
| 63 | 1 | LE,T,UH | 72 | 80 | 10 |

*Core stations are 33 and 55. Any regularly scheduled depth at a core station closest to a thermocline depth sample will be replaced by the appropriate thermocline depth sample. Any regularly scheduled B-10 depth sample within 3 meters of a thermocline depth sample will be omitted. The total number of samples between 1M and 100M will be six samples.

+In each basin, a station and depth will be randomly selected for field duplicate sampling (2 Niskin samples taken from the same depth). A second station will be randomly selected for field blank analysis. These field quality control samples will result in three duplicates and three field blanks for analysis. A laboratory split (duplicate) of a sample from a randomly chosen depth will be analyzed at each station. An integrated sample is included in sample total.

Table 10-A
Lake Superior Sampling Depths (Unstratified)
(April)

Sampling Depths in Meters

| Station # | Surface | B-10 | B-2 | Maximum Number of Samples |
|-----------|---------|---|-----|------------------------------|
| 779800 | 1 | Other Sampling Depths to be Determined During Sampling | | |
| 811500 | 1 | | | |
| 811700 | 1 | | | |
| 843800 | 1 | | | |
| 844000 | 1 | | | |
| 875900 | 1 | | | |
| 876100 | 1 | | | |
| 876300 | 1 | | | |
| 909000 | 1 | | | |
| 909400 | 1 | | | |
| 942500 | 1 | | | |
| 942700 | 1 | | | |
| 976400 | 1 | | | |
| 976600 | 1 | | | |
| 1010700 | 1 | | | |
| 1010900 | 1 | | | |
| 1011100 | 1 | | | |
| 1045600 | 1 | | | |
| 1080700 | 1 | | | |

Table 10-B
Lake Superior Sampling Depths (Stratified)

| Station # | Surface | Thermocline | B-10 | B-2 | Maximum Number of Samples+ |
|-----------|---------|-------------|------|-----|-------------------------------|
| 779800 | 1 | | | | |
| 811500 | 1 | | | | |
| 811700 | 1 | | | | |
| 843800 | 1 | | | | |
| 844000 | 1 | | | | |
| 875900 | 1 | | | | |
| 876100 | 1 | | | | |
| 876300 | 1 | | | | |
| 909000 | 1 | | | | |
| 909400 | 1 | | | | |
| 942500 | 1 | | | | |
| 942700 | 1 | | | | |
| 976400 | 1 | | | | |
| 976600 | 1 | | | | |
| 1010700 | 1 | | | | |
| 1010900 | 1 | | | | |
| 1011100 | 1 | | | | |
| 1045600 | 1 | | | | |
| 1080700 | 1 | | | | |

Table 11-A
Saginaw Bay Sampling Depths (Unstratified)
(April)

Sampling Depths in Meters

| Station # | Surface | B-10 | B-2 | Maximum Number of Samples |
|-----------|---------|------|-----|------------------------------|
| 1 | 1 | | | |
| 2 | 1 | | | |

Table 11-B
Saginaw Bay Sampling Depths (Stratified)

| Station # | Surface | Thermocline | B-10 | B-2 | Maximum Number of Samples+ |
|-----------|---------|-------------|------|-----|-------------------------------|
| 1 | 1 | | | | |
| 2 | 1 | | | | |

Any regularly scheduled depth between the surface and B-2 sample within 3 meters of a thermocline sample depth will be dropped in favor of the thermocline sample depth. There are no I sample at these stations. A duplicate Niskin bottle sample and a field blank sample will be taken. A lab split will be done at each station at a randomly selected depth.

2.0 PROJECT ORGANIZATION AND RESPONSIBILITY

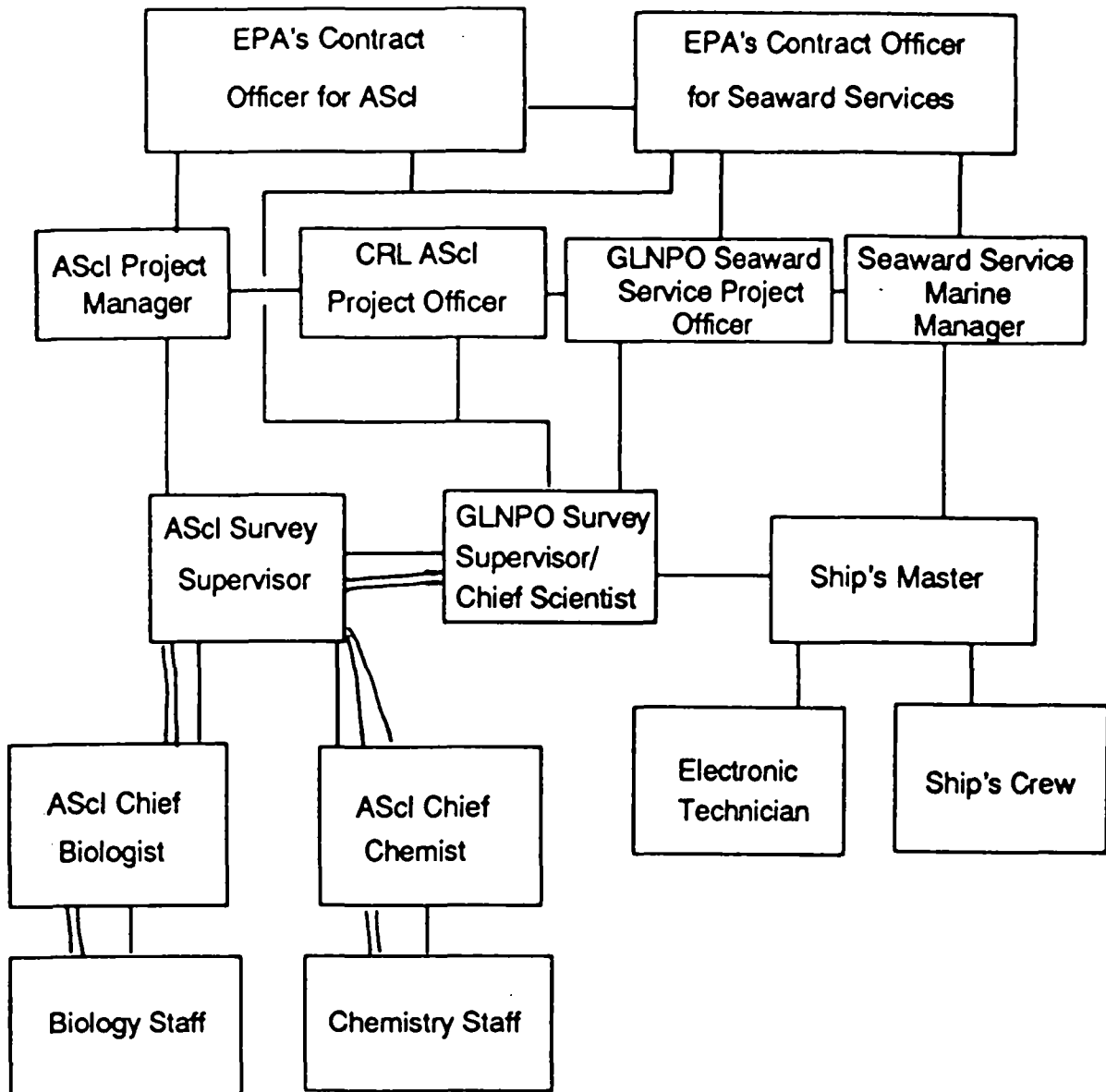
Project planning and operation requires close cooperation between GLNPO, CRL, and Contractor's personnel. GLNPO will designate an EPA supervisor for each survey, who will be the official point of contact for survey planning activities, as well as for shipboard supervision of one shift. GLNPO will provide supervision for each shift, Contractor will designate a Biology Supervisor, a Chemistry Supervisor and a Survey Supervisor. Contractor's Survey Supervisory role may include one of the other supervisory roles. Figure 2-1a illustrates the administrative reporting lines of communication for the parties involved in the operation, while figure 2-1b illustrates the scientific lines of communication.

Quality control responsibility rests with each analyst. Quality control overview of chemical analyses is the responsibility of the Contractor's chemistry supervisor. Coordination of corrective action will involve the GLNPO survey supervisor when sampling activities may need to be interrupted. Corrective action if a back log of chemistry samples develops is addressed in section 13.

Spill clean up is the responsibility of each analyst if quantity is less than one pint. Spills of larger quantities should be reported immediately to Contractor's shift supervisor personnel and EPA shift supervisor personnel. Spill clean up personnel shall take corrective action to contain spill or vapors or evacuate lab. Situation shall be reported to the ship's bridge. In addition to the above lab personnel, the spill clean up team includes ship personnel who will be activated in case of major spill. This includes two ship personnel trained in the use of self-contained breathing respirators and the electronic technician.

