Quality Assurance Project Plan For
106 Water Quality Monitoring Project

Lac Courte Oreilles Reservation
Hayward, Wisconsin

Revision 1 and Final QAPP for
Grant ID#I-00E05801 and I-00E57501

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INTRODUCTION

This Quality Assurance Project Plan (QAPP) describes the procedures for water quality monitoring regarding the EPA Section 106 Grant Work Plan for the Lac Courte Oreilles (LCO) Reservation. The purpose of this project is to gather information on the quality of surface water found on the LCO Reservation. Since the last approved LCO QAPP, certain water quality parameters have been added to the program. All QA/QC information can be found in this document.

Water quality information gathered from this project will be used to determine water quality management needs. Results from the project will support the LCO Water Monitoring Database and will allow for reliable trend analysis in the future.

SECTION ONE: PROJECT DESCRIPTION

1.1 SITE DESCRIPTION

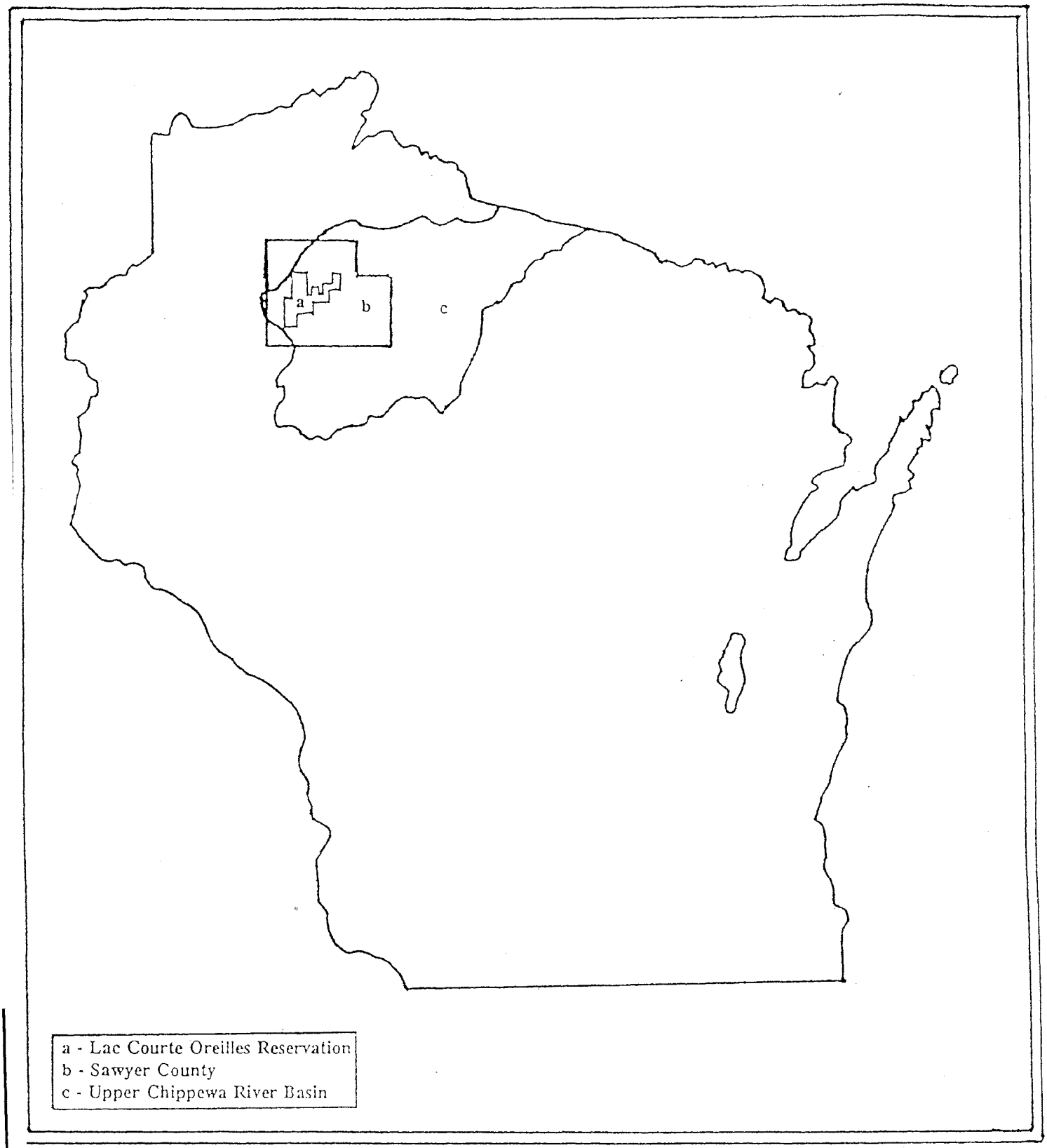
1.1.1 Location and General Information

The 76,464-acre Lac Courte Oreilles Reservation is located in west-central Sawyer County in Northern Wisconsin (see Figure 1). The Reservation is about 60 miles southeast of Duluth, MN, 150 miles north of Minneapolis, MN and the small town of Hayward, WI is six miles from the northwest corner of the Reservation.

According to the 2000 U.S. Census Bureau, there are approximately 2,900 people living within the Reservation boundaries and off-Reservation trust lands. Of the 2,900 individuals, roughly 74% are American Indian. There are currently 30 sub-communities spread out across the Reservation. The majority of these communities are located within a few miles of the main infrastructure of the Reservation. Other communities like Signor, New Post and Six Mile are more rural.

Figure 1

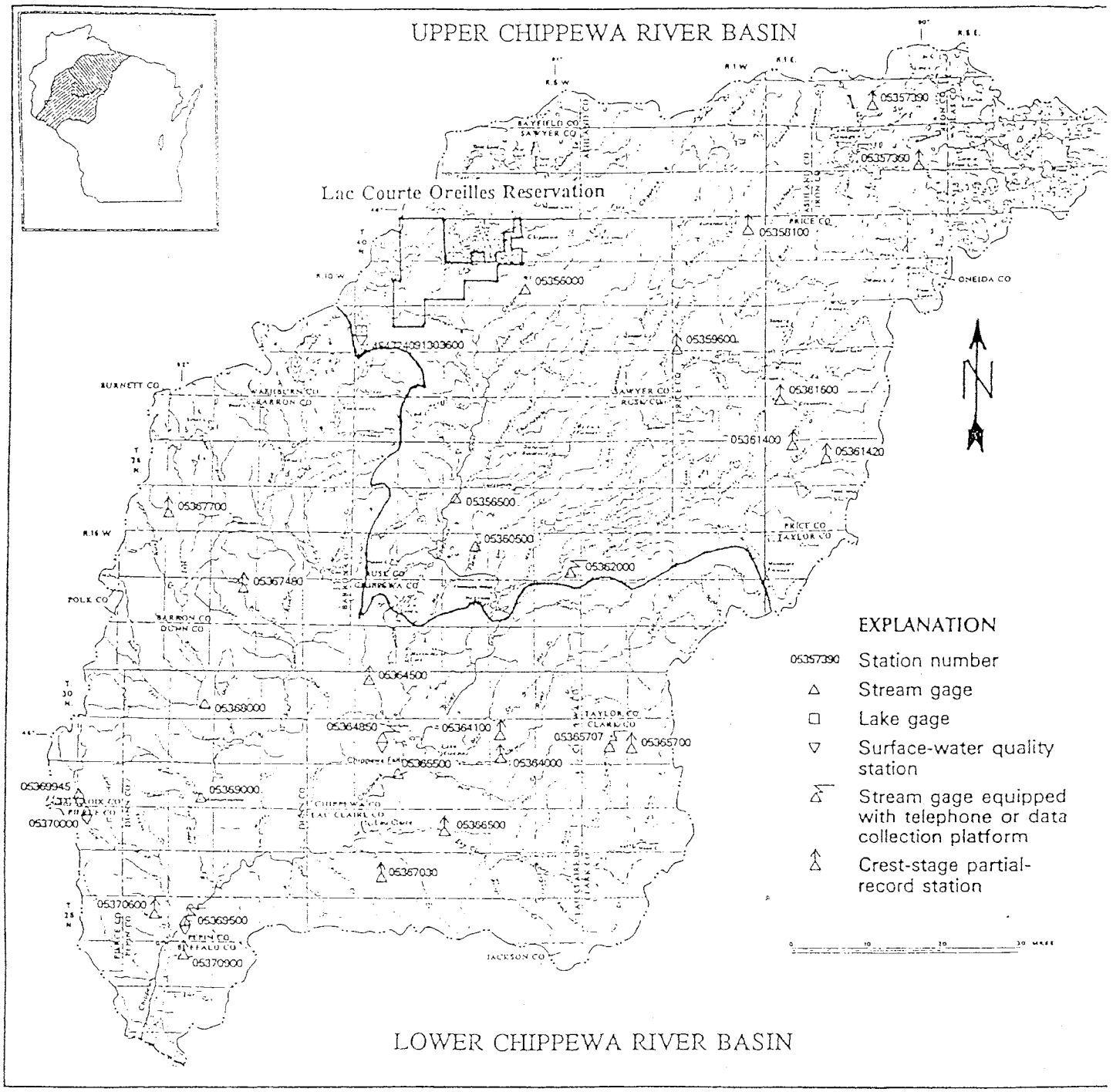
Location of the Lac Courte Oreilles Reservation



The LCO Reservation in located in Sawyer County in northwest Wisconsin. The waters of the reservation are part of the Upper Chippewa River Basin.

Figure 2

USGS Gaging Stations in the Chippewa River Basin



Source: USG

The stations shown provide data year-round.

The LCO Reservation is a "water rich" environment located entirely within the Upper Chippewa Watershed (see Figure 2). Twenty-five lakes (including six that form part of the Chippewa Flowage) and forty-three miles of rivers and streams are found on the Reservation, and over 7,500 acres of the Reservation are classified as wetlands.

The largest lake found on the LCO Reservation is the Chippewa Flowage which is an impoundment of the East and West forks of the Chippewa River. The Chippewa Flowage has a surface area of over 15,300 acres and a maximum depth of 92 feet, which makes it Wisconsin's third largest lake.

1.1.2 Site History

Baseline water quality data has been gathered under the EPA 106 program for the past several years on the Lac Courte Oreilles Reservation. Virtually all of the surface waters of the Reservation have been monitored in some capacity for the following parameters: total phosphorus, water clarity, chl. a, phytoplankton, zooplankton, macro-invertebrates and invasive species monitoring. This QAPP covers all the SOP's pertaining to these activities and others which have been added to the new work plan.

1.3 PROJECT OBJECTIVES

1.3.1 Problem Statement

The state of Wisconsin designates the Chippewa Flowage and the majority of the waters on the Reservation as outstanding water resources. Compared to lakes in the Southern region of the state this may be the case, but it is the feeling of the LCO Tribal Council and the LCO Conservation Department (LCOCD) that surface water found on the LCO Reservation is being degraded due to non-point sources from new development, damaged septic systems, increased impervious surfaces, cranberry farming, lack of shoreline protection and heavy recreational traffic.

The LCOCD is also concerned with the influx of potentially harmful invasive species found on the Reservation which include Eurasian Water Milfoil (*Myriophyllum spicatum*), Purple Loosestrife (*Lythrum Salicaria*), Curly Leaf Pondweed (*Potamogeton Crispus*), and Zebra Mussels (*Dreissena polymorpha*), and the threat of Viral Hemorrhagic Septicemia (VHS) on certain fish species. Continual monitoring and treatment of these invasive species is vital towards protecting the integrity of Reservation waters.

Effluent discharged from cranberry marshes adjacent to Musky Bay on Big Lac Courte Oreilles Lake continues to be a major problem. Sample results throughout the ice-up period, particularly discharge periods, continue to show elevated nutrient levels compared to other bays and basins in the lake. Total phosphorus levels of over 1,000 ppb have been observed, and the LCOCD feels strongly that cranberry nutrient loads are having a direct effect on the density and diversity of plant growth within

the bay.

The LCO Tribe relies heavily on the subsistence of fish from local waters in their diet. Fish advisories are in affect to some degree on all Reservation lakes. The ability to sample mercury in the lake sediment will allow the LCOCD to determine which lakes may have higher levels of exposure.

In order for the LCOCD to determine water quality trends, scientific data must continue to be gathered. What is the basic water quality of LCO Reservation lakes and streams over the next five years? This project will monitor and collect data on surface water found on the Reservation, and use that data to analyze water quality trends and identify polluted waters.

Data gathered from this project will be analyzed and modeled by the Project Managers. LCOCD Water Resource Technicians will be responsible for the water monitoring procedures, data gathering and other project services.

1.3.2 Decision

The LCOCD will determine whether there is cause for concern regarding the effects of increased development, invasive species, cranberry farming, increased impervious surfaces and heavy recreational traffic on the surface waters of the Reservation. Water quality parameters will be used as indicators that may prescribe for a more comprehensive study on a certain water body in the future. Also, data gathered will be compared to reference site water bodies that are considered not impacted by human activities to determine if the water quality is being degraded. If the water quality is found to be degraded, lake/stream management plans will be developed to protect the integrity of that water body. If the water quality is found not to be degraded, then no further action will be taken at that time.

1.3.3 Inputs to Decision

This plan includes for the monitoring of the following parameters for Reservation water bodies: dissolved oxygen, pH, total dissolved solids, temperature, water clarity, specific conductance, Microcystin-LR sampling, diatom assemblage and core dating, total nitrogen, total phosphorus, total suspended solids, chl. *a*, and mercury sediment analysis. Most all rivers, lakes, and streams found on the Reservation will be monitored.

Point source discharges within the Reservation boundaries will continue to be inventoried using the Reservation's Global Positioning System and mapped with GIS. All off-reservation point sources that discharge to receiving waters flowing onto the Reservation, or are immediately adjacent to it, will be identified and mapped also.

A year-end report will be prepared indicating the trends observed in water quality for that year with

recommendations for sampling and monitoring for the next year.

1.3.4 Study Boundaries

Profiles of the water quality parameters will be recorded for each water body at various locations throughout the lake or stream. Tables 1&2 provide the names of the lakes and streams to be monitored along with their location, number of monitoring sites and the surface water monitoring parameters.

Some potential constraints or obstacles that may possibly interfere with the study are: extreme weather conditions on the scheduled sampling date, mechanical difficulties, or the inability to gain access to the site due to poor landing conditions.

1.3.5 Decision Rule

One of the LCOCD's main water quality concerns is the negative effects cranberry farming is having on the water quality of certain lakes within the Reservation borders. Thermal pollution, nutrient loading and dissolved oxygen fluctuations due to discharges are threatening ecosystems and negatively impacting crucial spawning habitat, and littoral zone complexes. The LCOCD is currently working with the LCO Lake Association to conduct a plant survey in Musky Bay which will determine species presence, density, and diversity as another tool to identify pollution concerns in the bay. Continued water quality monitoring needs to be conducted as well as surveying and identification of invasive species in the area.

Monitoring dissolved oxygen levels in Reservation trout streams must continue. **If DO levels drop below 7 mg/l in trout streams, investigative procedures will be taken to determine if proper agricultural practices (mainly forestry) are being conducted, or if nuisance beaver problems are occurring.**

Invasive species in certain lakes have had a direct impact on habitat, and natural spawning areas. The LCOCD, along with the LCO Community College, have been very pro-active towards mapping and monitoring Eurasian Milfoil and Purple Loosestrife coverage within Reservation Borders. The LCOCD has also chemically treated certain high traffic areas to reduce the potential spread of EWM. **If certain invasive species are detected, and pose a significant risk to the resource, then control methods will be explored, and treatment will be considered.**

If total phosphorus levels reach the eutrophic or hyper-eutrophic range, management plans will be devised to determine the cause of the impact.

If elevated total suspended solids levels are found in Reservation streams, investigatory measures will be taken to determine whether the cause is from high flow rates, soil erosion,

beaver problems, urban runoff, wastewater and septic system effluent, or other means. Management plans will be developed in the future to address these concerns.