Figure 2-1a

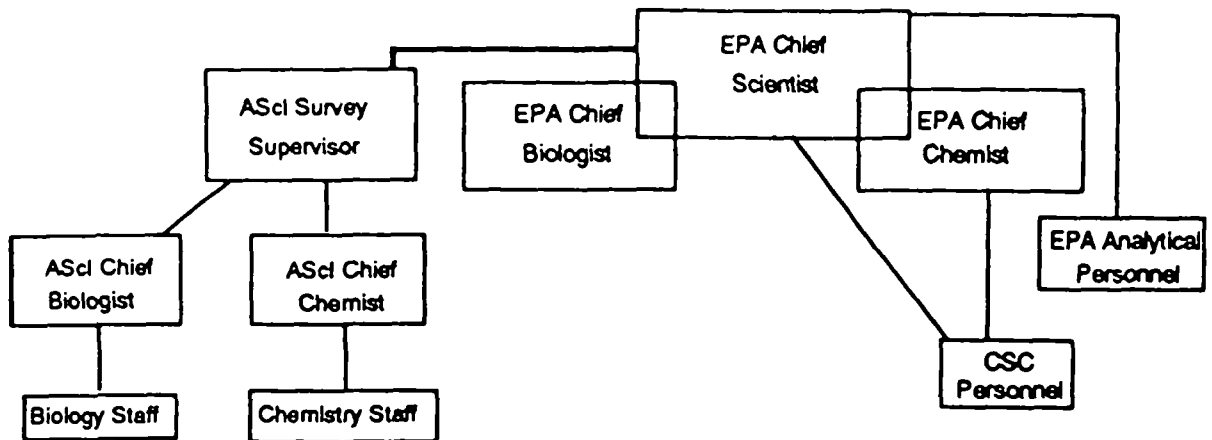
Contract Administration Lines of Reporting



— management
= QA

Figure 2-1b

Scientific Communication



3.0 QA OBJECTIVES FOR MEASUREMENT DATA IN TERMS OF PRECISION, ACCURACY, COMPLETENESS, REPRESENTATIVENESS AND COMPARABILITY

- 3.1 Precision - A measure of mutual agreement among multiple measurements of the same property, usually under prescribed similar conditions. Precision can be evaluated from duplicate analyses and expressed as the mean difference or more commonly as the standard deviation or variance (the square of the standard deviation) of the differences, either absolute or relative. 3.1
- 3.2 Accuracy - The degree of agreement between a measurement (or an average of measurements of the same thing), and the amount actually present. Since the amount actually present in real samples is not generally known, the evaluation of accuracy is performed from spike recovery data. The differences between the two samples (the original sample and the spiked sample) can be calculated from the known amount added, with a high degree of precision, and the interferences present in the normal sample (in contrast to the lack of interfering substances in standards) are present in the original sample and the spiked sample. Therefore, if the procedure is generating accurate results on real samples, the result from the spiked sample should be nearly equal to the result from the original sample plus the spike. The average difference should be numerically equal to the average difference between duplicate analyses. For those parameters capable of being evaluated, the accuracy goal is an average spike recovery of 90 to 110 percent.
- 3.3 Completeness - A measure of the amount of valid data obtained from a measurement system compared to the amount that was expected to be obtained under correct normal conditions. Our completeness goal for physical parameters is 100% and for chemical analyses is 95%.
- 3.4 Representativeness - Expresses the degree to which data accurately and precisely represent characteristics of a population, parameter variations at a sampling point, a process condition, or an environmental condition. Representativeness with respect to the present study is a measure of the parameter variation at a sampling point and is evaluated by collecting random duplicate samples.
- 3.5 Comparability - Express the confidence with which one data set can be compared to another. The comparability of the cruise data with previous cruise data is maintained by maintaining the same procedures as much as is reasonable. When a procedure or an instrument is changed, a comparison is made to verify that

the data is identical or more precise or accurate.

- 3.3 Completeness - A measure of the amount of valid data obtained from a measurement system compared to the amount that was expected to be obtained under optimal conditions.
- 3.4 Representativeness - Expresses the degree to which data accurately and precisely represent characteristics of a population, parameter variations at a sampling point, a process condition, or an environmental condition.
- 3.5 Comparability - Express the confidence with which one data set can be compared to another.

Table 3-1. QA OBJECTIVES FOR MEASUREMENT DATA IN TERMS OF PRECISION, ACCURACY, COMPLETENESS, REPRESENTATIVENESS AND COMPARABILITY

| PARAMETER | PRECISION GOAL From Duplicate Analysis $ x_1 - x_2 $ diff or 8% whichever is larger | | ACCURACY GOAL | COMPLETENESS GOAL |
|-----------------------------|--|---------|--|-------------------|
| | | | | |
| Air Temperature | $\pm 0.5^\circ\text{C}$ | | $\pm 0.5^\circ\text{C}$ | 100% |
| Wind Speed | ± 1 nautical mph | | $\pm (1 \text{ nautical mph} + 20\% \text{ times measured value})$ | 100% |
| Wind Direction | $\pm 10^\circ$ | | $\pm 10^\circ$ | 100% |
| Secchi Depth | $\pm .5 \text{ m}$ | | $\pm (.2 \text{ m} + 20\% \text{ times measured value})$ | 100% |
| Wave Height | $\pm .5 \text{ m}$ | | $\pm (.3 \text{ m} + 30\% \text{ times measured value})$ | 100% |
| Water Temperature | $\pm .1^\circ\text{C}$ | | $\pm 0.5^\circ\text{C}$ | 100% |
| Optical Transmittance | | | $\pm 5\%$ | 95% |
| Turbidity | 0.12 | .18 | $\pm (0.1 + 10\% \text{ times measured value})$ | 95% |
| Specific Conductance | .5uS | .5uS | (control std.) $\times \pm 3s$ | 95% |
| pH | .2SU | .6SU | (control std.) $\times \pm 3s$ | 95% |
| Total Alkalinity | | | (control std.) $\times \pm 3s$ | 95% |
| Total Ammonia Nitrogen | .6mg/L | 0.8mg/L | (control std.) $\times \pm 3s$ | 95% |
| Total Kjeldahl Nitrogen | .5ppb | 0.5ppb | (control std.) $\times \pm 3s$ | 95% |
| Total Kjeldahl Nitrogen | 20ppb | 22ppb | (control std.) $\times \pm 3s$ | 95% |
| Dissolved Nitrate & Nitrite | | | (control std.) $\times \pm 3s$ | 95% |
| Total Phosphorus | 3ppb | 3ppb | (control std.) $\times \pm 3s$ | 95% |
| Dissolved Orthophosphate | .6ppb | 1ppb | (control std.) $\times \pm 3s$ | 95% |
| Total Chloride | .2ppm | 0.5ppm | (control std.) $\times \pm 3s$ | 95% |
| Total Sulfate | .3ppm | 0.5ppm | (control std.) $\times \pm 3s$ | 95% |
| Total Dissolved Phosphorus | .6ppb | 1.0ppb | (control std.) $\times \pm 3s$ | 95% |
| Dissolved Reactive Silica | 5ppb | 8ppb | (control std.) $\times \pm 3s$ | 95% |
| Particulate Organic Carbon | $< (+ 2s)$ | | (control std.) $\times \pm 3s$ | 95% |
| Dissolved Organic Carbon | not established | | not established | 95% |
| Na | | | $x \pm 2s$ | 95% |
| K | | | $x \pm 2s$ | 95% |
| Ca | | | $x \pm 2s$ | 95% |
| Mg | | | $x \pm 2s$ | 95% |
| Dissolved Oxygen | $\pm .2 \text{ ppm}$ | 0.6ppm | $\pm 0.5 \text{ mg/L}$ or $\pm 10\% \text{ times measured value}$ | 95% |
| Phytoplankton | see method varies with algae type | | NA | 95% |
| Zooplankton | not established | | NA | 95% |
| Aerobic Heterotrophs | not established | | NA | 95% |
| Chlorophyll "a" | RPD $< 7\%$ | | $\pm 10\%$ or $\pm .3 \text{ ug/L}$ whichever is greater | 95% |

NA = Not Applicable

RPD = Relative Percent Difference

= difference between duplicates (lab splits)

= average difference between lab splits

$$= \frac{m=n \quad x_m - x_n}{n} \quad \text{where } x_i \text{ and } x_j \text{ are duplicate samples}$$

$$m=1$$

Figure 4-1b. Integrated Sample Flowchart

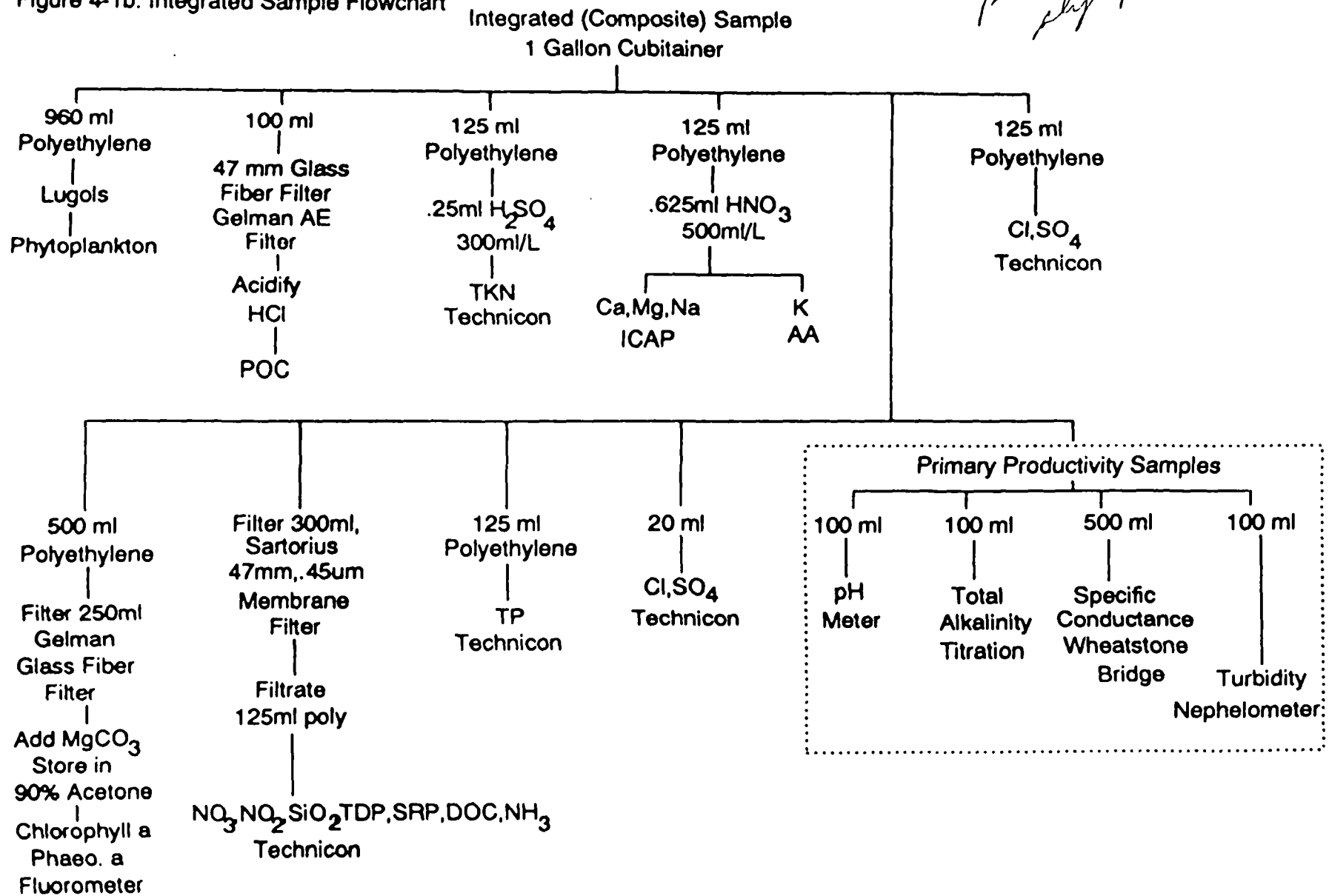
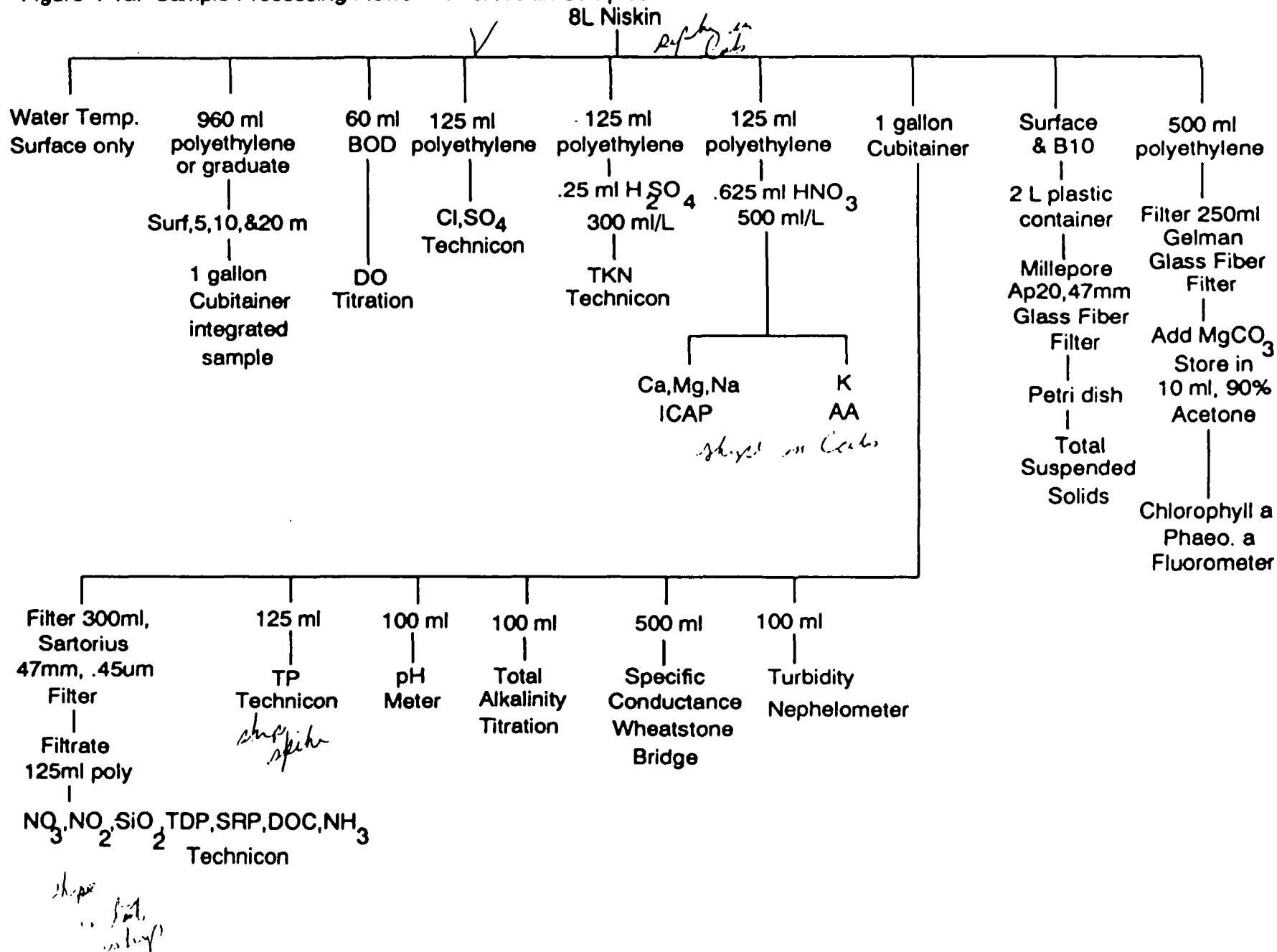


Figure 4-1a. Sample Processing Flowchart - 8l Niskin Samples



sample bottle and preservative dispenser. Dissolved oxygen samples are "set up" immediately. This involves filling the bottle to overflowing, allowing overflowing to continue 5 seconds before adding, in series, the first two reagents, allowing the floc to settle, mixing and allowing floc to settle again. D.O. samples are then completed in the main laboratory.

4.3 Sampling Equipment

4.3.1 Rosette Sampler - General Oceanics Model 1015-12-8 with EBT guideline Model 8705

A 12-bottle Rosette sampler system (General Oceanics Model 1015-12-8) will be used to collect water sample. A submersible bottle mounting array enables an operator to remotely actuate a sequence of up to 11 water sampling bottles. This system consists of an EBT (Guideline Model 8705) attached to the twelfth bottle position of the array, an A-frame, 1000 feet of multi-conductor cable, and a 5HP variable speed winch. The bottles can be sequentially closed remotely from the deck of the vessel while the array is submerged at the various sampling depths. The Rosette will accommodate any of the General Oceanics rigid PVC 1010 Niskin sampling bottles up to the 8 liter size.

✓ *denw* The Guildline EBT is factory calibrated, so that the only way that erroneous values can be obtained are through improper placement of the suppression, zero, volts/unit controls, or the Recorder controls. A variable zero control for the depth (pressure) is necessary to compensate for atmospheric pressure variability. The zero control for temperature should not be manipulated once it is properly set with an ice water bath prior to the cruise (Guideline manual). Temperature will be plotted along the horizontal axis at 50 ft/in. to 500 ft. at which point the scale will be shifted to 125 ft/in. After the samples are collected and the Rosette is brought on board by use of the A-frame, the samples are distributed to the various sample storage bottles while the Niskin bottles remain attached to the Rosette.

4.3.2 x,y Plotter-Hewlett Packard Model 7046A

Since the selection for sampling depths is influenced by the temperature-depth profile (Tables 1-6A to 1-10B), the temperature vs. depth graph is recorded by an x,y plotter (Hewlett Packard Model 7046A) as the Rosette is lowered to the bottom. Collection of the samples (close the Niskin bottles) is done primarily as the Rosette is raised to the surface. Care should be taken to assure that the Hewlett Packard recorder vernier controls (on the range selector switches) are set on the cal position, and that the suppression controls on the Guideline console are set at zero.

4.3.3 Microbiology Samplers

Microbiological samples are to be collected by means of a hydrographic winch, with 5/32 in. 5x7 stranded stainless steel aircraft cable, terminated with a 50 lb. steel weight. In the event of a failure of the Rosette system, water quality samples will be taken using this system. At depths less than 100-m, ZoBell microbiology samples are triggered at the designated depths by General Oceanics bronze messengers Model M1009MG. At depths greater than 100-m, General Oceanics "butterfly" or "chopstick" samplers are used, triggered in the same way.

The samplers and messengers are designed so that each sampler the descending messenger encounters causes that sampler to release a messenger to close the subsequent sampler. This sequence continues until the lowest sampler is encountered. Sterile pre-evacuated 250 ml ZoBell bottles (APHA, 1975) are used for microbiology samples collection.

As the bottle handler attaches the Niskin bottle or ZoBell sampler for the bottom sample, the winch operator sets the depth on the metering wheel to coincide with the sampling depth. The winch operator then lowers the cable until the metering wheel indicates the next sampling depth. The cable is then stopped and the second Niskin or ZoBell sampler is attached to the cable along with a messenger.

This sequence continues until all sampling depths are represented. Then the winch operator lowers the cable until the metering wheel indicates minus two meters (or however high the bottle handler is above the surface of the water). A messenger is attached to the cable and released by the bottle handler. By touching the cable, the bottle handler can feel an impact as each messenger triggers its intended sampler. When all samples are triggered, the bottle handler signals the winch operator to raise the cable until the upper bottle can be retrieved and placed in a carrying container for transfer to the microbiology laboratory.

4.4 Sampling Protocol

4.4.1 Depth Control

The depth at which samples will be collected is determined by a pressure transducer on the Rosette sampler. To assure that the controls on the depth measuring equipment are properly set, the bottom sounding will be compared to the Rosette sample reading at each station. The Rosette winch operator obtains a depth sounding from the bridge and writes this on the chart under observations and marks the chart at the appropriate location on the depth axis edge. The Rosette sampler will then be raised. Three minutes will pass to allow the sampler to drift away from the disturbed area before the B-2 sample is taken. The Rosette sampler will be lowered to B-2 and the sample taken.

A duplicate sample will be taken prior to the B-2 sample. Additional time intervals of three minutes are allowed to elapse prior to taking the thermocline sample and the lower epilimnion sample. These intervals provide time for water equilibration within the Niskins.

The knees of the EBT temperature depth trace will be determined by trisecting the angle between the epilimnion and mesolimnion temperature traces (upper knee) and the angle between the mesolimnion and hypolimnion temperature traces (lower knee). The upper knee is the upper 1/3 angle intercept, the lower knee is the lower 1/3 angle intercept. The lower epilimnion sample is one meter above the upper knee. The upper hypolimnion sample is one meter below the lower knee.