If *microcystin*-LR levels are found above 1 ug/L (drinking water guidance standard from WHO), then the LCOCD will construct boat landing signs, or provide educational materials to the public about health concerns associated with the toxin.

Water clarity (secchi disc), total phosphorus, and chl. a monitoring is used to determine trophic status for each reservation lake. **Trend analysis is performed annually for each water body. If trophic status trends start to deteriorate, then management plans will be developed for each respective water body to improve water quality.**

In the future, if trend analysis of the other study parameters indicate noticeable environmental problems, management plans will be developed to correct the problem. Management plans will also be developed to reduce the impacts of point-source discharges and non-point source pollution on Reservation resources.

No action level has been set by the LCOCD for total mercury concentrations in the sediments. Lake sediments with higher concentrations of total mercury will result in a higher priority for fish tissue analysis studies.

Diatom analysis and core dating will provide historic information to the LCOCD, identifying periods of natural and cultural disturbances in the ecosystem. Data gathered from this sampling regime will be used as a reference tool towards educating riparian owners and lake association groups about water quality.

1.3.6 Limits on Decision Errors

In order to specify tolerable limits on decision errors, the errors must be identified and a null hypothesis must be chosen. Both types of decision errors must be defined and the true nature for each must be established. The LCOCD has determined that the two decision errors are (i) deciding that the water quality of LCO's surface waters is degrading when it truly is not, and (ii) deciding that the water quality of LCO's surface waters is not degrading when it truly is. The true state of nature for decision error (i) is that the surface water quality is not degrading. The true state of nature for decision error (ii) is that the surface water quality is degrading. The consequences of deciding that the surface water is degrading when it truly is not will be slight because the ability to generate data by monitoring the resource is vital in determining future surface water degradation. The consequences of deciding that the LCO's surface waters are not being degraded when they truly are will be that the resource does not receive adequate protection from contamination sources. The LCOCD has concluded that decision error (ii) has the more severe consequences since the risk of

surface water degradation clearly outweighs any type of risk from the surface waters not being degradated at this time.

Therefore, the baseline condition or null hypothesis (H_o) is "water quality of LCO's surface waters indicates degradation." The alternative hypothesis (H_a) is "water quality of LCO's surface waters does not indicate degradation." The more serious error, then, would be the false positive. The errors are something the LCOCD is willing to accept when making decisions based upon the outcome of the study.

The sampling design for this project was constructed by the LCOCD which is based upon previous knowledge of the water resources of the Reservation, and is in accordance with the sample design outlined in the EPA's "Lake and Reservoir Restoration Guidance Manual" (U.S. EPA, 1990). The sampling plan was designed to develop a formidable and accurate data collection process. The LCOCD will also be conducting statistical analysis of the project parameters in comparison to similar reference sites.

1.3.7 Design for Obtaining Data

The sample design for this project was carefully constructed to provide the most resource-effective data collection process possible. Sample site locations were based upon the above objectives and concerns; the sample design includes lakes, rivers and streams located on the Reservation.

Surface water monitoring locations can be found in Tables 1&2. Monitoring for DO in the winter months may occur on lakes found on the Reservation.

1.4 PROJECT TARGET PARAMETERS and INTENDED DATA USAGE

This plan includes for the monitoring of the following parameters for all Reservation water bodies:

- dissolved oxygen,
- water clarity,
- pH,
- total dissolved solids,
- temperature,
- specific conductance,
- Microcystin-LR,
- diatom assemblage and core dating,
- total nitrogen,
- total phosphorus,
- total suspended solids,

- chl. a, and
- mercury sediment analysis.

Profiles of these parameters will be recorded for each water body at various locations throughout the lake or stream. Intended data usages of these parameters over time will allow for reliable trend analysis of the background water quality data.

Diatom assemblage and core dating will be studied to understand how each lake on the reservation has changed over time. The central questions are: what were the past conditions of the lake, did the conditions of the lake change, when did this occur, and what were the causes? Reconstruction of historical diatom assemblages through analysis of sediment cores can be useful for determining historical changes in nutrient outputs. Diatoms, a diverse and usually abundant type of algae that possess siliceous cell walls, are especially useful in sediment-core analysis because they are ecologically diverse and well preserved in sediments; moreover, the ranges of favorable environmental conditions are known for several species.

Mercury sediment analysis is being sampled to understand concentrations of mercury for selected lakes. Are some reservation lakes more susceptible to mercury in fish tissue? Limited data has been gathered on certain reservation lakes from the Great Lakes Fish and Wildlife Service (GLIFWC) in recent years. Data from this study will help supplement those findings and provide important information to LCO tribal members.

Accurate background water quality data is also essential in order for the Reservation to develop and implement its own water quality standards and criteria for the Reservation. The development and enforcement of these standards will help to maintain the necessary water quality of tribal waters needed for subsistence fishing, gathering and ricing.

1.5 SAMPLE NETWORK AND RATIONALE

The sampling locations and depths for analyses are associated directly with the properties of the lake. For example, in a lake that is mostly shallow and almost round (Gurno Lake), a single station over the deepest point is adequate. In deep, stratified lakes (Grindstone and Lac Courte Oreilles) several sample stations will be used to monitor the deepest part of the lake, the shallower areas and prominent bays. Rivers, streams and creeks found on the Reservation will be monitored monthly in the ice-free period as well. The profiling of each sample site will begin at the surface and continue at each vertical meter until near bottom.

1.6 PROJECT SCHEDULE

1.6.1 Anticipated Date of Project Mobilization

This project period runs from October 1st, 2006 through September 30th, 2008. Targets of this project and dates:

- Submit updated QAPP for Approval-January 2008
- Data collection/field sampling June 1st-Sept. 1st 2007 & 2008
- Submit Final Technical Report to EPA-December 2008

SECTION TWO: PROJECT ORGANIZATION AND RESPONSIBILITY

2.1 MANAGEMENT RESPONSIBILITIES

- Lac Courte Oreilles Conservation Department, 13394 W. Trepania Rd., Hayward, WI 54843 (715) 865-2329
- Project Managers- Lac Courte Oreilles Conservation Department, Environmental Engineer, Dan Tyrolt & Environmental Specialist, Brett McConnell
- Field Technicians- Lac Courte Oreilles Conservation Department, Water Resource Technicians, Brett McConnell and Bill Nebel

The Project Managers are responsible for project planning, data validation, report preparation and project budget management. The Field Technicians are responsible for the preparation of the QAPP, following all SOPs and other monitoring plan requirements.

- USEPA Region V, AE-17 J, 77 W. Jackson Blvd, Chicago IL 60604-3590
- Project Officer- Irene Cook Phone: (312) 886-1823
- Technical Contact- Don Roberts Phone: (312) 886-1765

2.1.1 Field Responsibilities

The Project Manager and Field Technicians are responsible for insuring that all monitoring procedures are done correctly and consistently.

2.1.2 Laboratory Responsibilities

There are two contract laboratories affiliated with this project, the Natural Resources Research Institute in Duluth, MN, and the Wisconsin State Lab of Hygiene. Paul Garrison from the WDNR will be handling all diatom assemblage analysis and core dating. All SOPs for analysis of LCO's water quality samples are contained in this document.

2.1.3 Corrective Action

The Project Manager or the technicians will be responsible for initiating, developing, approving and implementing the corrective actions. The EPA technical contact will be responsible for providing technical advice and consultation regarding the corrective actions.

2.1.4 Project Organization Diagram

The Project Organization Diagram can be found in Figure 3.

2.2 QUALITY ASSURANCE RESPONSIBILITIES

The Project Manager and the Field Technicians will be responsible for following standard operating

Figure 3

Project Milestones and Associated Timeframes

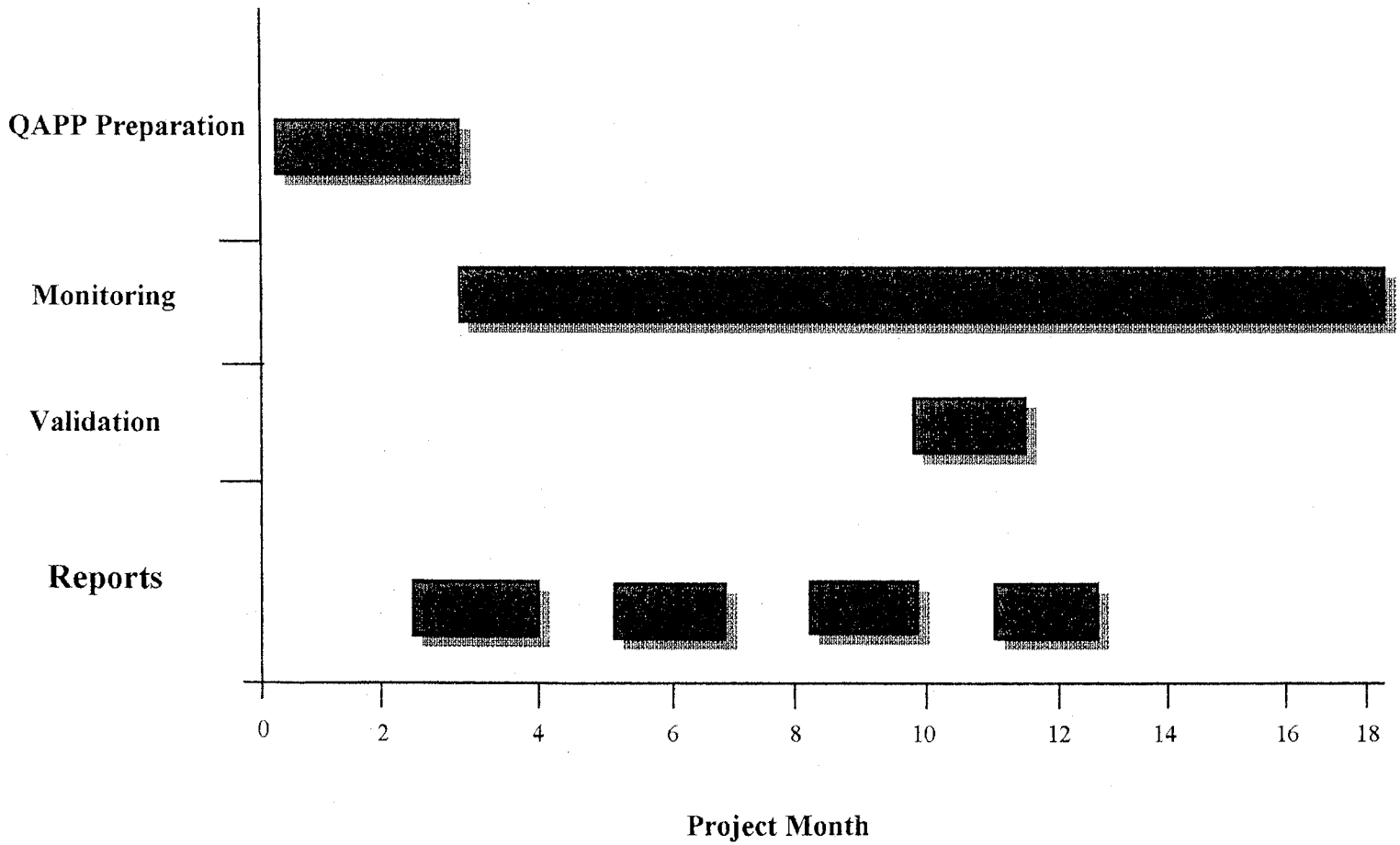
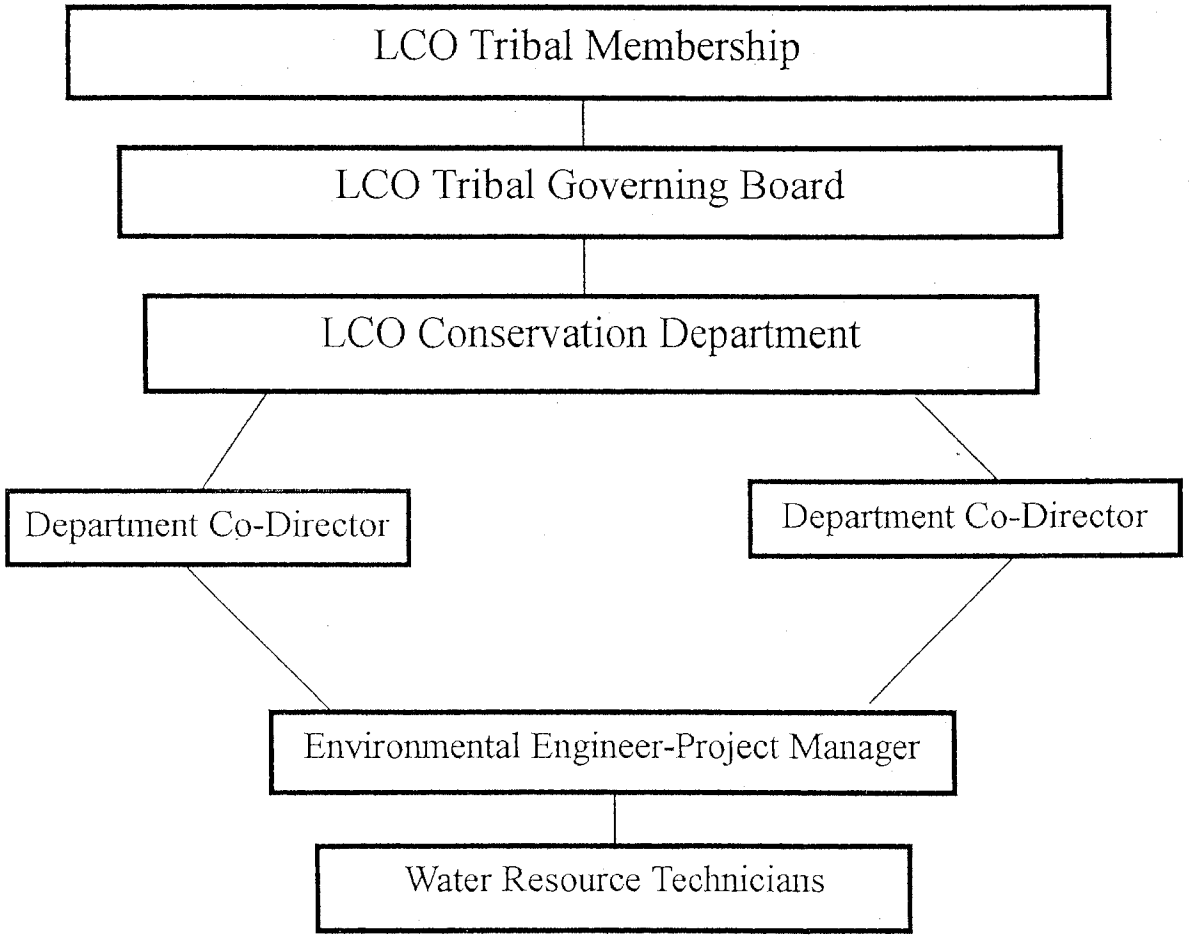


Figure 4

LCO Water Quality Project Organization Diagram



procedures and proper documentation of data in the field. Employees of the LCO Conservation Department have the following quality assurance responsibilities:

Project Manager:

- Validates data-entry errors before data sheets are filed away
- Conducts internal audits of calibration procedures and field activities
- Provides proper corrective action documentation and procedures
- Determines locations for Reservation DO monitoring
- Oversees project budget

Environmental Technicians:

- Conducts proper calibration and maintenance procedures for water quality meter
- Prepares draft QAPP for project to be submitted to EPA for review and approval
- Maintains field logbook documenting all information related to monitoring activities
- Documents and reports data collection process problems to the Project Manager

SECTION THREE: QUALITY ASSURANCE OBJECTIVES FOR MEASUREMENT DATA

3.1 DISCUSSION OF QUANTITATIVE QA OBJECTIVES

3.1.1 Precision

Precision is a measure of the degree to which two or more measurements are in agreement. Precision of data collected for this project will be determined by taking two separate readings at the same location once for each day of monitoring. The relative percent difference (RPD) will be calculated for each pair of readings as indicated below:

$$RPD = \frac{(S-D) \times 100}{(S+D)/2}$$

where:

S= first reading
D=second reading

Field Precision will be reported as the RPD between the two co-located readings for each depth interval.