4.4.2 Sequence of Sampling Events (Some events may be done simultaneously and event order will be subject to conditions)

Visual and physical station observations recorded:

Air temperature, wind speed, aesthetics, wind direction, depth, and wave height

- a) Run EBT down to define the temperature profile and determine the thermocline location during stratified situations
- b) Examine the EBT profile obtained in 4.4.2.a. Select sampling depths according to depth selection (Sec.1.8 and Sec. 4.4.1)
- c) Trigger sample bottle at correct depths, while verifying the temperature profile

- d) Split Rosette Niskin samples into the required sample bottles/preservatives. (See Figures 4-1A and 4-1B for details)

A composite 20m sample is taken for phytoplankton, chlorophyll a, pheophytin, DOC and POC by compositing Niskin samples at 1, 5, 10 and 20 meters.

- e) Send ZoBell sampler down to collect microbiological samples at the same depths as determined in 4.4.2.b.
- f) Conduct the 20 meter and B-2 vertical tows for zooplankton samples, rinse net and pour into 500 ml. polyethylene bottles with 10-15 ml club soda and 5% formalin as preservatives.

4.4.3 Nutrient Sample Filtration

Dissolved nutrient samples will be prepared by vacuum filtration (< 7 psi) of an aliquot from the PEC for onboard analyses within an hour of sample collection. A 47 mm diameter 0.45 um membrane filter (Sartorius) held in a polycarbonate filter holder (Gelman magnetic) with a polypropylene filter flask prewashed with 100 to 200 ml of demineralized water or sample water will be used. New 125 ml polyethylene sample bottles with linerless closures will be rinsed once with filtered sample prior to filling.

The aliquot for total dissolved phosphorus will be transferred to the digestion tube as soon as possible. The remainder of the processed sample water will be used for the other dissolved nutrient samples.

4.4.4. Suspended Solids Filtration

Samples for suspended solids (up to 2 liters) are taken from the surface and the B-10 Niskin bottles. Vacuum filtration (≤ 7 psi) through a 47mm millipore AP 20 glass fiber filter is performed within two hours of sampling. One field blank or lab blank is filtered for every four stations and one duplicate analysis is performed every four stations.

4.4.5 POC Filtration

Whatmann GFF 47-mm glass fiber filters are used to collect the particulates from the integrated sample at each station for POC analysis. For every four stations a field blank or lab blank will be filtered and a duplicate analysis will be performed.

4.5 QC Samples

4.5.1 Blanks

Field blanks will be collected in every basin during a survey. for a total of 20 stations See Tables 1-6A to 1-10-B for details.

Field blanks are collected exactly as the samples except they are taken from the deionized water tap instead of the Niskin bottle spigot. Field blanks are used to measure the level of contamination introduced by the sampling procedure but are not used to adjust or correct sample values.

Lab blanks will be taken directly from the reagent water source, a wash bottle or some other dedicated reagent water bottle.

4.5.2 Replicates

At 20 randomly selected stations, a depth is randomly selected to be sampled and analyzed in duplicate to evaluate sampling analytical variability.

A duplicate sample will be taken by firing a Niskin bottle at the designated depth as the Rosette sampler is being lowered to the bottom. This will be labeled "Duplicate." The primary sample is then collected as the sampler is raised to the surface as previously described. At another depth the primary sample from the QC depth will also be analyzed in duplicate in the laboratory (lab split) for each station.

Duplicate EBT profiles are not made using the Rosette sampler. However, the surface Niskin temperature is measured using a mercury thermometer and compared with the EBT profile at the surface depth. The Rosette temperature probe is calibrated using an ice water bath.

4.6 Sample Collection and Analysis

4.6.0 Brief Analytical Protocol

A list of parameters analyzed may be found in Table 4-1. Detailed analytical methods are in Section 7.

4.6.1 Air Temperature

Air temperature will be determined by use of the Maxi-Min. Temperature System RMS-Technology Inc. which will be read to the nearest 0.1°C.

4.6.2 Wind Speed and Direction

Wind speed and direction readings from a permanently mounted Danforth Marine type Wind Direction and Speed Indicator or a Wind Speed and Wind Direction Meteorological Meter Model F will be taken and recorded while the vessel is stopped to the nearest 1° (to the right of true north). Wind direction is accurate to $\pm 10^\circ$. The reading of speed will be estimated to the nearest nautical mile per hour and stored as miles per hour.

Table 4-1
Parameter List

| Parameter | STORET | Cruise | Stations | Depth | Sample |
|----------------------------|--------|--------|----------|------------|------------------|
| Air Temperature | 00020 | All | All | --- | Shaded from sun |
| Wind Speed | 00035 | . | . | --- | Onsite Measure |
| Wind Direction | 00040 | . | . | --- | . |
| Secchi Depth | 00078 | . | . | --- | . |
| Wave Height | 70222 | . | . | --- | . |
| Water Temperature | 00010 | . | . | All | Niskin, EBT, CTD |
| Optical Transmittance | 00074 | . | . | Continuous | CTD |
| Turbidity | 00076 | . | . | All | Niskin - PEC |
| Dissolved Oxygen | 00300 | . | . | . | . |
| Specific Conductance | 00095 | . | . | . | . |
| pH | 00040 | . | . | . | . |
| Total Alkalinity | 00410 | . | . | . | . |
| Dissolved Ammonia N | 00608 | . | . | . | - 125 PE |
| Total Kjeldahl N | 00625 | . | . | . | - 125 PE(S) |
| Diss. Nitrate+Nitrate N | 00631 | . | . | . | - 125 PE |
| Total Phosphorus | 00665 | . | . | . | or 125 PE |
| Total Dissolved P | 00666 | . | . | . | - 125 PE |
| Dissolved Ortho - P | 00671 | . | . | . | - 125 PE |
| Chloride | 00940 | . | . | . | . |
| Total Sulfate | 00945 | . | . | . | . |
| Diss. Reactive Silica | 01140 | . | . | . | - 125 PE |
| Total Suspended Solids | 00530 | . | . | Surf, B10 | . |
| Aerobic Heterotrophs | 31749 | . | . | All | Zobell Sampler |
| Chlorophyll a | 32209 | . | . | . | Niskin - PEC |
| Phaeophytin a | 32213 | . | . | . | . |
| Aesthetic-where applicable | | . | . | . | . |
| Phytoplankton | | . | . | Integrated | Niskin-960PE(L) |
| Zooplankton | | . | . | Integrated | #6net-500PE(C) |
| Primary Prod. Parameters | | . | Selected | Selected | . |
| Particulate Organic C | | . | All | All | Niskin - 125 PE |
| Dissolved Organic C | | . | . | . | . |
| Sodium | 00929 | August | . | All | (N) |
| Potassium | 00937 | . | . | . | . |
| Calcium | 00916 | . | . | . | . |
| Magnesium | 00927 | . | . | . | . |

EBT - Electronic Bathythermograph

CTD - Conductivity-Temperature-Depth (Sea Bird)

PEC - Polyethylene Cubitainer, 4 liter

PE - Polyethylene, preceding number indicates volume in milliliters

(S) - 1ml/l concentrated sulfuric acid added as preservative

(N) - 5ml/l concentrated nitric acid added as preservative

(L) - 8-10 ml/l Acid Lugols preservative

(C) - Club soda, 5% formalin

4.6.3 Secchi Disc Depth

Secchi Disc Depth will be estimated at each station on all cruises by use of a 30 cm, all-white Secchi disc. Secchi disc depths will be recorded to the nearest 0.5 meters.

4.6.4 Wave Height

Average wave height (valley to crest distance) and wave direction will be estimated at each station by the senior crew member on the bridge. Wave heights will be recorded to the nearest 0.5 ft.

4.6.5 Water Temperature

EBT temperature will be verified by uses of a mercury thermometer readable to 0.1 C (ASTM no. 90C). The thermometer shaft will be immersed in the full surface Niskin bottle or in the 960 ml plastic sample bottle. Readings will be estimated to the nearest 0.1 C. EBT temperature trace data will be used for in situ temperature readings for all sampling depths. The Niskin sampling bottles used on the Rosette may be fitted with Reversing Thermometer Assemblies (one on every other bottle) to use as a check on the EBT temperature probe readout.

4.6.6 Water Temperature and Light Transmission Profiles

Temperature vertical profiles may be determined from surface to bottom with the Sea Bird CTD.

The turbidity sensor uses a transmissometer technique of light attenuation. The sensor utilizes a constant LED light source and calibrated photosensor separated by a 25 centimeter path length. The attenuation of the light source by the turbid water is measured. The measurement is indicated in terms of percent transmission, or alternatively as an attenuation coefficient.

4.6.7 Turbidity

Turbidity will be measured with a Turner Turbidimeter. The turbidimeter will be calibrated before analysis of each set of samples using a standard within the anticipated range of turbidity. All turbidity samples will be heated to 25 C to avoid condensation on the sample cuvet. Readings on the 0-1 range will be recorded to the nearest 0.01 unit and readings from 1-20 range will be recorded to the nearest 0.1 unit. These reading are done after conductivity is determined (see 4.6.9) A portion of the conductivity sample is transferred to the curvette for turbidity measurement since the sample is already at 25 C

4.6.8 Dissolved Oxygen

Dissolved oxygen will be measured on water samples from all depths in Lake Erie and at the bottom depth in all other lakes, at each station on each survey. Analyses will be made by the azide modification of the Winkler test (EPA, 1974). The dissolved oxygen sample aliquot is obtained by inserting an 8 to 10 inch length of flexible plastic Tygon tubing connected to the Niskin bottle outlet plug to the bottom of a 60 ml glass BOD bottle. Flow will be regulated by the outlet plug so as to minimize turbulence and mixture of oxygen with the sample.

In addition, dissolved oxygen will be measured during the cast of the Sea Bird CTD with the built-in polarographic electrode.

4.6.9 Specific Conductance

Specific conductance will be determined using a YSI Model 35 conductivity bridge and a conductivity cell (YSI 3401 or YSE 3403, $K = 1.0$). An immersion heater (such as is used for heating a cup of water for instant coffee), connected to a manually operated switch, will be used to heat the sample in a 250 ml polypropylene beaker to 25.0 C. The temperature will be monitored with a mercury thermometer (ASTM 90C) with 0.1 C divisions. Rapid stirring will be accomplished with an immersion glass paddle attached to a small electric motor. The apparatus will be standardized daily against a standard KCl solution according to the equation of Lind et al. (1959).