3.1.2 Completeness

Completeness is a measure of the amount of valid data obtained from a measurement system compared to the amount that was expected to be obtained for that measurement. Data completeness will be assessed for compliance with the amount of data required for decision making. The percent completeness is calculated as indicated below:

$$\%Completeness = \frac{(number\ of\ valid\ measurements) \times 100}{number\ of\ measurements\ planned}$$

where "valid measurements" refers to numbers of investigational samples obtained for a specific purpose, or in order to satisfy a particular project objective.

3.1.3 Representativeness

Representativeness expresses the degree to which data accurately and precisely represent a characteristic of a population, parameter variations at a sampling point, a process condition, or an environmental condition. Representativeness is dependent upon the proper design of the sampling program and will be satisfied by ensuring that the field sampling plan is followed and that proper sampling techniques are used.

3.1.4 Comparability

Comparability is an expression of the confidence with which one data set can be compared with another data set. Field data will be comparable by following all QA/QC objectives documented in this QAPP.

3.1.5 Accuracy

Accuracy will be accomplished by following all calibration procedures for the YSI Multi-Parameter Water Quality Meter and Hydrolab instruments. Standard operating procedures for calibration of these water quality meters can be found in the Appendix.

SECTION FOUR: SAMPLING PROCEDURES

4.1 SAMPLING ACTIVITY SUMMARY

The monitoring activities used in this work plan will be consistent with project objectives. Lakes, rivers and streams to be monitored can be found in Tables 1 & 2. Water quality parameters will be analyzed by the Project Manager.

4.2 SAMPLING EQUIPMENT AND PROCEDURES

4.2.1 YSI Multi-parameter Water Quality Meter & Hydrolab Datasonde 4

A multi-parameter water quality meter will be used by the LCO Conservation Department to gather surface water quality data. Each site location will be profiled at the surface and at each subsequent meter until it is at near bottom. Parameters selected will be programmed into the data display unit to be shown simultaneously for each profiling location. Readings will be taken immediately following parameter stabilization.

Maintenance of the meter will occur once a month and calibration procedures will be done daily before monitoring activities begin.

Storage of the water quality meter will be done by placing 0.5 inches of water in the calibration and/or storage vessel, and placing the sonde with all probes in place in the vessel. The storage vessel will be sealed to prevent evaporation. A minimal amount of water will be used for storage so that the air in the chamber remains at 100 percent humidity. Also, the water level will be kept low enough so that none of the sensors are actually immersed. All YSI & Hydrolab maintenance SOPs will be followed. YSI & Hydrolab SOPs can be found in the Appendix.

4.2.2 Benthic Macro-invertebrate Sampling

Samples are collected by various methods depending on habitat and experimental design. In the littoral zone, samples will be collected using two methods, a 500um D-net, and a 3 ½ inch diameter acrylic corer, with the sample taken in the top 10 cm. A petite Ponar will be used in deeper areas. Generally, samples are washed through a 500um mesh net and placed in a sample container, and preserved. All macro-invertebrate samples will be preserved with a 10% formalin solution.

Each sample will contain an interior and exterior label. Sample labels identify: 1) project name, 2) site name or number, 3) sample number and number of containers (i.e. large samples that are placed in multiple containers, A-D), 4) gear type (Ponar, D-net, corer, etc.), 5) sieve size used to wash sample, and, 6) current date.

Labels may be coded or include limited information, but must be referenced with an accompanying log sheet that provides the required information from number 1 through 6. Interior labels written in pencil lead are required. Outside labels may also contain a brief description or code, but must include at least a unique identifier for lab sorting, prioritized processing, and archiving purposes.

4.2.3 Benthic Sample Inventory

A list of samples, including all label information, is completed in field notebooks as samples are collected. A sample list accompanies all samples returning to the laboratory. Chain of custody forms are completed and verified with the field sample list as in-coming samples are inventoried by laboratory personnel. Chain of custody forms and a field sample list are duplicated, filed with field notes or data sheets, and one copy placed in the project log book.

4.2.4 Benthic Sample Processing

Prior to processing, samples preserved in the field with 10% formalin are rinsed to remove the formalin preservative. This procedure is conducted under a ventilation hood. The rinsed sample is then re-preserved in 70% ETOH. Discarded preservatives are stored in containers labeled with appropriate hazardous waste information and transferred to Hazardous Chemical Storage.

Samples ready for processing are signed out of the project log book by lab personnel. Samples may contain multiple containers, so all containers for that sample are concurrently processed. All sample information contained inside the sample container should be verified with outside labels and project log book information. Due to the amount of material contained in a sample, it may be necessary to sub-sample or "split" various samples.

Sample materials are washed in the appropriate sieve and a final rinse is conducted in a wash pan. The remaining sample is rinsed into a sorting pan and any material remaining in the wash pan that passes through the sieve is discarded. Large amounts of material passing through the sieve are deposited in a waste receptacle and not discarded in the lab sink. Depending on the sediment type, samples can be washed using an elutriation device, colloidal silica bath, or other flotation procedures. These devices are designed to separate light organic material from heavier particles in a sample.

Once the sample has been thoroughly washed and sub-sampled accordingly, the sample is transferred to a tray, glass pan, or sorting dish. Sample material should be spread evenly throughout the pan. Large trays and glass pans should be sorted using a 2X magnification lens. A dissecting scope is used to process samples in a sorting dish.

Organisms are removed from detritus with a forceps and placed in labeled vials. Vial labels contain identical information as sample labels, with the addition of the amount of sample processed (i.e. 1/4, ½, or whole), a vial number, the total number of vials for that particular sample (e.g. 1 of 3), and

initials of lab personnel. The number of vials accompanying each sample will depend on the abundance of organisms, but one vial should be designated for only midge larvae. All samples will be subjected to QA/QC inspection.

4.2.5 Sample Identification

Sample vials containing processed macro-invertebrates are then signed out for identification using the vial chain of custody form. Organisms are identified to the lowest taxonomic level using appropriate keys, enumerated, and recorded on an identification data sheet. A reference collection is made for each individual taxa identified for the entire project. The collection is then subject to QA/QC guidelines that include re-identifying 30% of the collection. If more than 5% of the randomly selected taxa are questioned, the entire collection is re-identified.

Individual mounts

Individuals within the family Chironomidae (Diptera) are permanently mounted for further taxonomic identification. Generic identification requires head capsule decapitation to ensure ventral viewing of individual mouth parts. Organisms are soaked in 95% ETOH, preserved in euparal mounting medium, and placed under a cover slip. Generally, the number of individuals per slide depends upon body size. Individual placement on the slide and label information will follow standard template.

Individual Identification

Permanent slide mounts will be identified to the lowest taxonomic level under a compound microscope. Each individual will be assigned a particular slide number, position, and side, so a separate reference collection for these organisms is not necessary because location of individual organisms can be easily assigned. Chironomids will also be subjected to a 30% random re-identification for lab verification.

4.2.6 Macro-invertebrate Data Entry

Data from laboratory sheets will be entered in a Microsoft Access database, or entered in duplicate using a standard spreadsheet software. The data are subject to a 10% random evaluation according to the number of data records. An error rate greater than 1% will result in re-entry.

Data are merged with a database (bugspec.xls) in SAS to check for errors and provide higher taxonomic categories for all individuals identified. Individuals not listed in the database are either re-identified, or the current information and taxonomic name are compared to the ITIS system database for confirmation.

4.3 Phytoplankton Sampling

Phytoplankton assemblage requires 4-10 samples during the growing season to obtain a seasonal average. Counting of 300-500 cells to order will be done in the laboratory. The phytoplankton sample is preserved in the field with Lugol's solution. The sample is taken at the surface (.5m). Samples are fixed with 5% Lugol's Iodine and stored at 4 degrees Celsius.

4.4 Zooplankton Sampling

Zooplankton are sampled with vertical tows, using a plankton net equipped with a 7:1 reducing cone. A single, vertical tow from .5m above bottom to the surface is sufficient. The recommended approach is to sample 4 to 6 times during the growing season to obtain seasonal averages. Identification and counting of 100-200 organisms, and measurement of daphnia size will be done in the laboratory.

4.5 Total Suspended Solids (TSS)

When taking a TSS sample, a clean bottle must be used for sample collection. The sample must be taken from undisturbed water; when standing in the stream, reach upstream into the current to obtain the sample. Because sediment loads may be non-uniformly distributed in the water column, it may be wise to determine TSS from a composite of several samples.

4.6 Total Phosphorus and Total Nitrogen Sampling

Water samples are collected using an integrated sampler. The device is a PVC tube 6.6 feet (2 meters) long with an inside diameter of 1.24 inches (3.2 centimeters) fitted with a stopper plug on one end and a valve on the other. The device allows collection of water from the upper two meters of the water column (within the euphotic zone). If the euphotic zone is < 2.0m deep, the integrated sampler will be lowered only to the depth of the euphotic zone, and additional draws will be taken to collect the volume needed for the samples.

Prior to taking each sample, the rubber stopper is removed and the sampler is rinse by submerging it three times in the lake. With the valve open and the stopper off, the sampler is slowly lowered into the water as vertically as possible until the upper end is just below the surface. Cap and slowly raise the sampler. Close the valve when the bottom is near the surface. Empty the sample into sample bottle.

Laboratory methods pertaining to Total Phosphorus and Total Nitrogen analysis can be found in the Appendix in the NRRI "Quality Assurance and Quality Control Program."

4.7 Diatom Analysis /Core Dating & Mercury Sediment Analysis

Diatom analysis is a useful tool in examining the past history of a water body. Diatoms are a type of algae that grow abundantly and are well-preserved in sediments. Diatom species have unique features that enable them to be readily identified. Certain taxa are usually found under nutrient-poor conditions, whereas others are more common at elevated nutrient concentrations. Since ranges of favorable environmental conditions are known for many species, diatoms are especially useful in sediment-core analysis (Hall and Smol, 1999).

Mercury sediment analysis will help the LCOCD determine which lakes have higher mercury levels which may lead to higher consumption of methyl-mercury that accumulates in predator fish species like walleye pike, muskellunge and northern pike. The following are the protocols associated with diatom and mercury sediment sampling.

Diatom and mercury sediment samples will be taken together using the following procedure used by the USEPA "Survey of the Nation's Lakes" Field Operations Manual.

Collecting the Sediment Core from Natural Lake Using Modified KB Corer

1. Record the lake ID and the date on three sample labels. Mark one label for the top interval (TOP), one for the bottom interval (BOTTOM), and one smaller label (from a separate sheet) for the sediment sample (SED). Attach the labels to two small plastic containers (for diatoms) and one 20 mL plastic (PET) vial (for sediment). Record the bar code numbers on the collection form.
2. If the bottom has been disturbed during the intial depth determination or for any other reason, move at least 5 m to take the core. It is critical that the corer strikes undisturbed surface sediments.
3. Put on surgical gloves. They must be worn during sample collection because the sediments may contain contaminants.
4. Insert the core tube into the sampling housing apparatus and tighten the hose clamp steams to secure the tube.
5. Attach the messenger to the sampler line and slowly lower the corer through the water column until the bottom of the core tube is 0.5 m above the sediment surface. While maintaining a slight tension on the line, let the line slip through the hands and allow the corer to settle into the bottom sediments. Immediately after the corer drops into the sediments, maintain line tension to prevent the corer from tilting and disturbing the core sample. (the goal is to obtain a core 45 cm in length. If this core length is not obtained the first time, the operation might need to be repeated at a new site using a greater release height in order to improve penetration and attain a longer core.)

6. Trip the corer by releasing the messenger weight so that it slides down the line.
7. Slowly raise the corer back to the surface, until the core tube and rubber seal are just under the water.
8. While keeping the seal under water, slowly tilt the corer until you can reach under the surface and plug the bottom of the corer with a rubber stopper. To do this without disturbing the water-sediment interface, you cannot tilt the corer more than 45 degrees.
9. Keeping your hand under the stopper, raise the corer into the boat in a vertical position. Stand the corer in a large tub to prevent contaminating the boat with sediment material.

Process the Sediment Core

1. Detach the core tube from the corer. One person should hold the sampler in a vertical position while the second person dismantles the unit.
2. Measure the length of the core to the nearest 0.1 cm and record the interval on the Sample Collection Form and on the two sample labels.
3. Slowly extrude the sample. To do this, position the extruder under the stopper at the base of the coring tube. Supporting both the core tube and the extruder in a vertical position, slowly lower the coring tube until the sediment is approximately 1 cm below the top of the tube.
4. Remove the water above the sediment core by using a siphon tube with a bent plastic tip (or a small disposable pipette) so that the surface sediments are not disturbed.
5. Continue extruding the core slowly and gently until the top of the core is just below the top of the core tube.
6. Do not open the pre-washed "sampling kit" bag until its time to collect the sediment sample, and make sure the contents of the kit do not come into contact with anything other than the sediment sample.
7. Use the pre-washed 5-mL plastic pipette tip to collect a 1 cm3 sample from the center of the core. Use the wide end of the pipette tip like a corer and insert it into the core sample to the top of the collar on the tube (1 cm deep). Place your finger over the other end of the pipette tip to remove the sediment sample.
8. Transfer the removed sediment into the pre-labeled and pre-washed PET vial. Do not rinse the sample into the vial. Place the sediment sample on dry ice immediately to quick freeze the sample, and kep frozen until shipment. Pipette tips are not re-used, so they should be rinsed with lake water or DI water and disposed of properly.

If sampling a Reservoir, go to steps 12-13 below. If sampling a natural lake, continue with steps 10-13.

10. Before collecting the bottom section, remove the sectioning apparatus and rinse in lake water.

This procedure prevents contamination of the bottom sediment layer with diatoms from the upper portion of the core. This step is critical as a small amount of sediment contains millions of diatoms which would destroy the population structure needed to compare environmental conditions depicted by top and bottom core samples.

11. Continue extruding the sample, discarding the central portion in the tube, until the bottom of the stopper is approximately 5 cm (3 inches) from the top of the coring tube. Affix the sectioning apparatus to the top of the tube. Extrude the sample until the bottom of the stopper reaches the lower black line at the top of the tube (approximately 3 cm from the top of the tube). Section the extruded sediment (2cm) and discard. Rinse the sectioning tube with lake water. Without removing the sectioning apparatus from the coring tube, slightly tilt the tube and wash the sectioning stage with a small amount of water from a squirt bottle. Make sure the rinse water runs off the stage and not into the coring tube with sediment. Lower the tube until the top of the sediment is at the 1-cm mark on the sectioning tube. Collect the 1-cm section of core material in the second plastic container labeled for the BOTTOM interval. Record this interval on the Sample Collection Form and on the sample label for the bottom core. Discard the remaining 2 cm.
12. Cover the labels on each container completely with clear tape. Place containers in a cooler with bags of ice.
13. Rinse the corer, collection apparatus, and sectioning apparatus thoroughly with lake water. Rinse the tap water at the next sampling site.

4.8 Cyanobacteria Microcystin-LR Sampling

A 1-Liter amber glass bottle will be used and should be labeled before entering water. Gloves and waders will be worn; wade slowly to sampling location while trying to avoid agitating bottom sediment. Sampling should occur in water that is knee-deep. If a scum layer is present, samples should be collected there. Open the sampling bottle and grasp it at the base with one hand and plunge the bottle mouth downward into the water. The sampling depth should be approximately 3 to 6 inches below the surface of the water. Position the mouth of the bottle into the current away from your hand. If the water body is static, an artificial current can be created by moving the bottle horizontally with the direction of the bottle pointing away from you. Tip the bottle slightly upward to allow air to exit and the bottle to fill. Fill the bottle to about 1/3 full to allow room for expansion upon freezing. Tightly close the cap of the bottle.

Upon returning to shore, place the sample in a cooler with ice. Store and transport (to the State Lab of Hygiene) the sample on ice. Ship all samples on ice, in a cooler, to the Wisconsin State Laboratory of Hygiene the same day as samples were collected. Pack the bottles in the cooler carefully to inhibit breakage. Place laboratory slips in a zip-loc plastic bag in the cooler with the sample bottles.

Sample location on each lake will be determined by LCOCD staff.

4.9 DECONTAMINATION PROCEDURES

No heavy contamination is expected for this project. However, the water quality meter used will be decontaminated after each sampling location in order to avoid cross contamination between sites. The sonde will be rinsed with surface water from each sampling location before testing, and swung side-to-side at each sampling location depth interval.

Contaminant-free sample containers will be used for all sampling activities.

4.9.1 FIELD DUPLICATE COLLECTION

Duplicate profiling readings will be taken at one sampling location for each day of monitoring. Precision will be calculated by the RPD of each depth interval from the two readings.

Duplicate nutrient sampling will occur periodically throughout ice-out conditions, and during cranberry harvest discharge events.

SECTION FIVE: CUSTODY PROCEDURES

5.1 FIELD CUSTODY PROCEDURES

A field logbook will be used by the technicians to document all information related to surface water monitoring activities. Logbook entries will include: time, date, location, site description, weather conditions and personnel present. All pages will be signed and dated.

For samples that need to be shipped to the contract laboratory, all necessary chain of custody (COC) procedures will be followed. These include: properly labeling each sample with time, date, site code, sampler name and analytical parameter.

COC forms will be filled out, signed and dated by LCOCD staff. Copies of COC forms will be made and filed at the LCOCD.

5.1.1 Benthic Sampling Custody Procedures

Each sample will contain an interior and exterior label. Sample labels identify: 1) project name, 2) site name or number, 3) sample number and number of containers (i.e. large samples that are placed in multiple containers, A-D), 4) gear type (Ponar, D-net, corer, etc.), 5) sieve size used to wash sample, and, 6) current date.

Labels may be coded or include limited information, but must be referenced with an accompanying log sheet that provides the required information from number 1 through 6. Interior labels written in pencil lead are required. Outside labels may also contain a brief description or code, but must include at least a unique identifier for lab sorting, prioritized processing, and archiving purposes.

5.2 LABORATORY CUSTODY PROCEDURES

5.2.1 Laboratory Sample Inventory

A list of samples, including all label information, is completed in field notebooks as samples are collected. A sample list accompanies all samples returning to the laboratory. Chain of custody forms are completed and verified with the field sample list as in-coming samples are inventoried by laboratory personnel. Chain of custody forms and a field sample list are duplicated, filed with field notes or data sheets, and one copy placed in the project log book.

5.3 FINAL EVIDENCE FILE

A final evidence file will be created for all evidence and project-related data relevant to sampling activities described in this QAPP. The file will include (but not limited to) field notebooks, photographs, progress reports, COC forms, QA reports and all project-related documentation.

SECTION SIX: CALIBRATION PROCEDURE AND FREQUENCY

6.1 FIELD INSTRUMENT CALIBRATION

The field instruments to be used, the YSI 610 Display/Logger with 6-series sondes, and the Hydrolab Datasonde 4, will be calibrated prior to the beginning of each scheduled monitoring time. All YSI & Hydrolab standard operating procedures for calibration will be followed. Slight variations may occur with individual parameters. To maintain accurate results, calibration procedures will be done thoroughly and consistently before each monitoring period. YSI & Hydrolab SOPs can be found in the Appendix.

SECTION SEVEN: ANALYTICAL PROCEDURES

Surface water will be field analyzed for the following parameters: dissolved oxygen, specific conductivity, temperature, pH and total dissolved solids.

7.1 FIELD ANALYTICAL PROCEDURES

Field analysis will involve the use of the YSI and Hydrolab Multi-Parameter Water Quality Meters. The water meter is maintenanced on a monthly basis and calibrated each day before monitoring. The SOPs for the water meter can be found in the Appendix.

7.2 LABORATORY ANALYTICAL PROCEDURES

7.2.1 Benthic Sample Processing

Prior to processing, samples preserved in the field with 10% formalin are rinsed to remove the formalin preservative. This procedure is conducted under a ventilation hood. The rinsed sample is then re-preserved in 70% ETOH. Discarded preservative are stored in containers labeled with appropriate hazardous waste information and transferred to Hazardous Chemical Storage.

Samples ready for processing are signed out of the project log book by lab personnel. Samples may contain multiple containers, so all containers for that sample are concurrently processed. All sample information contained inside the sample container should be verified with outside labels and project log book information. Due to the amount of material contained in a sample, it may be necessary to sub-sample or "split" various samples.

Sample materials are washed in the appropriate sieve and a final rinse is conducted in a wash pan. The remaining sample is rinsed into a sorting pan and any material remaining in the wash pan that passes through the sieve is discarded. Large amounts of material passing through the sieve are deposited in a waste receptacle and not discarded in the lab sink. Depending on the sediment type, samples can be washed using an elutriation device, colloidal silica bath, or other flotation procedures. These devices are designed to separate light organic materials from heavier particles in a sample.

Once the sample has been thoroughly washed and sub-sampled accordingly, the sample is transferred to a tray, glass pan, or sorting dish. Sample material should be spread evenly throughout the pan. Large trays and glass pans should be sorted using a 2X magnification lens. A dissecting scope is used to process samples placed in a sorting dish.

Organisms are removed from detritus with a forceps and placed in labeled vials. Vial labels contain identical information as sample labels, with the addition of the amount of sample processed (i.e. 1/4, ½, or whole), a vial number, the total number of vials for that particular sample (e.g. 1 of 3), and initials of lab personnel. The number of vials accompanying each sample will depend on the abundance of organisms, but one vial should be designated for only midge larvae. All samples will be subjected to QA/QC inspection.

7.2.2 Macro-Invertebrate Sample Identification

Sample vials containing processed macro-invertebrates are then signed out for identification using the vial chain of custody form. Organisms are identified to the lowest taxonomic level using appropriate keys, enumerated, and recorded on an identification data sheet. A reference collection is made for each individual taxa identified for the entire project. The collection is then subject to QA/QC guidelines that include re-identifying 30% of the collection. If more than 5% of the randomly selected taxa are questioned, the entire collection is re-identified.

Individual Mounts

Individuals within the family Chironomidae (Diptera) are permanently mounted for further taxonomic identification. Generic identification requires head capsule decapitation to ensure ventral viewing of individual mouth parts. Organisms are soaked in 95% ETOH, preserved in euparal mounting medium, and placed under a cover slip. Generally, the number of individuals per slide depends upon body size. Individual placement on the slide and label information will follow standard template.

Individual Identification

Permanent slide mounts will be identified to the lowest taxonomic level under a copound microscope. Each individual will be assigned a particular slide number, position, and side, so a separate reference collection for these organisms is not necessary because location of individual organisms can be easily assigned. Chironomids will also be subjected to a 30% random re-identification for lab verification.

7.2.3 Macro-invertebrate Data Entry

Data from laboratory sheets will be entered in a Microsoft Access database, or entered in duplicate using a standard spreadsheet software. The data are subject to a 10% random evaluation according to the number of data records. An error rate greater than 1% will result in re-entry.

Data are merged with a database (bugspec.xls) in SAS to check for errors and provide higher taxonomic categories for all individuals identified. Individuals not listed in the database are either re-identified or the current information and taxonomic name are compared to the ITIS system database for confirmation.

7.2.4 Phytoplankton Sample Processing and Identification

Whole water samples are fixed with ~ 5% Lugol's Iodine and stored at 4 C. For counting, sample is mixed well and a 20-30 mL aliquot is poured into a 45 mL Utermohl chamber (made at NRRI) prefilled with ~ 20 mL tap water (see Sandgren and Robinson 1984). Samples are allowed to settle a minimum of 24 hrs.

Algal scans are made using an Olympus IM inverted microscope. The slide is scanned at 400x and cells are identified to genus and species if possible. Then % biomass is estimated at 200X based on cell size, growth form and density. Often, biomass estiamtes are difficult to make due in both high and low density samples. In some cases, several Genera within the same class are clumped together and given a group biomass estimate.

NRRI most commonly uses Prescott, 1982 to identify cells to genus/species. Willen et al and Anton and Duthie are used to identify Cryptomonads.

7.2.5 Zooplankton Sample Processing and Identification

Density estimates for each sample will be based on (1) quantitative sub-samples of 100 specimens from each of the taxonomic groups and (2) searches of at least half the sample for the rare taxonomic groups. Three major taxonomic groups, cladocerans, copepods, and rotifers, will be categorized and counted. Cladocerans are distinguished as *Daphnia, Bosmina, Diaphanosoma, Chydorus, Ceriodaphnia, Holopedium, or Leptodora kindti.*

Cladocerans are often referred to as water fleas and vary between 0.2 and 3mm in length. Cladocerans are common in northern temperate lakes especially in the summer, and all but *L. kindti* are primarily herbivorous.

Copepods, a second major group of zooplankton, are distinguished as either *Cylcopoid* copepods or *Calanoid* copepods for copepodid stages. Nauplii, immature copepods in the naupliar stage, are categorized as copepod nauplii.

Rotifers are the third major taxonomic group of zooplankton quantified. Rotifers are ubiquitous in freshwater and are a highly diverse taxonomic group in both size (40 um to 2.5mm) and feeding behaviors (herbivores, detritovores, and omnivores).

In addition to the three major taxonomic groups, *Chaoborus* and *Chironomids* will be quantified. These are aquatic stages of insects found in the plankton, which can be important predators of zooplankton. These invertebrate predators are known to migrate into the sediments during the day to avoid visual predation by fishes and therefore the data will be regarded as presence/absence information and not faithful density estimates.

Two density estimates will be provided for each sample, the number of each taxonomic group per

square foot, and the number of each taxonomic group per cubic foot. The latter takes into account the depth of the sampling site and is a common method to compare abundances across sites with different depths. A total density of zooplankton for each sample will also be provided.

Four total summary indices will be calculated for each sample, the Shannon Diversity Index, the Gannon Index, and two cladoceran size indices.

The Shannon Diversity Index is used to determine the diversity of each sample. This index uses the number of taxonomic groups and their relative abundance to estimate how much biological diversity is present at the site.

The Gannon Index is used to compare the productivity or trophic status of the sites sampled. This ratio is defined as the ratio of *Calanoid* copepod density to the sum of *Cyclopoid* copepod density and cladoceran density. The Gannon Index is useful in comparing the trophic status of multiple locations or sampling times in a single lake, or among different lakes. If the Gannon index is a smaller number, the productivity of a lake is high, or tends toward the more eutrophic side of the spectrum.

A size index will be used to compare the density of small cladocerans (*Bosmina, Ceriodaphnia*, and *Chydorus*) to the total density of cladocerans. A high value for this size index might indicate that size selective predation (SSP) by fish is intense and planktivorous fish are abundant.

The ratio of *Daphnia* to *Bosmina* will also be calculated. This ratio, although helpful in assessing SSP, is primarily an indication of food quality for herbivorous plankton. A high *Daphnia* to *Bosmina* ratio might indicate the predominance of lower quality phytoplankton.

7.2.6 TSS Sample Processing (NRRI)

A well mixed raw water sample is filtered through a weighed standard fiber filter and the residue retained on the filter is dried to a constant weight at 103-105 degrees Celsius. The increase in weight of the filter represents the total suspended solids.

Large floating particles or submerged agglomerates of nonhomogeneous materials from the sample are excluded if it is determined that this inclusion is not desired in the final result. Because excessive residue on the filter may form a water-entrapping crust, limit the sample size to that yielding no more than 200 mg residue. For samples high in dissolved solids, the filter is thoroughly washed to ensure the removal of the dissolved material. Samples must be filtered within 7 days and kept at 4 degrees Celsius. The limit of detection is based on the balance used in the analysis. Weights below 5 mg on a 4-place analytical balance should be considered unreliable. In such a case, more water should be filtered.

NRRI has traditionally used Whatman GF/C filters and has passed performance evaluation testing

using those filters. It is important that filter type be recorded during any extended study and that the type not be changed during the study.

Analytical Procedure

1. Preparation of glass-fiber filter: Insert filter with wrinkled side up on filtration apparatus. Apply vacuum and rinse filter with three successive 20-mL portions of deionized water (DIW). Continue scution to remove all traces of water, and discard rinse. Remove filter from filtration apparatus and transfer to a labeled aluminum weigh pan. Dry briefly at room temperature before drying the rinsed filters at 105 degrees Celsius for 2 hours. Lift the filter from the pan before placing it in the oven. This will prevent sticking.
2. If volatile solids are also to be measured, ignite filters in a muffle furnace. Cool to room temperature in a desiccator and weigh. Repeat cycle of drying or igniting, cooling, desiccating, and weighing until a constant weight is obtained or until weight loss is less than 0.5 mg between successive weighings. Store in desiccator until needed. Weigh immediately before use.
3. Sample analysis: Assemble filtering apparatus, seat filter and begin suction. Wet filter witha small volume of DIW to seat it. Filter a measured volume of well-mixed sample through the glass fiber filter. Wash with three successive 10-mL volumes of DIW, allowing complete drainage between washings and continue suction for about 3 minutes after filtration is complete. Carefully remove filter from filtration apparatus and transfer to an aluminum weigh pan as a support. Dry for at least 1 hour at 103-105 degrees Celsius in an oven, cool in a desiccator to room temperature, and weigh. Repeat the cycle of drying, cooling, desiccating, and weighing until a constant weight is obtained or until the weight loss is less than 4% of the previous weight or 0.5 mg, whichever is less.

Calculation: $\text{mg TSS/L} = \dfrac{(A-B) \times 1000}{\text{Sample volume, mL}}$

where:

A = weight of filter + dried residue, mg, and
B = weight of filter, mg.

QA/QC

1. Record temperature of drying oven and/or muffle furnace.
2. Record balance used.
3. Record type of filter used.

References

Standard Methods for the Examination of Water and Wastewater, Method 2541 D. 18th Ed. 1992. American Public Health Association, Washington, D.C.

7.2.7 Total Phosphorus and Total Nitrogen Analytical Procedures

Laboratory methods pertaining to Total Phosphorus and Total Nitrogen analysis can be found in the Appendix in the NRRI "Quality Assurance and Quality Control Program" Manual.

7.2.8 Sediment Diatom Methods

Laboratory methods for sediment diatom analysis can be found in the Appendix.

7.2.9 Cyanobacteria Toxin Analysis

Analysis of the Cyanotxin Microcystin by the Elisa Method can be found in the Appendix.

SECTION EIGHT: INTERNAL QUALITY CONTROL CHECKS

8.1 FIELD QUALITY CONTROL CHECKS

The QC procedure for dissolved oxygen, pH, specific conductance, total dissolved solids and temperature measurements of surface water involve the calibration of the water quality meter as described in the YSI and Hydrolab SOP's.

8.2 LABORATORY QUALITY CONTROL CHECKS

The Wisconsin State Lab of Hygiene and the Natural Resources Research Institute follow strict QA/QC protocols outlined throughout this document.

SECTION NINE: DATA REDUCTION, VALIDATION AND REPORTING

9.1 DATA REDUCTION

9.1.1 Field Data Reduction

Field data reduction procedures will be minimal due to the equipment being used. The YSI and Hydrolab Multi- Parameter Water Quality Meters will generate measurements that are directly read from its data display component. Information taken from the data display will be transferred onto site-specific surface water quality profiling data sheets immediately upon taking a reading.

9.2 DATA VALIDATION

The primary procedures that will be used to evaluate field data include checking for transcription errors and review of data sheets and data entry. It is the Project Manager's responsibility to validate data-entry errors before data sheets are filed away.

9.3 DATA REPORTING

Measurements taken from the field will be reported on data sheets; calibration activities performed in the field will be documented in a field logbook. The Project Manager will be responsible for field data recording, data entering and preparation of final reports. Data received from the contract laboratories will be downloaded into the LCO Water Quality database in Quattro Pro and Excel Spreadsheet format.