Conductivity will also be measured during the cast of the Sea Bird CTD. Raw conductivity measurements will be converted to specific conductance using empirically derived formulas.

4.6.10 pH

pH analyses will be made by electrometric measurement. pH meters will be standardized with pH 7.0 and 10.0 buffers, to bracket the pH of lake water. A combination Ross electrode with a platinum internal electrode element will be used. The pH measurement is taken by placing the pH probe in the water remaining in the conductivity sample (4.6.9) after the turbidity curvette (4.6.7) has been filled.

Measurements of pH will also be made during Sea Bird CTD casts.

4.6.11 Total Alkalinity as CaCO₃

Total alkalinity will be determined by titration to pH 4.5 with 0.02 NH_4SO_4 . The pH meter (Cole Parmer Model 5997), with Ross combination electrode, will be standardized daily with pH 4.0 and 7.0 buffers. The acid will be standardized against a standard Na_2CO_3 solution.

4.6.12 Dissolved Ammonia Nitrogen

Dissolved ammonia nitrogen analyses will be performed with a Technicon Autoanalyzer System II using a modification of Technicon's industrial method 154-71W/Tentative (Van Slyke and Hillen, 1933). The pump tube rates will be as follows: sample 0.80 ml/min, complexing agent 0.42 ml/min, alkaline phenol 0.23 ml/min, hypochlorite 0.16 ml/min, nitroprusside 0.23 ml/min, and flow cell 1.00 ml/min. The ammonia determinations will be performed on board as soon as possible, but always within 8 hours of sample collection. Samples will be maintained at 4 C until analyzed.

4.6.13 Total Kjeldahl Nitrogen

Total Kjeldahl nitrogen samples will be preserved for no longer than 90 calendar days by the addition of 0.40 ml of H_2SO_4 (310 ml/L) to each 125 ml. Preservative will be added to samples within 30 minutes of sample collection. Analyses will be made by an "ultramicro semiautomated" method (Jirka et al., 1976), in which a 10 ml sample is digested with a solution of K_2SO_4 , and HgO in a thermostated 370 C block digester. After cooling and dilution with water, the sample neutralization and ammonia determination (Berthelot Reaction) are accomplished on a Technicon Autoanalyzer System II.

4.6.14 Dissolved Nitrate and Nitrite Nitrogen

A Technicon Autoanalyzer will be used with Technicon's industrial method no. 158-71W (Armstrong et al., 1967; Grasshoff, 1969; FWPCA, 1969). In this procedure, nitrate is reduced to nitrite, in a copper cadmium column, which is then reacted with sulfanilamide and N-1-naphthylethylenediamine dihydrochloride to form a reddish purple azo dye. Nitrate and nitrite analyses will be performed within 48 hours of collection.

4.6.15 Total Phosphorus and Total Dissolved Phosphorus

Conversion of the various forms of phosphorus to orthophosphate is by an adaptation of the acid persulfate digestion method (Gales et al., 1966). Screw cap tubes containing samples and digestion solution will be heated in an autoclave at 15 psi (121 C) for 30 min. After cooling, the resulting orthophosphate is determined by the Technicon Autoanalyzer system II and Technicon's industrial method 155-71W (Murphy and Riley, 1962).

The sample storage bottle for total phosphorus will be agitated before sampling. Samples will be transferred to digestion tubes as soon as possible after sample collection.

4.6.16 Dissolved Orthophosphate

Samples will be analyzed for orthophosphate using a Technicon Autoanalyzer System II and Technicon's industrial method 155-71W (Murphy and Riley, 1962). This is the single reagent ascorbic acid reduction method in which a phosphomolybdenum blue complex is measured photometrically at 880 nm. Analyses will be performed on the filtered sample.

4.6.17 Chloride

A Technicon Autoanalyzer System II will be used with Technicon's industrial method No. 99-70W (Zall et al., 1956; O'Brien, 1962). In this method chloride ion displaces mercury from mercuric thiocyanate

forming unionized soluble mercuric chloride. The released thiocyanate reacts with ferric ion to form intensely colored ferric thiocyanate which is determined photometrically. Raw water samples, will be stored non-refrigerated in 125 ml or 250 ml polyethylene bottles with plastic closures.

4.6.18 Sulfate

Samples will be analyzed for sulfate with a Technicon Autoanalyzer using Technicon's industrial method 118-71W (Lazrus et al., 1965). In this procedure the sample is first passed through a cation-exchange column to remove interfering cations. The sample is then mixed with an equimolar solution of BaCl₂ and methylthymol blue (MTB). Sulfate reacts with Ba reducing the amount of Ba available to react with MTB. The free MTB is then measured photometrically. Raw water samples will be stored nonrefrigerated in 125 ml or 250 ml polyethylene bottles with plastic closures.

4.6.19 Dissolved (Reactive) Silica

A Technicon Autoanalyzer System II is used with Technicon's industrial method No. 186-72W/Tentative (Technicon, 1973). This method is based on the chemical reduction of a silicomolybdate in acid solution to "molybdenum blue" by ascorbic acid. Oxalic acid is added to eliminate interference from phosphorus. Analyses will be performed on the filtered samples.

4.6.20 Microbiology Parameters

Direct Observation of Bacteria by DAPI

DAPI is a highly specific stain for DNA and can be used to separate bacteria from non-living particles. By observing the nuclear material organisms, an estimate can be made of the number of organisms per unit volume of water. An aliquot of water collected with a nonmetallic sampling device is transferred into a sterile glass vial and preserved with glutaraldehyde. The sample is then exposed to DAPI, filtered onto a black membrane filter which has been treated to suppress autofluorescence, and then mounted on a microscope slide. A compound microscope equipped with an epifluorescence attachment is used to observe the filter. Random fields are counted and the resultant number is used in calculations to obtain a value in cells/unit volume.

Direct observation of bacteria by DAPI will be performed for all water samples in parallel with analyses for aerobic heterotrophs.

Aerobic Heterotrophs

Aerobic heterotrophic bacterial densities will be determined at several depths at all stations on all cruises by the membrane filtration technique, using Bacto Plate Count agar with aerobic incubation at $20^{\circ}\text{C} \pm .5^{\circ}\text{C}$ for 48 hours (APHA, 1971). Counts will be made with aid of a 10-power stereomicroscope. Counts will be made in accordance with Standard Methods, (APHA, 1975) except that total plate count agar plates, presolidified in petri dishes, type 50 x 15 mm, will be used in place of pour plates.

4.6.21 Chlorophyll "a" and Pheophytin

Samples for chlorophyll analysis (100 ml to 500 ml) will be taken from all depths at all stations and from the integrated or composite sample and will be filtered at $<7"$ of Hg vacuum along with 1 to 2 ml of MgCO_3 suspension (10 gm/l) usually within 30 minutes of sample collection. In some instances filtration may be delayed for as long as 2 hours. The filter (Gelman - Glass Fiber Filter type AE) will be retained in a capped glass tube containing 10 ml of 90% acetone at -10°C in the dark for up to 30 days prior to completion of the analysis. The tubes will be treated in an ultrasonic bath for 20 minutes and then allowed to steep for a minimum of 24 hours prior to fluorometric analysis with a fluorometer (Strickland and Parsons, 1972).

In situ chlorophyll a measurements will also be made during Sea Bird casts.

4.6.22 Aesthetics

Reports of any unusual visual conditions that exist at any station will be made. Conditions such as floating algae, detritus, dead fish, oil, unusual water color, or other abnormal conditions will be recorded in the field observations.

4.6.23 Phytoplankton

Phytoplankton samples will be collected from all stations on the regularly scheduled cruises as well as at master stations on supplemental cruises. The samples will be representative of the upper 20 meters of the water column and will be collected as follows: whole water will be collected by Niskin bottle from 1, 5, 10, and 20 meters.

Approximately 960 ml of sample from each depth (1, 5, 10, and 20 meters) will be mixed in a one-gallon cubitainer. Approximately 960 ml of the mixed sample will be transferred to a 960 ml bottle and immediately preserved with 10 ml of modified Lugol's solution for phytoplankton analysis. The remaining volume in the cubitainer will be designated the "Integrated Sample" and will be used for chemical analysis.

At CRL diatoms will be cleaned with 30% H₂O₂, plus K₂Cr₂O₇, and mounted in Hydrax. At least 500 frustules per sample will be enumerated and identified at 1250X. Other algal forms will be identified and enumerated at 500X using a modification of the Utermohl (1958) method.

Biovolumes will be determined for each sample by assigning an appropriate geometric shape and making the necessary measurement for the volume calculation. A minimum of 10 individuals of each common species will be measured in each sample. Less common organisms will be measured when they occur.

4.6.24 Zooplankton

Samples for crustacean zooplankton will be collected by vertical tow. Zooplankton tows will be made from B-2 meters to the surface and from 20 m to the surface at each station using a 62 micron mesh plankton net with a 0.5 meter mouth opening. At master stations, duplicate tows will be taken for evaluation of the representativeness of the tows collection of the zooplankton assemblages volume of water sampled for each tow will be determined by recording the before and after tow reading of a flow meter mounted in the mouth of the plankton net.

Following collection, the plankton net shall be hosed down (from the outside only!) to wash organisms adhering to the side of the net into the collection cup. The contents of the cup shall be rinsed twice with distilled or potable water and the washings added to the sample bottle. Ten to fifteen ml of the narcotizing agent (club soda) shall be added to each sample.

The bottle shall be inverted two or three times to assure mixing and then allowed to stand 10 or 20 minutes for narcotization to take effect. Samples will then be preserved with 5% formalin (10 ml concentrated formalin/250 ml sample). Each sample will be labeled with the regular station number and the depth at which the tow was begun. An entry will be made on the zooplankton field sheet indicating station number, date time, depth at which the tow was begun and the before and after tow flow meter reading, as well as wire angle during the tow.