SECTION TEN: PERFORMANCE AND SYSTEM AUDITS

10.1 FIELD PERFORMANCE AND SYSTEM AUDITS

Internal audits of calibration procedures and field activities will be performed by the Project Manager. The Project Manager will examine, verify, or correct all information monthly to ensure project consistency.

SECTION ELEVEN: PREVENTATIVE MAINTENANCE

11.1 FIELD INSTRUMENT PREVENTATIVE MAINTENANCE

Proper calibration and maintenance procedures for the water quality meter will be followed to prevent, or reduce down time. The main preventative maintenance concern is proper short-term storage of the sonde. The key for interim storage is to use a minimal amount of water so that the air in the chamber remains at 100 percent humidity, but the water level is low enough so that none of the sensors are actually immersed. Other preventative maintenance is to make sure the storage vessel is sealed, the data display unit is recharged daily, and the vessel is checked periodically to make certain that water is still present.

SECTION TWELVE: DATA QUALITY ASSESSMENT

It is the Project Manager's responsibility to perform data quality assessment. The quality of the data will be determined by its usability in decisions made regarding water quality management on the LCO Reservation.

Reference sites will be selected to compare and assess the monitoring data acquired in the study. Similar water bodies that are not currently developed or exposed to contamination sources will be chosen for comparison.

SECTION THIRTEEN: CORRECTIVE ACTION

13.1 FIELD CORRECTIVE ACTION

Corrective action may be required for field equipment problems. Re-calibration procedures and part replacement will all be documented in the field logbook. All corrective actions taken during the project will be maintained in the project file. The Project Manager is responsible for proper corrective action documentation and procedures.

SECTION FOURTEEN: QUALITY ASSURANCE REPORTS TO MANAGEMENT

A quality assurance report will be produced at the end of the project period. This report will contain: data validation and assessment results, field audit results, QA/QC problems and corrective actions taken during the project. Monthly reports will also be submitted to the LCO Project Manager to ensure that problems arising during the monitoring phase are investigated and corrected.

Table 1
Surface Water Monitoring Locations - Lakes

Lake Names	Location	# of Sample Sites	Monthly Monitoring	Action Level For Dissolved Oxygen	Surface Water Monitoring Parameters
Ashegon	T39NR8W	1	yes	5 mg/l	total phosphorus, chlorophyll a, secchi disc, exotic species, lake sediment mercury concentration, dissolved oxygen, pH, water temperature, specific conductance,diatom analysis & core dating top & bottom
Big Round	T41NR8W	3	yes	5 mg/l	total phosphorus, chlorophyll a, secchi disc, exotic species, dissolved oxygen, pH, water temperature, specific conductance
Blueberry	T39NR7W	1	yes	5 mg/l	total phosphorus, chlorophyll a, secchi disc, exotic specie s, dissolved oxygen, pH, water temperature, specific conductance
Chippewa Flowage	T40NR7W/6W	18	yes	5 mg/l	total phosphorus, chlorophyll a, secchi disc, lake sediment mercury concentration (8), dissolved oxygen, pH, water temperature, blue-green algae toxins (10), specific conductance, diatom analysis & core dating top & bottom(4)
Christner	T40NR9W/8W	1	yes	5 mg/l	total phosphorus, chlorophyll a, secchi disc, exotic species, lake sediment mercury concentration, dissolved oxygen, pH, water temperature, specific conductance, diatom analysis & core dating top & bottom
Devils	T39NR8W	1	yes	5 mg/l	total phosphorus, chlorophyll a, secchi disc, exotic species, lake sediment mercury concentration, dissolved oxygen, pH, water temperature, specific conductance
Green	T40NR8W	1	yes	5 mg/l	total phosphorus, chlorophyll a, secchi disc, exotic species, lake sediment mercury concentration, dissolved oxygen, pH, water temperature, blue-green algae toxins, specific conductance, diatom analysis & core dating top & bottom
Grindstone	T40NR8W/9W	1	yes	5 mg/l	total phosphorus, chlorophyll a, secchi disc, exotic species, dissolved oxygen, pH, water temperature, specific conductance
Gurno	T40NR8W	1	yes	5 mg/l	total phosphorus, chlorophyll a, secchi disc, exotic species, lake sediment mercury concentration, dissolved oxygen, pH, water temperature, blue-green algae toxins, specific conductance, diatom analysis & core dating top & bottom
Indian	T40NR8W	1	yes	5 mg/l	total phosphorus, chlorophyll a, secchi disc, exotic species, lake sediment mercury concentration, dissolved oxygen, pH, water temperature, specific conductance, diatom analysis & core dating top & bottom
Lac Courte Oreilles	T39NR9W	11	yes	5 mg/l	total phosphorus, chlorophyll a, secchi disc, exotic species, dissolved oxygen, pH, water temperature, hlue-green algae toxins (5), specific conductance

Little Lac Courte Oreilles	T39NR8W	1	yes	5 mg/l	total phosphorus, chlorophyll a, secchi disc, exotic species, lake sediment mercury concentration, dissolved oxygen, pH, water temperature, specific conductance,
Little Round	T41NR8W	1	yes	5 mg/l	total phosphorus, chlorophyll a, secchi disc, exotic species, lake sediment mercury concentration, dissolved oxygen, pH, water temperature, specific conductance
Lost	T40NR7W	1	yes	5 mg/l	total phosphorus, chlorophyll a, secchi disc, exotic species, lake sediment mercury concentration, dissolved oxygen, pH, water temperature, specific conductance, diatom analysis & core dating top & bottom
Sand	T39NR9W	1	yes	5 mg/l	total phosphorus, chlorophyll a, secchi disc, exotic species, dissolved oxygen, pH, water temperature, blue-green algae toxins, specific conductance
Spring	T40NR9W/8W	1	yes	5 mg/l	total phosphorus, chlorophyll a, secchi disc, exotic species, lake sediment mercury concentration, dissolved oxygen, pH, water temperature, blue-green algae toxins, specific conductance, diatom analysis & core dating top & bottom
Squaw(Osprey)	T40NR8W	1	yes	5 mg/l	total phosphorus, chlorophyll a, secchi disc, exotic species, lake sediment mercury concentration, dissolved oxygen, pH, water temperature, specific conductance, diatom analysis & core dating top & bottom
Two Boys	T40NR7W	1	yes	5 mg/l	total phosphorus, chlorophyll a, secchi disc, exotic species, lake sediment mercury concentration, dissolved oxygen, pH, water temperature, specific conductance
Whitefish	Y39NR9W	1	yes	5 mg/l	total phosphorus, chlorophyll a, secchi disc, exotic species, dissolved oxygen, pH, water temperature, specific conductance

Table 2
Surface Water Monitoring Locations - Rivers, Streams and Creeks

River, Stream, & Creek Names	Location	Monthly Monitoring	Action Level for Dissolved Oxygen	Surface Water Monitoring Parameters
Alder Creek (Between Ortwig and Tuscobia Trail)	T38NR8W	yes	7 mg/l	DO, pH, total dissolved solids, specific conductance, total phosphorus, temp, total suspended solids, fish assemblage survey, total nitrogen
Chippewa River-West Fork Area closer to Flowage	T40NR6W	yes	5 mg/l	DO, pH, total dissolved solids, specific conductance, total phosphorus, temp, total suspended solids, total nitrogen
Chippew River-East Fork Area Closer to Flowage	T39NR6W	yes	5 mg/L	DO, pH, total dissolved solids, specific conductance, total phosphorus, temp, total suspended solids, total nitrogen
Couderay River	T39NR8W/T38 NR7W	yes	5 mg/l	DO, pH, total dissolved solids, specific conductance, total phosphorus, temp, total suspended solids, total nitrogen
Eddy Creek Upper and Middle Sections	T39NR7W	yes	7 mg/l	DO, pH, total dissolved solids, specific conductance, total phosphorus, temp, total suspended solids, fish assemblage survey, total nitrogen
Gorman Creek	T40NR6W	yes	7 mg/l	DO, pH, total dissolved solids, specific conductance, total phosphorus, temp, total suspended solids, fish assemblage survey, total nitrogen
Grindstone Creek Upper Section Fish All Sections Water Chem.	T40NR8W	yes	7 mg/l	DO, pH, total dissolved solids, specific conductance, total phosphorus, temp, total suspended solids, fish assemblage survey, total nitrogen
Pipestone Creek	T39NR7W	yes	7 mg/l	DO, pH, total dissolved solids, specific conductance, total phosphorus, temp, total suspended solids, fish assemblage survey, total nitrogen

Demon Creek (Reserve Rd. Creek) Closer to Little LCO	T39NR8W	yes	5 mg/l	DO, pH, total dissolved solids, specific conductance, total phosphorus, temp, total suspended solids, fish assemblage survey, total nitrogen
Surette Creek	T40NR6W	yes	7 mg/l	DO, pH, total dissolved solids, specific conductance, total phosphorus, temp, total suspended solids, fish assemblage survey, total nitrogen

APPENDICES

APPENDIX A
NRRI QA/QC Program Manual
(LCO's Contract Laboratory)

Natural Resources Research Institute
Quality Assurance and Quality Control Program
Manual

Quality Assurance and Quality Control Program

General

One of the fundamental responsibilities of water management is the establishment of continuing programs to insure the reliability and validity of data. Effective research in water pollution and management depends on a valid laboratory data base, which in turn may contribute to sound evaluations of both the progress of the research itself and the viability of available water pollution and management alternatives.

Quality Assurance and Quality Control (QA/QC)

Primary functions:

1. Continuous monitoring of the reliability (accuracy and precision) of the results reported (i.e., determination of quality).
2. Control of quality, meeting the requirements for reliability.

Quality assurance and quality control start with sample collection and are not complete until data is reviewed and accepted. Each method has a rigid, referenced protocol. Similarly, QA/QC associated with the test must include specific steps for monitoring the test and ensuring that its results are correct. All experimental variables that affect the final results should be considered, evaluated, and controlled.

Several types of water samples are gathered and analyzed as part of continuing programs at the Natural Resources Research Institute (NRRI). These include water from precipitation, streams, wetlands, lakes and septic system effluent and sediments or other particulate matter. Concentrations of many chemical constituents are in the low µg/l (ppb) range, therefore some of our methods are specifically adapted for very low nutrient and low ionic strength samples. Although they may not be certifiable by the Minnesota Department of Health, they are currently used extensively by limnological and oceanographic research centers.

Sample Collection

Sample containers are cleaned by prescribed methods that are documented to insure proper and consistent preparation prior to use (See Table I-1).

Sample Holding and Preservation

Most analyses must be completed within a specified time in order to ensure that true concentrations are measured. Holding time and type of preservation based on Environmental Protection Agency (EPA) recommendations are given in Table I-2. Parameters with short holding periods, 24 hours or less, are given priority and analysis is completed as quickly as possible. When all of the analyses are completed and the report is completed, each sample is stored according to its preservation criterion for a period of at least 8 weeks. See Table I-2.

Table I-1. Typical Bottle Preparation Protocols[1,2]

pH-ANC-EC	250 ml	MQW soak 48 hours, rinse 3x MQW
Major Anions	125 ml	MQW soak 48 hours, rinse 3x MQW
DOC	125 ml	Rinse 10% HCL, 3x MQW , soak MQW 24 hours, rinse 2x MQW
Major cations and other metals†	60-125ml	Soak 15% HNO3 24 hours, rinse 4x MQW , soak MQW 24 hours, rinse 2x MQW
Nutrients (N and P-series)	125 ml	Rinse 10% HCL, 3x MQW , soak MQW 24 hours, rinse 2x MQW
Cubitainers	1-4 liters	Rinse 3x MQW , soak MQW 49 hours, rinse 3x MQW
All samples	250 ml	Rinse 10% HCL, 3x MQW , soak MQW 24 hours, rinse 2x MQW
Other parameters	variable	See specific analyte

[1]If not specified, prep bottles according to Standard Methods 1992,1996
[2]MQW = Millipore "Milli-Q" deionized water or equivalent (ASTM Type I, > 15 megohm/cm)
†Laboratory bottle blanks are analyzed for metals on each lot

Bottle Preparation References

Standard Methods for the Examination of Water and Wastewater, 18th Ed. 1992. American Public Health Association, Washington DC.

Brown, J.M. and C.D. Goodyear. 1987. Acid Precipitation Mitigation Program: research methods and protocols. U.S. Fish Wild. Serv. National Ecology Center, Leetown, WV. NEC-87/27. V.P.

U.S. EPA, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio. 1979. Handbook for Analytical Quality Control in Water and Wastewater Laboratories. EPA-600/4-79-019.

U.S. EPA, Acid Deposition and Atmospheric Research Division, Washington, D.C. 1987. Handbook of Methods for Acid Deposition Studies - Laboratory Analysis for Water Chemistry. EPA-600/4-87-026.

Tracking Samples

The majority of samples received or collected for analysis at NRRI do not require a formalized chain of custody. Samples are preserved and refrigerated or frozen according to batch or date (depending on the project). Sample tracking charts are prepared and customized according to project. A record is kept of the analyst and date for each parameter for each sample.

If the samples require a specific chain of custody, a procedure does exist for handling these samples. See Table I-2.

Analytical Equipment: Calibration and Maintenance Schedules

A preventive maintenance program is followed to ensure that instruments used for analysis are in optimum condition for operation. Personnel available within the lab are well trained in routine cleaning and maintenance of the instrumentation. This in-house maintenance is supported by service contracts with the instrument manufacturer for annual preventive maintenance or relatively quick response should a breakdown occur. Calibration and maintenance are archived in the QA/QC files and instrument logs. Lists of maintenance schedules for equipment can be found on Table I-3.

Glassware

A separate set of glassware is maintained for each parameter that is routinely analyzed in the lab. In addition, care is taken to prevent glassware used for waters with high analyte concentrations from being used for very dilute waters. Glassware for standards is typically stored in 0.1N HCl unless otherwise stated (i.e. chloride, buffers, chlorophyll). Stored glassware is rinsed at least three times with lab deionized water (> 1 megohm/cm) and then three times with "Milli-Q" water before use (MQW=Milli-Q water, > 15 megohm/cm from a Millipore Milli-Q deionizing system).

Standard Solutions

For all wet chemistry techniques, a liquid stock is prepared as per the specific method. In most cases the stock is then stored refrigerated in the dark. Working standards are prepared by diluting from the stock with Class A pipettes or volume verified variable pipettes and are either stored in the same manner as the stock or made fresh daily.

Reagents

Chemicals used for reagents are ACS grade or better, unless otherwise noted in a specific method. Reagents made with chemicals from new lots of chemicals are generally checked against reagents made with the previous lot to check for possible analyte background, especially if lower grades of chemicals are used. Use of chemicals below ACS grade is carefully evaluated before incorporation into operating protocols.

General QC Parameters

All analysts use some form of qualitative QA/QC to produce credible results, however, a good QC program consists of at least six elements:

1. Recovery of known additions
2. Analysis of externally supplied standards
3. Analysis of reagent blanks
4. Calibration with standards
5. Analysis of duplicates
6. Maintenance of control charts and QC logs

A seventh element exists which may be the most important to a successful QA/QC program. This is a working understanding of the purpose of the first six so that identification of "out-of-control" situations can be made quickly and corrections executed with minimal down-time of the analysis.

Recovery of Known Additions

"Recovery of Known Additions"or addition of an analyte spike to a sample is part of our regular methodology. Concentration of the known additions are 1 to 50 times the limit of detection (See Limit of Detection section) and fall within the linear range of the method. Concentrated solutions are used for additions so that volume change in the sample is negligible. See Table I-4 for frequency of additions. Recovery is expressed as a percentage and is calculated as follows:

$$\% \text{ Recovery} = \left[\frac{\text{Spiked Sample} - \text{Sample}}{\text{Spike conc.}}\right] \times 100$$

Analysis of Reagent Blanks and Blank Spikes

Reagent blanks are run for each standard curve and may be inserted after samples with high concentrations to identify carryover to more dilute samples. At least one reagent blank per run is spiked with analyte at the same level as the samples and the percent recovery is calculated as per known additions to verify spiking level.