4.6.25 Particulate Organic Carbon

Particulate matter from a sample of variable volume is collected on a 47 mm glass fiber filter (Whatman GF/F) which has been pretreated by firing at 500 C. The material is washed with 0.1 NHCl acid to remove inorganic carbon, and the 47 mm filter is folded in quarters and placed in a petrie dish. The petrie dish and filter are stored in a freezer. The entire filter is later subjected to elemental carbon analysis at CRL.

4.6.26 Dissolved Organic Carbon

Organic carbon will be determined on all filtered samples at all stations using a Technicon Autoanalyzer System II and Technicon's industrial method No. 451-76W. In this method, the acidified sample is purged with CO₂-free gas and then subjected to short wave UV radiation to convert carbon compounds to CO₂. The generated CO₂ is measured with a nondispersive CO₂ detector.

4.6.27 Sodium, Potassium, Calcium, Magnesium

Samples are to be analyzed at CRL using flame Atomic Adsorption AA for potassium and Inductively Coupled Plasma analysis for sodium, calcium, and magnesium. Samples are preserved with .625 ml of 1/1 nitric acid per 125 ml of sample.

4.6.28 Primary Productivity Parameters

Samples for analysis of primary productivity will be collected at selected sites in parallel with those for phytoplankton enumeration: during the summer survey a separate sample from the M3 depth will be taken for analysis also. Approximately 4L of composited water sample will be collected into a darkened carboy or cubitainer, and the carboy placed immediately in a light-tight insulated chest for transportation to the shipboard laboratory. The water sample will be transferred to 300 ml incubation bottles and inoculated with a known quantity of bicarbonate substrate which is labeled with the radiotracer ¹⁴C. Samples from the same water source are incubated at temperatures approximating ambient, at various light intensities for 2 to 4 hours, after which the algal cells are separated from the water by filtration.

The filters are immersed in a scintillation cocktail and returned to CRL for counting in a liquid scintillation counter. Because the measured radio activity of each filter will be proportional to the quantity of carbon fixed by the algae into organic material, the metabolic activity of the algae community can be established.

Calculation of the productivity parameters also require information about the total inorganic carbon available in the incubation vessel, the length of time of incubation, the chlorophyll content of the incubated sample and the specific activity of the radiotracer.

4.6.29 Suspended Solids

Samples for analyses of suspended solids will be collected in separate containers marked for surface (1M) and bottom (B10). A weighed filter contained within a petri dish will be used to collect suspended materials from up to 2 liters of sample. Filtration at <7" of Hg psi vacuum will be done within 30 minutes of sample collection. The filter (47mm Millepore AP20 glass fiber filter) on

the spring/summer survey will be weighed at CRL after drying at 105 C for a minimum of 1 hour. The Millepore AP20 filters will be replaced by Whatman GFF filters beginning Summer 1992.

4.7 Holding Times

Maximum holding times, preservation or storage methods, and ship board operational storage methods and holding times are displayed in Table 4-2.

TABLE 4-2. SAMPLE PRESERVATION AND HOLDING TIMES

| | <u>Max. Holding Time Unpreserved</u> | <u>Preservative/ Storage Method</u> | <u>Max. Holding Time Preserved</u> | <u>Operational Storage Method & Holding Time Limits</u> |
|--|--|--|--|---|
| Turbidity | unstable Perform ASAP | Refrig. 4 C | 48 hr (1) | 2 hr. |
| D.O. | | None | 8 hr (1) | 1st 2 reagents immediately Add Acid within 8 hr. Titrate within 30 min. of acid addition |
| Specific Cond. | | Refrig. 4 C | 28 days(1) | 2 hr. |
| pH | | None | 2 hr (1) | 2 hr. |
| Alkalinity | | Refrig. 4 C | 14 days(1) | 2 hr. |
| NH ₃ -N* | 24 hr. | 1 ml H ₂ SO ₄ /l and Refrig. 4 C | 28 days(1) 90 days(2) | 48 hr. (4 C) At CRL < 90 days |
| TKN | | 1 ml H ₂ SO ₄ /l | 28 days(1) 90 days(2) | At CRL < 90 days |
| NO ₃ -NO ₂ * TDP | 24 hr. | 1 ml H ₂ SO ₄ /l in filtered sample (orange label) | 28 days(1) 90 days(2) | 48 hr. (4 C) At CRL < 90 days |
| TP | 24 hr. | 1 ml H ₂ SO ₄ /l in unfiltered sample (yellow label) | 28 days(1) 90 days(2) | At CRL < 90 days |
| SRP* | unstable | Refrig. 4 C | 48 hr. (1) | 48 hr. |
| Cl | indefinite | None | 28 days(1) | indefinite |
| SO ₄ | indefinite | None | 28 days(1) | indefinite |
| SiO ₂ * | indefinite | None | 28 days(1) | 48 hr. (4 C) |
| POC | | | not estab. | At CRL not estab. |
| DOC* | 48 hr. | 1 ml H ₂ SO ₄ /l | 28 days(1) 90 days(2) | 48 hr. |
| Na,K,Mg, Ca | | 1 ml HNO ₃ /l | 6 mo. (1) | At CRL < 90 days |
| Aerobic hetero- trophs | ASAP | Refrig. 4 C | not estab. | 6 hr. (4 C) |
| Sample filtration | ASAP | None | | 1 hr. |

(1) EPA 40 CFR, Part 136 Holding Time.

(2) Recommendation of EPA CRL. Although there are no data to indicate that this type of sample is unstable, a 90-day holding time is recommended.

4.8 Analysis Priority Ranking

If it appears that onboard holding time goals will not be reached, the ASCI Chemistry Supervisor and the EPA Survey Supervisor will be notified. The EPA Survey Supervisor will assign priority to backlog analysis. Suggested prioritizations are listed in Table 4.3. Sample collection will be interrupted until the back log is reduced so that on board holding times are met.

Suggested order of biological analysis is:

- 1) aerobic heterotrophs
- 2) productivity
- 3) chlorophyll
- 4) DAPI, sample preservation

Table 4-3. Prioritization and Preservation of Chemistry Samples

| PRIORITY | PARAMETER | OPERATIONAL MAXIMUM HOLDING TIME | PRESERVATIVE/ STORAGE | COMMENTS |
|----------|--|--|--|---|
| 1 | physical tests, turbidity, DO, Cond., pH, alk., All filtration | Perform ASAP | None | Unstable |
| 2 | SRP | 48 hr. | 4°C/Iced | Unstable |
| 2* | NH ₃ | 48 hr. | 4°C/Iced | TKN samples may be used but AVOID CONTAMINATION |
| 3* | NO ₂ + NO ₃ | 48 hr. | 4°C/Iced | " |
| 3* | TDP, DOC | 48 hr. | 4°C/Iced | Filter immediately |
| 4* | TP | 48 hr. | 1 ml H ₂ SO ₄ /L | TKN samples may be used |
| 5 | POC, TKN, Na, K, Ca, Mg | Analyzed at CRL | Analyzed at CRL | Analyzed at CRL |

Within these restrictions, backlogged samples will be analyzed on the Guardian on a "first-in-first-out" schedule.

*When these samples are returned to the CRL, they will be analyzed within 90 days of the collection date.

5.0 SAMPLE CUSTODY

Chain-of-custody procedures do not apply for lake samples. None of the lake data is intended to be used for litigation.

Prior to each survey, numbered sample bottle labels will be printed by computer. The sample bottle label will contain the following information:

CRL sample number (see below)
 Lake
 Station number
 Survey date
 Preservation used
 Parameter to be measured
 QC sample depth

CRL sample numbers are of the following format:

| | |
|--------------------|--------------------------------|
| Primary samples | (n)(n) G (a) (n) (n) S (n) (n) |
| Integrated | G I |
| Duplicate | G D |
| Field Blank | G R |
| Duplicate Analysis | G C |
| Spike | G X |
| Laboratory Blank | G B |

where (n) indicates a number and (a) indicates a letter. The first 2 numeric spaces are used to designate the fiscal year. The second letter (a) specifies the lake (A = Michigan, B = Huron, C = Erie, D = Connecting Channels, E = Ontario), and the remaining numeric spaces indicate series and sample number.

Labels will be color coded to indicate the preservation used, and to identify filtered samples ie. Yellow for Sulfuric acid (total nutrient), Orange for Sulfuric Acid (total dissolved nutrients), Green for Nitric acid (metals), and white for unpreserved.

✓ Prior to arrival at a sampling station, those station labels will be segregated and applied to the sampling bottles. When sample bottling and preservation are completed, a record of the numbers on the labels used will be made on analysis request sheets.

All on-board results will be recorded in data files on floppy diskettes on the on-board Intel computer. Back-up diskettes will be updated at the end of each shift. Master sheets will also be available for data recording as needed (samples attached) (Figures 5-1A to 5-1C). Physical parameters will be recorded on similar sheets (sample attached) (Figure 5-2). Results generated at the CRL will be reported on CRL data forms.

6.0 Calibration Procedures and Frequency

| INSTRUMENT | REFERENCE OF CALIBRATION PROCEDURE | CALIBRATION STANDARD | FREQUENCY |
|--|------------------------------------|---|-----------|
| EBT Guildline Model 8705 | Factory Calibrated | Factory Calibrated | 2 Years |
| Maxi-Min Temp. System, RMS Technology, Inc | - | - | - |
| Danforth Marine Indicator - Wind Speed and Direction, Meteorological Meter Model F | - | - | - |
| Secchi Disk | None Required | - | - |
| Turner Turbidimeter | Instrument Manual | Formazin | Daily |
| YSI Model 35 Conductivity Bridge | Instrument Manual | Shunts | - |
| Jenco 6071 pH Meter | Instrument Manual | Buffers pH 7 and pH 10 | Daily |
| Cole Parmer 5997 pH Meter | Instrument Manual | Buffers pH 4 and pH 7 | Daily |
| Technicon - NH ₃ | Technicon Manual | 4 Conc. NH ₄ Cl & Blank | Daily |
| Technicon - TKN | Technicon Manual | 4 Conc. Glutamic Acid & Blank | Daily |
| Technicon - TP & TDP | Technicon Manual | 4 Conc. KH ₂ PO ₄ & Blank | Daily |
| Technicon - NO ₂ -NO ₃ | Technicon Manual | 4 Conc. KNO ₃ , KNO ₂ & Blank | Daily |
| Technicon - DRP | Technicon Manual | 4 Conc. KH ₂ PO ₄ & Blank | Daily |
| Technicon - Cl | Technicon Manual | 8 Conc. NaCl & Blank | Daily |
| Technicon - SO ₄ | Technicon Manual | 8 Conc. Na ₂ SO ₄ & Blank | Daily |
| Technicon - SiO ₂ | Technicon Manual | 4 Conc. Na ₂ SiO ₃ & Blank | Daily |
| Technicon - DOC | Instrument Manual | Potassium Biphthalate | Daily |
| Turner Dual Mono. Spectrofluorometer | CRL Method | Chlorophyll <u>a</u> Chlorophyll <u>b</u> | Daily |
| ICP - Ca, Na, Mg | CRL Method | NBS | Daily |
| AA - K | | NBS | |

7.0 ANALYTICAL PROCEDURES

Methods for the following analytical procedures may be found in Appendix 1.

7.1 R/V Lake Guardian Methods Manual: Shipboard Analyses

Contents:

- 1) GLNPO SOP Dissolved Nutrients Filtration
- 2) GLNPO SOP Total Alkalinity Titration
- 3) GLNPO SOP Ammonia Nitrogen
- 4) GLNPO SOP Chloride
- 5) GLNPO SOP Dissolved Organic Carbon
- 6) GLNPO SOP Chlorophyll "a" and Pheophytin "a"
- 7) GLNPO SOP Specific Conductance
- 8) GLNPO SOP Nitrate and Nitrite Nitrogen
- 10) GLNPO SOP Dissolved Oxygen, Winkler Titration
- 11) GLNPO SOP Electrometric pH
- 12) GLNPO SOP Soluble Reactive Phosphorus (Orthophosphate)
- 13) GLNPO SOP Total and Total Dissolved Phosphorus
- 14) GLNPO SOP Soluble Reactive Silica
- 15) GLNPO SOP Standards and Spikes preparation(autoanalyzers)
- 16) GLNPO SOP Sulfate
- 17) GLNPO SOP Suspended Solids
- 18) GLNPO SOP Technicon Operation
- 19) GLNPO SOP Turbidity
- 20) Methodology for Aerobic Heterotrophs, Total Coliforms, Fecal Coliforms, Fecal Streptococci
- 21) Method for Determining Primary Production Parameters using Carbon 14 Radiotracer
- 22) GLNPO SOP Quality Control Schedule

7.2 Other Analytical Procedures

Contents:

- 1) CRL SOP for Total Kjeldahl Nitrogen
- 2) CRL SOP for Analysis of Particulate Organic Carbon in Lake Water
- 3) Proposed Method for Direct Observation of Bacteria by DAPI
- 4) CRL SOP for the Analysis of Phytoplankton
- 5) CRL SOP for the analysis of Zooplankton
- 6) CRL: The Determination of Calcium, Magnesium, Potassium and Sodium in water by Flame AA
- 7) CRL: The Determination of Total Calcium, Magnesium, Potassium and Sodium in Water By ICAP

8.0 DATA REDUCTION, VALIDATION & REPORTING

8.1 Calculations and Units

All calculations used to reduce raw data to its final form are presented in each analytical method. Units are also specified in each method.

8.2 Raw Data

All shipboard generated strip charts, bench records, and computer printouts will be kept in a folder, indexed by station, until the remaining samples eg. Metals, TKNs and reruns are transferred to the CRL. A master folder will be prepared to hold all sample information and additional data as it is generated, reviewed and approved. All raw data will be assembled and indexed by parameter by lake and by survey leg. Analogue charts and digital conversion printouts will be stapled together. Each parameter will be put in a manilla folder and given to GLNPO.

8.3 Data Validation

All data generated will go through the same review process required by the ASCI QA Project Plan. This entails the following (Figure 8-1): No data, whether generated on board or in the laboratory will be released to GLNPO without this review.

8.4 Out of Control Criteria

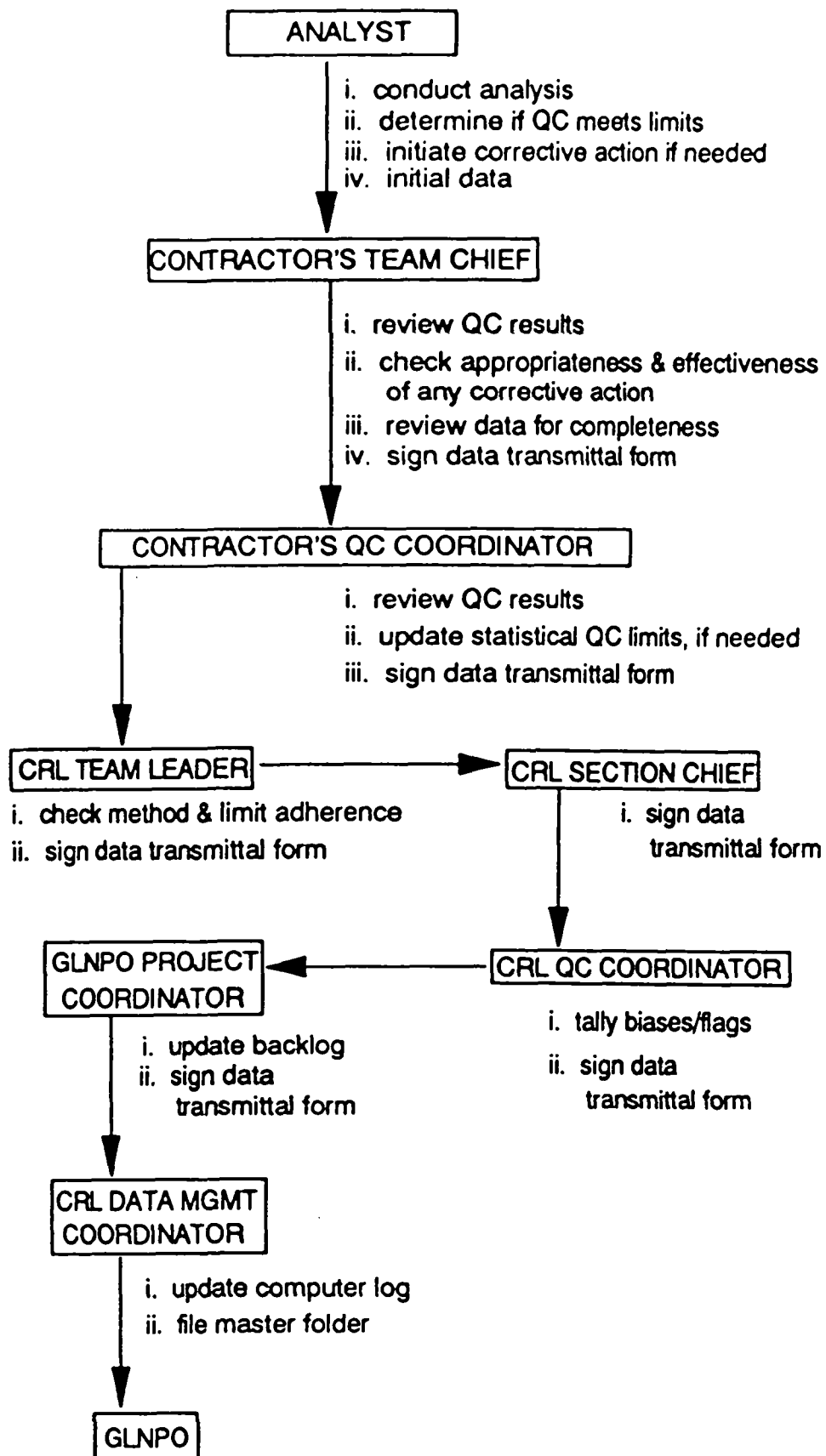
All QC audit results falling outside the statistically established control limits (see method or Table 3-1) are outliers, the analytical system should not generate data on any real samples until it has been determined whether the outlier is a normal low probability result or the system is out of control. If the outlier is a simply a low probability result in an otherwise properly operating system, then the samples and QC audit results should be retained. If the system is out of control, then the associated samples and QC audit results should be discarded, and the system brought into a properly operating mode prior to rerunning the subject samples.

GLNPO will provide control limits based upon more than fifteen years of previous experience using trained personnel aboard the RV Simons. Current numerical limits will be recorded in the system log for each method. The contractor QC coordinator will evaluate the variance and means for each audit by cruise. This will provide a basis for revisions to the GLNPO control limits.

8.5 Computer Support

User documentation for A/D transfer of data and down loading of concentrations is found in appendix 2.

Figure 8-1. Data and QC Review



9.0 INTERNAL QC CHECKS AND FREQUENCY

9.1 Type & Frequency of Audits

Each method delineates the exact type, frequency & limit for each audit. Unless otherwise indicated a pair of control standards, a laboratory blank and a duplicate analysis will be run with each group of samples from one or two non-master stations.

- 9.1.1 High Control and the Low Control standards are dilutions of the particular analyte in reagent water selected such that their values fall at the upper and lower end of the range of values normally found in the lake water or the range used for the analysis.
- 9.1.2 Laboratory reagent blanks are prepared from reagent water and are processed like aliquots removed from the sample storage bottle. Laboratory blanks do not go through the filtering operation nor sample storage bottles.
- 9.1.3 Duplicate analysis is performed at the conclusion of an analytical run and the regular analysis of the same sample is performed at the usual position within the run. For filtered samples, the filtering is considered a part of the analysis. Separate sample storage bottles are used for the regular filtered sample and the duplicate analysis filtered sample.
- 9.1.4 Spiked samples are prepared from aliquots from the sample storage bottle and a concentrate traceable to the calibration standard concentrates. For filtered samples, one sample storage bottle is used for the filtered sample, and another for the filtered sample for the spiked sample preparation.
- 9.1.5 Between Shift Duplicate Analysis - Optional. The last sample run on the shift will be reanalyzed by the next shift to check inter analyst precision.