Analysis of Externally Supplied Standards

Quality control (QC) samples[1] with a certified known concentration are analyzed with each batch of samples. QC samples run at the beginning and end of each batch can show drift in the analytical run. These samples are prepared to fall within the linear range of the method. The assigned identification number or lot number of the external quality control standard should be recorded with each data set to allow tracking in the event determined concentrations show drift beyond control limits.

Passing ranges for QC samples are posted in the quality assurance/quality control (QA/QC) data sheets and are updated for each new standard. A percent recovery is calculated by:

$$\% \text{ Recovery} = \frac{\text{Determined concentration}}{\text{Certified concentration}} \times 100$$

Acceptable limits for these standards are 90-110% (± 10%). If ± 10% cannot be achieved, the instrument must be re-calibrated and the analysis repeated. See Table I-4.

Calibration with Standards

Working standards are prepared by diluting a stock solution. For each run a minimum of three different concentrations spanning the expected range and a blank are prepared. Concentrations of individual samples are calculated from a regression of the measured parameter (e.g., spectral absorbance) against the standard concentration. If a sample concentration is greater than the highest standard of the standard curve the sample must be diluted so its concentration falls within the mid range of the standard curve. Milli-Q water (MQW) is used for all blanks, standards, reagents, and final rinsing of glassware.

Analysis of Duplicates

When samples have measurable levels of the constituent being determined, analysis of duplicate samples is used to estimate precision. In most cases, duplicates are run on 10% of the samples. See Table I-4 for frequency of duplicates.

Maintenance of Control Charts and QA/QC Logs

Quality control charts are essential for quality control. There are several parameters that must be defined for use and maintenance of quality control charts.

Limit of Detection (LOD): This is the lowest concentration of an analyte that the analytical process can reliably detect. The LOD can further be defined as three times the variability (i.e., standard deviation) in the gross signal of the reagent blanks. The LOD is calculated every 25 runs or quarterly, whichever comes first.

[1]Available from Analytical Products Group (APG), 2730 Washington Blvd, Belpre, Ohio 47514

As the LOD is approached, the variance typically increases. This requires us to have what is termed the Limit of Quantification (LOQ) for a method.

Limit of Quantification: The LOQ is defined as the value for an analyte great enough to produce <15% RSD for its replication.

$$LOQ = 10(S.D.)$$

where 10(S.D.) is 10 times the standard deviation of the gross blank signal.

Lower and Upper Control Limits (LCL and UCL):
To monitor drift in the calibration curves, warning limits are established and plotted. The Upper Control Limit (UCL) is the highest acceptable range of occurrence for a particular QA/QC parameter. The Lower Control Limit (LCL) is the lowest acceptable range of occurrence for a particular QA/QC parameter. UCL and LCL can be calculated as:

$$UCL = \bar{X} + 3(S.D.)$$
$$LCL = \bar{X} - 3(S.D.)$$

where:

$\bar{X}$ = the mean value of the parameter
3(S.D.) = three times the standard deviation of the parameter

We apply control limits by plotting them as absolute boundaries for the acceptable range of occurrence. The mean value ($\bar{X}$) becomes the central line of the control chart. Control charts are continuously updated and evaluated every 25 runs or quarterly, whichever comes first.

Percent Relative Standard Deviation of Replicates (% RSD): Ten percent of a run of samples are run in duplicate and the % RSD, also called the coefficient of variation, is calculated by:

$$\%RSD = 100 \times \frac{(S.D.)}{\bar{X}}$$

where:

S.D. = standard deviation of the replicates
$\bar{X}$ = mean of the replicates

A % RSD below 15% for most replicates is considered acceptable. If the 15% RSD is exceeded, the samples will be reanalyzed. %RSD normally applies where the number of replicates is greater than 3.

Relative Percent Difference (RPD): While our standard laboratory convention is to analyze 10% of the samples in duplicate and use %RSD of the duplicates as a guide for accepting or rejecting the data, another measure of the variation of duplicates is RPD or:

$$RPD = \frac{|X_1 - X_2|}{\frac{(X_1 + X_2)}{2}} \times 100$$

Where:

X_1 = Value of duplicate 1, and
X_2 = Value of duplicate 2

If the RPD exceeds 15%, the sample will be reanalyzed.

Midpoint Check Standard: This refers to the placement of a mid range standard into the sample run. The value obtained should show less than 10% deviation from its true value. See Table I-5 for frequency of midpoint check standards.

"Out-of-control" Situations: In examining control charts and other QA/QC parameters, any of the following conditions would indicate an "out-of-control" situation.

1. Any point on a control chart beyond the control limits (i.e., LCL and UCL).
2. Seven successive points on the same side of the central line (mean) of the control chart.
3. A % RSD for duplicates greater than 15% above the LOQ.
4. A QC check standard beyond its passing range.
5. Failure of a calibration curve where "failure" is defined as a r^2 of 0.99 or less.
6. Midpoint check standard failure.

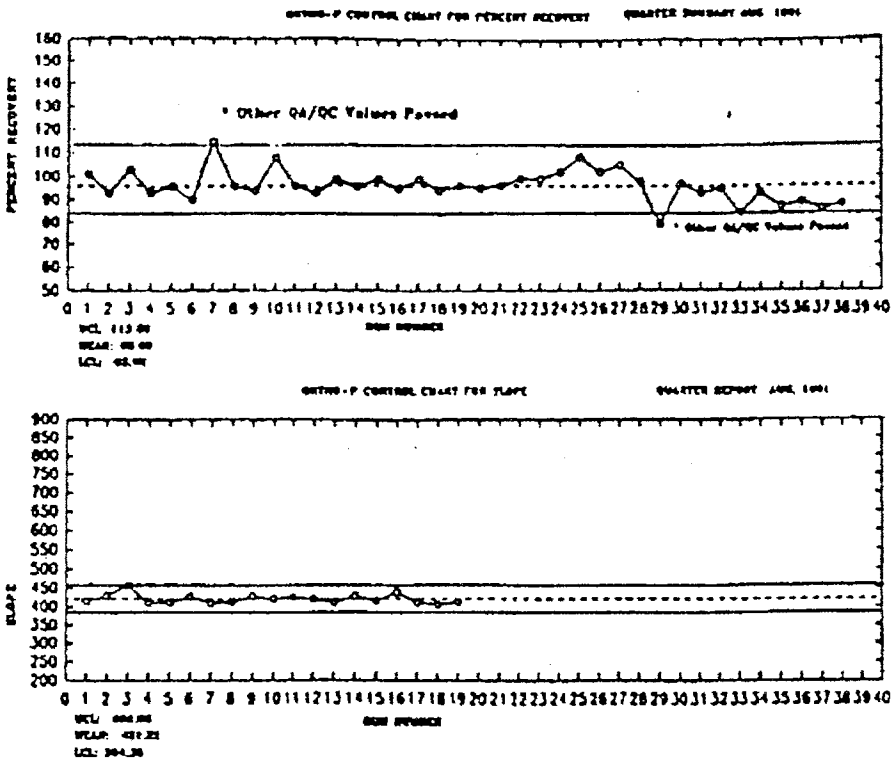
When an "out-of-control" situation occurs, the analyses must be stopped until the problem has been identified and resolved. A decision may be made to eliminate certain standards or spikes if the analyst can support this decision based on previous experience, knowledge of the aquatic system and an examination of other QA/QC information for that run. See Figure 1.

Performance Evaluations

Periodic audit and reference samples are received from a Minnesota Department of Health approved provider. We also analyze samples in a round robin laboratory comparative study with the Lake Superior Association of Environmental Laboratories (LSAEL) every four months. See Table I-4.

Data Handling and Reporting

Figure 1



After completion of an analysis, the control sheets are filled out. These sheets are located in a filing cabinet under the heading QA/QC. If a section is left blank, a comment section is filled out as to why. The comment section is also used to indicate any change in the analysis (i.e., path length, new standards and change in stock solutions). All control chart parameters are manually plotted. Quick reference sheets are provided and updated periodically. These sheets include LCL, UCL, LOQ, and EPA or APG QC values. Special tests (spikes, method modifications, etc.) are included in the QC files, and quarterly reports are generated and reviewed. All data is entered into electronic data sheets for QA tracking. Files are saved on NRRI network backup system each week.

Raw Data

Original raw data is stored, by analysis, under raw data files. A copy of this data is archived by project. A second copy of raw data is placed in a ring-binder for laboratory reference and data entry. Ring-bound data is updated and readily available to lab managers and project heads. Project heads may request a copy of the raw data, but this data should not interfere with standard archiving procedures. Updates of spreadsheets are also filed by project. All lab books are centrally located when not in use. Notebooks do not leave the lab and data is entered ASAP. All raw data should have clear identification including sample ID, name of analyst, type of analysis, date of sample collection, QA/QC sample lot number and date of analysis.

Data Reporting

All data is entered into computerized spreadsheets within 5 days. If a sample falls below the LOD, it is reported as < LOD. Spreadsheets are reviewed by lab managers and project heads prior to release. In addition, data sheets must contain comments if a sample has been incorrectly collected, preserved or has passed its holding time.

Safety

Workplace safety is important at NRRI. NRRI has an active safety committee that meets monthly to discuss ways of improving safety and problems such as accident reports that have occurred. Meetings are also held with project supervisors on a monthly basis to pass on information from the committee and provide them with information on topics from safe driving to ergonomics in the workplace. The committee is supported by the administration with a budget for materials and its own set of laboratory safety slide-tape presentations used for Employee Right to Know training.

The Central Analytical Laboratory (CAL) is an active participant in the programs of the committee and benefits from the safety awareness promoted there.

Initial training of NRRI laboratory personnel to meet the requirements of the Minnesota Employees Right to Know Act (MERTKA) and the OSHA Laboratory Standard is provided by their laboratory supervisor. The program was developed by the Environmental Health and Safety officer at UMD. It is a two hour series of tape-slide presentations from the National Safety Council and the University of Minnesota Environmental Health and Safety Department. The topics covered are:

1. Working with chemical and your health. National Safety Council
   a. General Concepts
   b. Acids and Bases
   c. Solvents
   d. Toxic Metals.
2. Principles of Laboratory Safety, Parts 1 and 2. University of Minnesota

Additional tapes on many topics are available in a safety cubicle on the third floor for many specialized topics of laboratory safety. Programs on radiation safety are required for personnel working with isotopes (Carbon-14 and Tritium) are available along with programs on other topics from the UMD Audio-Visual department in the University library. Laboratory specific information such as the location of available safety equipment, location of material safety data sheets (MSDS), location of chemical storage and hazardous waste storage areas, etc. are also discussed with the employee. Supervisors are expected to train employees in the individual procedures they are performing and advise them of any hazards involved. Documentation of training is on a standard University form and records are kept in the employees file and by the UMD Health and Safety Officer.

Standard safety equipment is available to all laboratory employees. This includes chemical splash goggles, aprons, chemical protecting face shield, rubber and autoclave gloves as personal protection gear. A hearing protection and respirator fit program are in place at the Institute if these are required for specific projects. Eye washes, chemical showers, fire blankets and fume hoods are available in laboratory areas.

Small lots of chemicals are stored in a room near the laboratories that is not actively used as a preparation or analytical area. Solvents, oxidizers and general chemicals are stored by group in separate cabinets. More solvent storage and corrosive chemical storage is in vented cabinets below the laboratory fume hoods. Working mixed reagents are usually stored near their point of use or in a compatible area if they are flammable (hood), produce fumes (hood) or are thermally labile (refrigerator). Case lots of acids or solvents are stored on the first floor of the building in rooms specifically designed for such storage.

Master collections of MSDS for the Institute are maintained in the office of the NRRI laboratory safety officer and the NRRI Library. MSDSs for specific procedures are also available in laboratory areas. MSDS's are available to all Institute employees.

The laboratory maintains a chemical list of all chemicals currently in the Institute laboratories. It lists the chemicals, quantities available, storage location and the National Fire Protection Association coding for hazard and flammability. It is provided to the Hermantown Volunteer Fire Department to aid them in knowing what chemicals are stored in the building as well as what the hazard may be. The list is updated annually.

Hazardous waste produced by laboratory procedures is bottled and held for short term storage in specific areas in the laboratory. It is then transferred to the Hazardous Waste Storage room on the first floor for packaging, manifesting and removal through the University of Minnesota Hazardous Waste Program. The Institute has an EPA Hazardous Waste Generator number. Radioisotope waste produced by the laboratory is handled and stored according to University of Minnesota procedures that have been approved by the Nuclear Regulatory Commission. Assistance in recognizing and dealing with hazards from stored chemicals as well as mixed wastes is always available from the University Environmental Health and Safety program if it is not available "in house."

The NRRI Analytical Chemistry Laboratory complies with the current OSHA laboratory standard. A copy of the modified University of Minnesota Chemical Hygiene Plan is on file in the office of the NRRI Laboratory Safety Officer, NRRI Center offices and the NRRI Library. The Chemical Hygiene Plan covers the general laboratory practices recommended by the University of Minnesota and more specific Institute policies and operating procedures for the laboratory.

Hazard Definitions:

Chemical hazards. Any chemical, especially in concentrated form, that can have a detrimental effect on the health of an individual represents a chemical hazard. For purposes of this manual, chemical hazards have been divided into two categories:

1. Chemical hazard **[*C]**: The reactivity of the chemical or chemicals with each other or tissue involved through contact may create a reaction that is potentially injurious through the creation of heat, explosion, toxic gases and/or destruction of exposed tissue.

   Examples of chemicals included would be corrosives (strong acids and bases, phenol), oxidizers (peroxides, and peroxide forming chemicals), water reactive (sodium), etc. Chemicals designated as having particularly hazardous properties should be handled only by experienced and trained individuals wearing proper protective clothing and equipment. Use of a fume hood for mixing reactive chemicals is advised. MSDS should be consulted for the hazard potential of unknown materials.

2. Toxicity hazard **[*T]**: This is a type of chemical hazard but is flagged separately since the chemical may be extremely toxic to biological systems if ingested or inhaled as a gas or particulate. A toxicity flag may indicate the chemical itself is toxic or a reaction of chemicals may create a product that is toxic, e.g., adding nitroprusside waste to a bottle containing dilute or concentrated acid will produce cyanide gas. Special handling procedures are outlined in the method or a supervisor and the MSDS should be consulted for additional information if questions arise. Use a fume hood and proper protective equipment if chemicals are flagged.

3. Physical hazard **[*P]**: Hazards that can have detrimental health effects on an individual that are not related to the chemical properties but to ionizing radiation, heat, electrical and physical contact. Instruments with high temperature ovens have a thermal hazard and contact should be avoided. Radioactive materials require special handling and knowledge to avoid exposure to the ionizing radiation. Ultraviolet light from UV sources such as deuterium lamps may damage the retina of the eye if proper protective glasses are not worn. Electrical hazards are present any time an instrument is opened for trouble shooting or internal adjustments. When physical hazards are flagged, special knowledge and documented training are required.

Hazardous Waste

Hazardous wastes created by the procedures in this manual are disposed of through the University of Minnesota Hazardous waste program. Analysts are responsible for properly identifying, labeling and storing hazardous waste. Supervisors are responsible for having laboratory personnel trained in proper handling of wastes.

1. Wastes created by any procedure should not be mixed with those from other procedures.
2. Waste containers should be compatible with the wastes they contain. In general, aqueous wastes should be stored in plastic containers and solvent wastes in metal or glass containers. Containers must have sealable caps and not capped with aluminum foil or other mismatched cover.
3. Aqueous wastes stored in laboratory satellite storage must be segregated by pH.
4. Solvent waste bottles must be capped. No solvents shall be evaporated in the fume hoods.
5. Waste containers must be labeled with hazardous waste labels before wastes are added. The labels must be fully filled out with the name of the generator, the generators telephone number, the starting date for the bottle and a complete list of components of the waste along

with approximate concentrations. Chemical names must be complete. Abbreviations such as "MeOH" or "Mercury analysis waste" are unacceptable. Sample labels with the necessary information are included with many of the procedures in this manual.