9.2 Recording and plotting of QC Data

Analysts will make every attempt to make maximum effective use of QC data. Specific steps toward this end include prompt recording of AQC results in the system log and plotting that data on the appropriate control charts. Implementation for each survey will include the following steps.

- 9.2.1 Preparation of system log books and control charts. Prior to the survey, the lab contractor's QC Coordinator will be responsible for assuring that the system logs are available and current. He/she will assure that the control charts, covering low check standards, high check standards, duplicate analyses, spike recovery, duplicate samples, field blanks and laboratory reagent blanks are available with the proper limits. The limits used will

be those obtained from GLNPO.

A sample control chart is attached (Figure 9-1). Each parameter will have at least one control chart constructed for an associated audit (i.e., spike recovery, control standard value).

- 9.2.2 Responsibility for Charting. Each analyst will maintain the logs and control charts for their assigned parameters on an ongoing basis. Each analyst will regularly evaluate whether the analytical system is in control. Each analyst will report actual or suspected impending out-of-control situations to the contractor shift supervisor. Corrective action for beyond-limit situations are discussed in section 13.0. Charts are to include the date the point was generated, the associated station number and notations of extraordinary situations. On the Hi, Lo, and Blk control charts, entries should be made to indicate the preparation of new batches of control standards and calibration standards and the calibration points.
- 9.2.3 Training. All analysts participating in the survey will receive training in the use of the logs and charts before the survey by the contractor's QC coordinator.

9.3 Field Audits

Duplicate samples and field blanks will be collected at random depths and stations at the rate of one each for lake basin.

- 9.3.1 Field Blank. Reagent water from the ship's distilled water tap will be dispensed into the sample storage bottle and handled exactly like the associated samples.
- 9.3.2 Duplicate Samples. The duplicate sample Niskin bottle is triggered as the EBT/Rosette is deployed(on descent). The regular sample Niskin bottle for the duplicate is triggered as the EBT/Rosette is retrieved(on ascent).

10.0 PERFORMANCE AND SYSTEM AUDITS AND FREQUENCY

10.1 Training and Certification

The survey scientists provided by the Contractor will be trained at the Central Regional Laboratory (CRL). All instrumentation will be assembled and tested at the CRL before it is sent to the R/V Lake Guardian for each Survey. Testing will consist of checking all control standards on the assembled systems to (1) verify proper concentration, and (2) demonstrate that all analytical systems to be used on the RV Simons are capable of running within the limits required using the current standards and reagents.

10.2 Dry Run

After the equipment is installed on the R/V Lake Guardian, the Contractor's QC Coordinator will accompany the Contractor's survey staff while they test all equipment prior to beginning the survey. At that time, the QC Coordinator will evaluate the autoanalyzer systems and advise the GLNPO survey supervisor of the status of the equipment and personnel readiness.

10.3 Performance Evaluation

Periodically, Round Robin samples from the IJC will be analyzed. These results will be reported to the Data Quality Work Group. Upper Great Lakes reference group QC samples will also be obtained from the QAO by the Contractor's QC Coordinator to evaluate accuracy in an actual lake matrix. These samples are used to evaluate the comparability of the data to other data generators, not to set accuracy and precision limits.

11.0 PREVENTIVE MAINTENANCE/SCHEDULE

After each survey, all on board instruments will be inspected for worn parts or erratic behavior as indicated by QC results.

An on board back up recorder, sampler, colorimeter, pump, manifold, tubing supply and small replacement parts will be kept. Contractor Survey coordinator will maintain an inventory on this equipment.

To prevent equipment misuses, the lab Contractor will assure that its employees follow all operational procedures for each instrument utilized. All personnel will be "checked-out" on an instrument by either their direct supervisor or another knowledgeable individual, as directed by the EPA Project Officer.

Preventative maintenance is necessary to keep analytical instruments and other equipment in good working condition and to decrease the amount of major repairs and downtime. Most analytical instrument and equipment manuals have a section dealing with preventive maintenance. These sections will be read by each person operating the equipment. All preventative maintenance performed will be noted in the system logbook.

The lab contractor will maintain the system logbooks on each instrument used. All calibration procedures performed on the instrument and a record of all maintenance (including installation of new pump tubes) performed will be documented. The Contractor's Project Manager or the QC Coordinator will inspect these logbooks after each survey to determine the instrument's condition and performance. Any failure/breakdowns will be reported immediately to both the Contractor's Project Manager and the EPA Project Officer. This action will be the responsibility of the individual operating the instrument when such an event occurs.

The laboratory contractor will operate within all established CRL Quality Assurance procedures for equipment, glassware and reagents. Parts that need periodic replacement will be requested at a rate to ensure that parts are always on hand.

The lab contractor will have at least one employee attend each CRL Safety Meeting to ensure that all safety concerns are addressed promptly.

12.0 SPECIFIC ROUTINE PROCEDURES TO BE USED TO ASSESS DATA PRECISION, ACCURACY, AND COMPLETENESS OF SPECIFIC MEASUREMENT PARAMETERS INVOLVED

12.1 Precision

The precision will be evaluated by performing duplicate analyses, and expressed as the standard deviation of duplicates. This is the square root of the sum of the squares of the differences, the sum being divided by the total number of pairs. If a determination requires dilution of the sample in order to bring it into the working range of the SOP, then the precision statement is applicable only to the diluted sample. The control charts are plotted using the result from the duplicate analysis minus the result from the regular analysis.

12.2 Accuracy

The accuracy of the determinations will be derived from the mean difference between the spiked sample results and the original sample results. The average spike recovery will be calculated at the conclusion of the cruise, but the individual spike recovery results will be obtained as soon as possible and plotted so as to eliminate or reveal any operator error while the details of the analytical session may still be recalled. The control chart should have the same limits as the duplicate analysis control charts, or possibly higher by 2% of the amount the spike increases the concentration. The value plotted is the spiked sample result minus the result from the original sample corrected for the spike, or the error in absolute recovery.

$$\% \text{ recovery} = 100 * ((R + 1) * CX - R * CS) / X$$

where CX = analytical result of spiked sample
 CS = analytical result of original sample
 R = (volume of sample before spike)/(vol of spike)
 X = concentration of spike

$$\text{absolute recovery} = CX - CS$$

$$\text{error in absolute recovery} = CX - (X + CS * R) / (1 + R)$$

12.3 Completeness

Completeness for most analyses should be 100% since the samples are available for reanalysis in the event that the analytical procedure goes out of control for some reason. To maintain a high completeness for those parameters with a limited shelf life, the procedure must either be maintained in control or the capability for corrective action must be such as to allow the samples to be reanalyzed within the allotted time limit if 100% completeness is to be maintained. For each parameter the completeness equals:

$$\text{completeness} = \text{number of analyses in control} / \text{number planned}$$

12.4 Representativeness

Representativeness of sampling is evaluated by analysis of duplicate samples, and is represented by the standard deviation of duplicates.

12.5 Comparability

Comparability is not assessed on a regular basis by GLNPO. Comparability with previous cruises is maintained by using the same analytical procedures, traceable to Standard Methods and EPA methods of analysis. Periodically GLNPO participates in round robin studies by the IJC.

13.0 CORRECTIVE ACTION

Any indication that a system is out of control will be brought immediately to the attention of the Contractor's shift supervisor by the analyst. If an audit is beyond the prescribed limits, the analyst will first determine that an error was not made in sample placement or calculations. The next step is to run two of more of the offending audits using the original standardization. If the procedure is still suspect, and the offending audit is a check standard or spike, then fresh working check standards or spike material will be prepared and analyzes performed using the original standardization. For further direction, see the flow chart figure 13-1. The flow chart is an aid to the analyst, not a restriction. If information is available that would indicate a speedier resolution of the problem, it should be pursued. Regardless of the course of action, there are three possibilities; 1. the procedure is declared to have been in control, in which case the original samples, and QC audit results are accepted, 2. the procedure is determined to be out of control, in which case, modifications are made to correct the situation, and a hard copy of the original data along with an explanation of the problem and its resolution is placed in the system log. The original samples are then rerun and the new results of the samples and QC audits replace the original data. 3. if it is inconclusive whether the system was in control or not, but it is operating properly at the present, then continue as in 2 above.

Feedback to the employees and suggestions for corrective actions will be the supervisor's responsibility. In the event that the only way that the procedure can be brought under control is by a procedure modification, this must be reported to the Contractors QC Coordinator and Contractor's Survey Supervisor. Documentation will be in the form of a written variance to the establish procedure. Written documentation will be presented to, Contractor's project officer and to EPA's survey supervisor and project officer.

Contractor's Survey Coordinator and EPA's Survey Supervisor can stop the analysis if the system cannot be brought into control.

If a back log of samples develops such that it can not be cleared within the sample time controls if additional samples are taken, then the collection of samples will be interrupted until the back log is cleared. The recommendation to halt sampling will be made by Contractor's Survey Coordinator. The decision to stop sampling will be made by EPA's Survey supervisor or shift supervisor.

14.0 QUALITY ASSURANCE REPORTS TO MANAGEMENT

After each survey, the contractor's Biology and Chemistry supervisors will compile a summary of the survey output, technical problems, corrective actions and QC results. The Contractor's QC Coordinator will evaluate the overall level of quality based on these reports and offer suggestions for improvement on the next survey in a formal report. This report will be reviewed by the Contractor's Project Manager who will provide a copy to the EPA Project Officer and the Contractor's Corporate QAO. An annual summary report will be submitted by the Contractor's QC Coordinator discussing the success and problems of the QA program, including the open lake surveys. The report will be sent to the EPA Project Office.

APPENDIX 1

7.0 ANALYTICAL PROCEDURES

Great Lakes Survey Studies

USEPA Great Lakes National Program Office

APPENDIX 2

A User Manual of Laboratory Automation Program

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