6. Waste containers should only be filled to the shoulder of the bottle and not filled to the cap. A space must be left for expansion of the contents.
7. When containers are full, a manifest form should be filled out according to instructions in the **Hazardous Chemical Waste Management Manual**. The NRRI hazardous waste officer should be notified of the full container so that it can be checked for proper labeling and manifesting before being transported to hazardous waste storage for shipping. A copy of the manifest is attached to the waste container, a copy is given to the Hazardous Waste Officer and the remaining copies are forwarded to the UMD Hazardous Waste Officer.

Waste Reduction

This laboratory is concerned about the quantity of waste produced and the costs of disposal.

1. Analytical procedures that minimize the quantity of waste will be used as long as the limit of detection is adequate for the project.
2. Chemicals needed for procedures should be purchased on the basis of quantity needed rather than completely on price.
3. Excess chemicals should be made available to other projects .

References

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Revised

J.J. Ameel, E.M. Ruzycki, 01/00, J.J. Ameel, 01/01

Table I-2. QA/QC Summary Table - Handling and Preservation

Parameter	Minimum Recommended Sample Vol. (mL or g)	Filtered (Type) or Raw Water	U.S. EPA Recommended Preservation Method [1]	Container Type	Container Preparation	U.S. EPA Recommended Hold Time [1]	NRRI Method	Detection Limit
Physical II								
Color	100	Raw: Apparent GF/C: True	Refrigeration @ 4°C	Plastic	48 hrs. MQW 3x MQW	48 hours	II.0.10 - II.0.11	5 color units
Conductivity	100	Raw	Refrigeration @ 4°C	Plastic	48 hrs. MQW 3x MQW	28 days	II.0.20	
Residue - Filterable (TDS)	200	GF/C	Refrigeration @ 4°C	Plastic	48 hrs. MQW 3x MQW	7 days	II.0.30	0.005 g
Residue - Total Suspended (TSS)	200	Filter on to GF/C	Refrigeration @ 4°C	Plastic	48 hrs. MQW 3x MQW	7 days	II.0.40	0.005 g
Residue - Total	200	Raw	Refrigeration @ 4°C	Plastic	48 hrs. MQW 3x MQW	7 days	II.0.50	0.005 g
Residue - Volatile (VSS)	200 or 2 g	Filter on to GF/C	Refrigeration @ 4°C	Plastic	48 hrs. MQW 3x MQW	7 days	II.0.60	0.005 g
Turbidity	100	Raw	Refrigeration @ 4°C	Cubitainer	48 hrs. MQW 3x MQW	24 hrs.	II.0.70	0.10 NTU
Inorganic, Metallic III								
Flame								
Aluminum	125	Raw: Total [8] 0.45 µm: Dissolved [7]	0.5% Nitric Acid	Plastic	15% HNO_3 - 24 hrs, 4x MQW, 24 hrs MQW, 2x MQW	6 mo.	III.0.20	0.1 mg/L
Calcium	125	Raw: Total [8] 0.45 µm: Dissolved [7]	0.5% Nitric Acid	Plastic	15% HNO_3 - 24 hrs, 4x MQW, 24 hrs MQW, 2x MQW	6 mo.	III.0.30-III.0.33	0.08 mg/L
Copper	125	Raw: Total [8] 0.45 µm: Dissolved [7]	0.5% Nitric Acid	Plastic	15% HNO_3 - 24 hrs, 4x MQW, 24 hrs MQW, 2x MQW	6 mo.	III.0.40	0.02 mg/L
Magnesium	125	Raw: Total [8] 0.45 µm: Dissolved [7]	0.5% Nitric Acid	Plastic	15% HNO_3 - 24 hrs, 4x MQW, 24 hrs MQW, 2x MQW	6 mo.	III.0.50-III.0.53	0.007 mg/L
Potassium	125	Raw: Total [8] 0.45 µm: Dissolved [7]	0.5% Nitric Acid	Plastic	15% HNO_3 - 24 hrs, 4x MQW, 24 hrs MQW, 2x MQW	6 mo.	III.0.70-III.0.72	0.01 mg/L

Table 1-2. Continued.

Parameter	Minimum Recommended Sample Vol. (mL or g)	Filtered (Type) or Raw Water	U.S. EPA Recommended Preservation Method [1]	Container Type	Container Preparation	U.S. EPA Recommended Hold Time [1]	NRRI Method	Detection Limit
Sodium	125	Raw: Total [8] 0.45 µm: Dissolved [8]	0.5% Nitric Acid	Plastic	15% HNO_3 - 24 hrs, 4x MQW, 24 hrs MQW, 2x MQW	6 mo.	III.0.80-III.0.82	0.005 mg/L
Zinc	125	Raw: Total [8] 0.45 µm: Dissolved [7]	0.5% Nitric Acid	Plastic	15% HNO_3 - 24 hrs, 4x MQW, 24 hrs MQW, 2x MQW	6 mo.	III.0.90	0.005 mg/L
Graphite Furnace								
Aluminum	125	Raw: Total [8] 0.45 µm: Dissolved [7]	0.5% Nitric Acid	Plastic	15% HNO_3 - 24 hrs, 4x MQW, 24 hrs MQW, 2x MQW	6 mo.	III.2.10-III.2.21	0.1 µg/L
Arsenic	125	Raw: Total [8] 0.45 µm: Dissolved [7]	0.5% Nitric Acid	Plastic	15% HNO_3 - 24 hrs, 4x MQW, 24 hrs MQW, 2x MQW	6 mo.	III.2.25	0.1 µg/L
Cadmium	125	Raw: Total [8] 0.45 µm: Dissolved [7]	0.5% Nitric Acid	Plastic	15% HNO_3 - 24 hrs, 4x MQW, 24 hrs MQW, 2x MQW	6 mo.	III.2.30	0.1 µg/L
Chromium	125	Raw: Total [8] 0.45 µm: Dissolved [7]	0.5% Nitric Acid	Plastic	15% HNO_3 - 24 hrs, 4x MQW, 24 hrs MQW, 2x MQW	6 mo.	III.2.35	0.1 µg/L
Copper	125	Raw: Total [8] 0.45 µm: Dissolved [7]	0.5% Nitric Acid	Plastic	15% HNO_3 - 24 hrs, 4x MQW, 24 hrs MQW, 2x MQW	6 mo.	III.2.40	0.1 µg/L
Iron (soil)	125	Raw: Total 0.45 µm: Dissolved	0.5% Nitric Acid	Plastic	15% HNO_3 - 24 hrs, 4x MQW, 24 hrs MQW, 2x MQW	6 mo.	III.2.50	0.1 µg/L
Iron (water)	125	Raw: Total [8] 0.45 µm: Dissolved [7]	0.5% Nitric Acid	Plastic	15% HNO_3 - 24 hrs, 4x MQW, 24 hrs MQW, 2x MQW	6 mo.	III.2.51-III.2.52	0.1 µg/L
Lead	125	Raw: Total [8] 0.45 µm: Dissolved [7]	0.5% Nitric Acid	Plastic	15% HNO_3 - 24 hrs, 4x MQW, 24 hrs MQW, 2x MQW	6 mo.	III.2.60	0.1 µg/L
Manganese	125	Raw: Total 0.45 µm: Dissolved	0.5% Nitric Acid	Plastic	15% HNO_3 - 24 hrs, 4x MQW, 24 hrs MQW, 2x MQW	6 mo.	III.2.70-III.2.71	0.2 µg/L

Table I-2. Continued.

Parameter	Minimum Recommended Sample Vol. (mL or g)	Filtered (Type) or Raw Water	U.S. EPA Recommended Preservation Method [1]	Container Type	Container Preparation	U.S. EPA Recommended Hold Time [1]	NRRI Method	Detection Limit
Nickel	125	Raw: Total 0.45 µm: Dissolved	0.5% Nitric Acid	Plastic	15% HNO_3 - 24 hrs, 4x MQW, 24 hrs MQW, 2x MQW	6 mo.	III.2.80	0.1 µg/L
Zinc	125	Raw: Total 0.45 µm: Dissolved	0.5% Nitric Acid	Plastic	15% HNO_3 - 24 hrs, 4x MQW, 24 hrs MQW, 2x MQW	6 mo.	III.2.90	0.05 µg/L
Mercury	125	Tissue/sed water	Water: 0.5% Nitric Acid Tissue/sed: freeze	TFE-Low mercury or glass	>95°C in HNO_3 2x MQW; 1% HCl 50°C, store in 1% HCl	1 mo.	III.5.10	0.2 µg/L
Inorganic, Non-metalics IV								
Acidity	200	Raw	Refrigeration @ 4°C	Plastic	48 hrs. MQW 3x MQW	24 hrs.	IV.0.10	0.5 mg as $CaCO_3$
Alkalinity (ANC)	200	Raw	Refrigeration @ 4°C	Plastic	48 hrs. MQW 3x MQW	24 hrs.	IV.0.20-IV.0.25	0.5 mg as $CaCO_3$
Carbon, Dissolved Inorganic	50	Raw	Refrigeration @ 4°C	Plastic syringe	48 hrs. MQW 3x MQW	24 hrs.	IV.0.30-IV.0.31	0.5 mg/L
CHN	10g	Sediment, soil, sediment trap	Dry wt. over desiccant	LSC vial over desiccant	3x MQW Air dry	6 mo.	IV.0.40	3-5 mg dry wt/1% of wt
Chloride - Argentometric	100	0.45 µm	Refrigeration @ 4°C	Plastic	48 hr. MQW 3x MQW	7 days	IV.0.51	0.02 mg/L
Fluoride Electrode	500	0.45 µm	Refrigeration @ 4°C	Plastic	48 hr. MQW 3x MQW	7 days	IV.0.60	0.005 mg/L
Ammonium - Auto-Salicylate	250	0.45 µm	H_2SO_4 to pH < 2 @ 4°C or frozen	Plastic	Rinse 10% HCl 24 hr. MQW 3x MQW	28 days	IV.1.10	0.005 mg/L
Ammonium - Manual-Salicylate	250	0.45 µm	H_2SO_4 to pH < 2 @ 4°C or frozen	Plastic	Rinse 10% HCl 24 hr. MQW 3x MQW	28 days	IV.1.11	0.005 mg/L
Ammonium - Auto-Phenate	250	0.45 µm	H_2SO_4 to pH < 2 @ 4°C or frozen	Plastic	Rinse 10% HCl 24 hr. MQW 3x MQW	28 days	IV.1.12	0.01 mg/L

Table I-2. Continued.

Parameter	Minimum Recommended Sample Vol. (mL or g)	Filtered (Type) or Raw Water	U.S. EPA Recommended Preservation Method [1]	Container Type	Container Preparation	U.S. EPA Recommended Hold Time [1]	NRRI Method	Detection Limit
Sodium	125	Raw: Total [8] 0.45 µm: Dissolved [8]	0.5% Nitric Acid	Plastic	15% HNO_3 - 24 hrs, 4x MQW, 24 hrs MQW, 2x MQW	6 mo.	III.0.80-III.0.82	0.005 mg/L
Zinc	125	Raw: Total [8] 0.45 µm: Dissolved [7]	0.5% Nitric Acid	Plastic	15% HNO_3 - 24 hrs, 4x MQW, 24 hrs MQW, 2x MQW	6 mo.	III.0.90	0.005 mg/L
Graphite Furnace								
Aluminum	125	Raw: Total [8] 0.45 µm: Dissolved [7]	0.5% Nitric Acid	Plastic	15% HNO_3 - 24 hrs, 4x MQW, 24 hrs MQW, 2x MQW	6 mo.	III.2.10-III.2.21	0.1 µg/L
Arsenic	125	Raw: Total [8] 0.45 µm: Dissolved [7]	0.5% Nitric Acid	Plastic	15% HNO_3 - 24 hrs, 4x MQW, 24 hrs MQW, 2x MQW	6 mo.	III.2.25	0.1 µg/L
Cadmium	125	Raw: Total [8] 0.45 µm: Dissolved [7]	0.5% Nitric Acid	Plastic	15% HNO_3 - 24 hrs, 4x MQW, 24 hrs MQW, 2x MQW	6 mo.	III.2.30	0.1 µg/L
Chromium	125	Raw: Total [8] 0.45 µm: Dissolved [7]	0.5% Nitric Acid	Plastic	15% HNO_3 - 24 hrs, 4x MQW, 24 hrs MQW, 2x MQW	6 mo.	III.2.35	0.1 µg/L
Copper	125	Raw: Total [8] 0.45 µm: Dissolved [7]	0.5% Nitric Acid	Plastic	15% HNO_3 - 24 hrs, 4x MQW, 24 hrs MQW, 2x MQW	6 mo.	III.2.40	0.1 µg/L
Iron (soil)	125	Raw: Total 0.45 µm: Dissolved	0.5% Nitric Acid	Plastic	15% HNO_3 - 24 hrs, 4x MQW, 24 hrs MQW, 2x MQW	6 mo.	III.2.50	0.1 µg/L
Iron (water)	125	Raw: Total [8] 0.45 µm: Dissolved [7]	0.5% Nitric Acid	Plastic	15% HNO_3 - 24 hrs, 4x MQW, 24 hrs MQW, 2x MQW	6 mo.	III.2.51-III.2.52	0.1 µg/L
Lead	125	Raw: Total [8] 0.45 µm: Dissolved [7]	0.5% Nitric Acid	Plastic	15% HNO_3 - 24 hrs, 4x MQW, 24 hrs MQW, 2x MQW	6 mo.	III.2.60	0.1 µg/L
Manganese	125	Raw: Total 0.45 µm: Dissolved	0.5% Nitric Acid	Plastic	15% HNO_3 - 24 hrs, 4x MQW, 24 hrs MQW, 2x MQW	6 mo.	III.2.70-III.2.71	0.2 µg/L

Table I-2. Continued.

Parameter	Minimum Recommended Sample Vol. (mL or g)	Filtered (Type) or Raw Water	U.S. EPA Recommended Preservation Method [1]	Container Type	Container Preparation	U.S. EPA Recommended Hold Time [1]	NRRI Method	Detection Limit
Nickel	125	Raw: Total 0.45 µm: Dissolved	0.5% Nitric Acid	Plastic	15% HNO_3 - 24 hrs, 4x MQW, 24 hrs MQW, 2x MQW	6 mo.	III.2.80	0.1 µg/L
Zinc	125	Raw: Total 0.45 µm: Dissolved	0.5% Nitric Acid	Plastic	15% HNO_3 - 24 hrs, 4x MQW, 24 hrs MQW, 2x MQW	6 mo.	III.2.90	0.05 µg/L
Mercury	125	Tissue/sed water	Water: 0.5% Nitric Acid Tissue/sed: freeze	TFE-Low mercury or glass	>95°C in HNO_3 2x MQW; 1% HCl 50°C, store in 1% HCl	1 mo.	III.5.10	0.2 µg/L
Inorganic, Non-metalics IV								
Acidity	200	Raw	Refrigeration @ 4°C	Plastic	48 hrs. MQW 3x MQW	24 hrs.	IV.0.10	0.5 mg as $CaCO_3$
Alkalinity (ANC)	200	Raw	Refrigeration @ 4°C	Plastic	48 hrs. MQW 3x MQW	24 hrs.	IV.0.20-IV.0.25	0.5 mg as $CaCO_3$
Carbon, Dissolved Inorganic	50	Raw	Refrigeration @ 4°C	Plastic syringe	48 hrs. MQW 3x MQW	24 hrs.	IV.0.30-IV.0.31	0.5 mg/L
CHN	10g	Sediment, soil, sediment trap	Dry wt. over desiccant	LSC vial over desiccant	3x MQW Air dry	6 mo.	IV.0.40	3-5 mg dry wt/1% of wt
Chloride - Argentometric	100	0.45 µm	Refrigeration @ 4°C	Plastic	48 hr. MQW 3x MQW	7 days	IV.0.51	0.02 mg/L
Fluoride Electrode	500	0.45 µm	Refrigeration @ 4°C	Plastic	48 hr. MQW 3x MQW	7 days	IV.0.60	0.005 mg/L
Ammonium - Auto-Salicylate	250	0.45 µm	H_2SO_4 to pH < 2 @ 4°C or frozen	Plastic	Rinse 10% HCl 24 hr. MQW 3x MQW	28 days	IV.1.10	0.005 mg/L
Ammonium - Manual-Salicylate	250	0.45 µm	H_2SO_4 to pH < 2 @ 4°C or frozen	Plastic	Rinse 10% HCl 24 hr. MQW 3x MQW	28 days	IV.1.11	0.005 mg/L
Ammonium - Auto-Phenate	250	0.45 µm	H_2SO_4 to pH < 2 @ 4°C or frozen	Plastic	Rinse 10% HCl 24 hr. MQW 3x MQW	28 days	IV.1.12	0.01 mg/L

Table I-2. Continued.

Parameter	Minimum Recommended Sample Vol. (mL or g)	Filtered (Type) or Raw Water	U.S. EPA Recommended Preservation Method [1]	Container Type	Container Preparation	U.S. EPA Recommended Hold Time [1]	NRRI Method	Detection Limit
Ammonium - Manual - Phenate	250	0.45 µm	H_2SO_4 to pH < 2 @ 4°C or frozen	Plastic	Rinse 10% HCl 24 hr. MQW 3x MQW	28 days	IV.1.13	0.005 mg/L
TKN	250	0.45 µm	H_2SO_4 to pH < 2 @ 4°C or frozen	Plastic	Rinse 10% HCl 24 hr. MQW 3x MQW	28 days	IV.1.15	Lachat 0.10 mg/L
Nitrate-Nitrite [2]	100	0.45 µm	Refrigeration @ 4°C	Plastic	48 hr. MQW 3x MQW	48 hrs.	IV.1.20	Lachat 0.003 mg/L
Oxygen Dissolved	300	Raw	Determine on-site	Glass	48 hr. MQW 3x MQW	No holding	IV.2.00	Winkler, 0.025 mg/L
pH - Open	200	Raw	Refrigeration @ 4°C	Plastic	48 hr. MQW 3x MQW	8 hr.	IV.2.10	± 0.1 unit
pH - Closed	200	Raw	Refrigeration @ 4°C	Plastic syringe	48 hr. MQW 3x MQW	8 hr.	IV.2.11	± 0.1 unit
Ortho-Phosphorus (Auto)	100	0.45 µm	Refrigeration @ 4°C	Plastic	48 hr. MQW 3x MQW	48 hr.	IV.3.01	0.005 mg/L
Ortho-Phosphorus (Manual)	100	0.45 µm	Refrigeration @ 4°C	Plastic	48 hr. MQW 3x MQW	48 hr.	IV.3.00	0.002 mg/L
Total Phosphorus (Manual)	100	Raw	Refrigeration @ 4°C	Plastic	48 hr. MQW 3x MQW	24 hr.	IV.3.00	0.002 mg/L
Total Phosphorus (Auto)	100	Raw	Refrigeration @ 4°C	Plastic	48 hr. MQW 3x MQW	24 hr.	IV.3.10	0.005 mg/L
Bio-A-Phosphorus	100g sediment [3] 20 g trap [3]		Refrigeration @ 4°C	Plastic	48 hr. MQW 3x MQW	28 days	IV.3.20	0.002 mg/L
Sediment TP By Digest	100g sediment [3] 20 g trap [3]		Refrigeration @ 4°C	Plastic	48 hr. MQW 3x MQW	28 days	IV.3.21	0.002 mg/L
Sediment TP By Ignition	100g sediment [3] 20 g trap [3]		Refrigeration @ 4°C	Plastic	48 hr. MQW 3x MQW	28 days	IV.3.22	0.002 mg/L
Silica	50	0.45 µm	Refrigeration @ 4°C	Plastic	48 hr. MQW 3x MQW	28 days	IV.4.11	0.1 mg/L
Sulfide	200	0.45 µm	2 ml Zinc Acetate	Glass	48 hr. MQW 3x MQW	24 hr.	IV.5.00 IV.5.10	0.1 mg/L

Table I-2. Continued.

Parameter	Minimum Recommended Sample Vol. (mL or g)	Filtered (Type) or Raw Water	U.S. EPA Recommended Preservation Method [1]	Container Type	Container Preparation	U.S. EPA Recommended Hold Time [1]	NRRI Method	Detection Limit
Sulfite	50	Raw	Determine on-site	Glass	48 hr. MQW 3x MQW	No Holding	IV.5.12	0.1 mg/L
Anions by Dionex V								
Chloride	100	0.45 µm	Refrigeration @ 4°C	Plastic	48 hr. MQW 3x MQW	7 days	V.0.10	0.01 mg/L
Nitrate	100	0.45 µm	Refrigeration @ 4°C	Plastic	48 hr. MQW 3x MQW	48 hr.	V.0.10	0.01 mg/L
Sulfate	100	0.45 µm	Refrigeration @ 4°C	Plastic	48 hr. MQW 3x MQW	7 days	V.0.10	0.01 mg/L
Fluoride	100	0.45 µm	Refrigeration @ 4°C	Plastic	48 hr. MQW 3x MQW	48 hr.	V.0.10	0.005 mg/L
Organics								
BOD	250	Raw	Refrigeration @ 4°C	Glass	48 hr. MQW 3x MQW	No Holding	VI.0.10	1 mg/L
Sediment Oxygen Demand (SOD)	100 g [4]		Refrigeration @ 4°C	Plastic	48 hr. MQW 3x MQW	No Holding	VI.0.20	1 mg/L
Carbon, Organic, Total (TOC) or Dissolved (DOC)	50	TOC - Raw DOC- Filtered, 0.45 µm	4°C, analyze within 2 hr or H_2SO_4 to pH <2	Glass preferred	Rinse HCl, MQW, bake 550°C, 1 hr Caps, detergent wash, rinse MQW, bake, 100°C	30 days (acidified)	VI.0.30	1 mg/L
Biological								
Chlorophyll	1000 [5]	Filter on to GF/C	Frozen filter	Foil	48 hr. MQW 3x MQW	14 days	VII.0.10	0.001 abs. units for spectro-photometry [6]

[1] It has been shown, according to the EPA, that samples properly preserved may be held for extended periods beyond the recommended holding time.
[2] Nitrite can be derived with same method, Nitrate can be found by Nitrite-Nitrate minus Nitrite.
[3] The amount of sediment/trap material used will depend on the concentration of phos. in the system.
[4] The amount of sediment used and the size of the jar is dependent on the type of sediment used.
[5] Detection limits for chlorophyll-a are dependent on the amount of water filtered.
[6] Detection limits are much lower for flurometric assays.
[7] Water samples should be held at least 17 hours after preservation before analysis.
[8] Samples for total cations should be digested if their turbidity is 1 NTU or visible particulate matter is present.

Chain of Custody Record

Collector (s):

Type of samples:

Sample ID	Collection Time		Arrived at Lab			Store	Analysis		Store	Re-Analysis		Store	Disposed		notes:
	Date	Time	Date	Time	Rec'd By	Date	Date	Analyst	Date	Date	Analyst	Date	Date	Initials	
1.															
2.															
3.															
4.															
5.															
6.															
7.															
8.															
9.															
10.															
11.															
12.															
13.															
14.															
15.															
16.															
17.															
18.															
19.															
20.															

Comments:

Sample Transmittal:

Name of Person sending samples: _____ Company: _____ Address: _____ City: _____ State: _____ Zip _____

Samples shipped to lab on (date) ____/____/____ at time _____

Ship to:
NRRI-Central Analytical Lab
5013 Miller Trunk Highway
Duluth, MN 55811

Via (carrier name):

Person accepting for carrier:

Scheduled arrival at lab: ____/____/____
Time: _____

Figure I-2: Chain of custody form (rev. 1/16/01, JJA)

TABLE I-3: MAJOR EQUIPMENT

EQUIPMENT	YEAR	MFR SERIAL I.D. #	U of M I.D. #	MAINTENANCE
ATOMIC ABSORPTION SPEC. -VARIAN SPECTRA-30A GRAPHITE FURNACE	1985	5121750	198609879	M
AUTO ANALYZER -LACHAT QC8000	2000	A83000-1512	200004151	IH/M
BALANCE				
-SARTORIOUS 1264	1980	2909074	198007236	IS
-SARTORIOUS 1702 ELECTROBALANCE	1985	3412269	198508969	IS
-CAHN 25 ELECTROBALANCE	1978	55592	197812236	NIS
CARBON-HYDROGEN-NITROGEN ANALYZER - LECO CHN-800	1985	107	198511605	CIH
CENTRIFUGES				
-IEC, Clinical	1989	42830436	198903531	M
-CENTRA 4	1986	23820719	8601334	M
DISSOLVED OXYGEN METER				
-YSI MODEL 58	1988	8005385	198806171	M
-YSI MODEL 50	1990	906016849	199009913	M
-YSI MODEL 85	1998	98a0211	199811566	M
ENVIRONMENTAL CHAMBER				
-NORLAKE WALKIN	1986	8507742	198601842	IS
REFRIGERATOR				
-PRECISION 183, FLAMMABLE	1986	10AT10	198610937	IS
-NORLAKE MINI-ROOM	1986	8507747	8511761	IS
FLUOROMETER				
-SEQUOIA TURNER DESIGNS MODEL 10	1988	5810	8805775	M
GAS CHROMATOGRAPH				
-H-P 5890-A	1989	2916A22281	148610636	NIS
-H-P 5890	1990	2361A00872	8610636	NIS
INCUBATOR				
-BOD FISHER SCIENTIFIC	1980	1906	198109925(?)	IS
-PERCIVAL LIGH/TEMP	1985	88J3382.12	8814291	IS
-FISHER ISOTEMP	1998		199801796	IS
ION CHROMATOGRAPH -DIONEX 2000I/SP AUTOSAMPLER; INTEGRATOR	1985	085/20667-014 854208	198511416 198511417 198511418	IN/M

TABLE I-3 (Continued)

EQUIPMENT	YEAR	MFR SERIAL I.D. #	U of M I.D.#	MAINTENANCE
LIQUID SCINTILLATION SYSTEM				
-BECKMAN LS6000SE	1990	7060576	8814398	MA
MICROSCOPE				
-OLYMPUS BH-2 W/ UV FLUORESCENCE	1990	236200	199011074	IS
-CARLO DISSECTING SCOPE	1990	UNK	199000267	IS
-OLYMPUS IMT INVERTED SCOPE	1983	UNK	UNK	IS
OVEN				
-GRAVITY THERMLYNE 0035325	1985	39200125	198510105	IS
-LINBERG BOX FURNACE	1986	UNK	740876	IS
PH METER				
-CORNING 150	1986	2331	198600429	M
-CORNING 250	1988	2795	198807412	M
-BECKMAN ϕ11	1987	UNK	UNK	M
STERILIZER				
-CONSOLIDATED STILLS & STERILIZERS	1974	39174	7408137	IS
STEREOSCOPE				
-OLYMPUS SZ60	1990	UNK	199000267	IS
SPECTROPHOTOMETER				
-PERKIN-ELMER LAMBDA 3B	1990	81536F		IS
TURBIDIMETER				
-HF INSTRUMENTS DRT-100-B	1985	16662	8510015	M
FREEZER				
-KELVINATOR ULTRA-COLD (-80 C)	1985	402558	198606233	NIS
-KENMORE CHEST	1985	E5295218		M
-KENMORE UPRIGHT	1989	937.089961	19900940	M
-KENMORE UPRIGHT	1990	UNK		M
WATER PURIFIER				
-MILLIPORE MILLI-Q	1982	21043-6	198208166	IH

CIH = CERTIFIED IN HOUSE MAINTENANCE
IH= IN-HOUSE SERVICE
IS = INDEPENDENT MAINTENANCE
M = MANUFACTURER MAINTENANCE
MA= MANUFACTURER'S MAINTENANCE AGREEMENT
NIS = NOT IN SERVICE
UW = UNDER WARRANTY

Table I-4: Parameter QC summary

	SPIKE FREQUENCY	REPLICATION FREQUENCY	MIDPOINT STANDARD FREQUENCY	EXTERN/AL QC FREQUENCY	ARCHIVED QC DATA	CONTROL CHART
PHYSICAL II						
Color	N/A	10%	N/A	N/A	Yes	No
Conductivity	N/A	10%	10%	Batch	Yes	No
Residue - Filterable (TDS)	N/A	*Batch	N/A	N/A	Yes	No
Residue - Total Suspended	N/A	*Batch	N/A	N/A	Yes	No
Residue - Total	N/A	*Batch	N/A	N/A	Yes	No
Residue - Volatile (VSS)	N/A	*Batch	N/A	N/A	Yes	No
Turbidity	N/A	10%	10%	Quarterly	Yes	No
INORGANIC, METALICS III						
Flame						
Aluminum	10%	10%	10%	Batch	Yes	No
Calcium	10%	10%	10%	Batch	Yes	No
Copper	10%	10%	10%	Batch	Yes	No
Magnesium	10%	10%	10%	Batch	Yes	No
Potassium	10%	10%	10%	Batch	Yes	No
Sodium	10%	10%	10%	Batch	Yes	No
Zinc	10%	10%	10%	Batch	Yes	No
Graphite Furnace						
Aluminum	10%	10%	10%	Batch	Yes	No
Copper	10%	10%	10%	Batch	Yes	No
Iron (soil)	10%	10%	10%	Batch	Yes	No
Iron (water)	10%	10%	10%	Batch	Yes	No
Lead	10%	10%	10%	Batch	Yes	No
Manganese	10%	10%	10%	Batch	Yes	No
Nickel	10%	10%	10%	Batch	Yes	No
Zinc	10%	10%	10%	Batch	Yes	No
Mercury	10%	10%	10%	Batch	Yes	No
INORGANIC NON-METALICS IV						
Acidity	N/A	*10%	N/A	Quarterly	Yes	No
Alkalinity (ANC)	N/A	*10%	N/A	Quarterly	Yes	No
Dissolved Inorganic Carbon	10%	10%	10%	N/A	Yes	No
CHN	N/A	10%	10%	N/A	Yes	No

TABLE I-4 (Continued)

	SPIKE FREQUENCY	REPLICATION FREQUENCY	MIDPOINT STANDARD FREQUENCY	EXTERN/AL QC FREQUENCY	ARCHIVED QC DATA	CONTROL CHART
Chloride - Auto	10%	10%	10%	Tray	Yes	Yes
Chloride - Argentometric	10%	10%	10%	Day	Yes	Yes
Fluoride - Electrode	10%	10%	10%	Day	Yes	Yes
Nitrate-Nitrite	10%	10%	10%	Tray	Yes	Yes
Ammonia - Manual UV	10%	10%	10%	Day	Yes	Yes
Ammonia - Auto Phenol	10%	10%	10%	Tray	Yes	Yes
Ammonia - Auto-Sal	10%	10%	10%	Tray	Yes	Yes
Oxygen - Dissolved	N/A	*Batch	N/A	N/A	Yes	No
pH - Open	N/A	*Batch	N/A	Quarterly	Yes	No
pH - Closed	N/A	*Batch	N/A	N/A	Yes	No
Ortho-phosphorus (Auto)	10%	10%	10%	Tray	Yes	Yes
Ortho-phosphorus (Manual)	10%	10%	10%	Batch	Yes	Yes
Total - Phosphorus (Manual)	10%	10%	10%	Batch	Yes	Yes
Total - Phosphorus (Auto)	10%	10%	10%	Tray	Yes	Yes
Bio-A-Phosphorus	10%	*Batch	10%	N/A	Yes	No
Sediment TP by Digest	10%	*Batch	10%	N/A	Yes	No
Sediment TP by Ignition	10%	*Batch	10%	N/A	Yes	No
Silica	10%	10%	10%	Tray	Yes	Yes
Sulfide	N/A	*10%	N/A	N/A	Yes	No
Sulfite	N/A	*10%	N/A	N/A	Yes	No
ANIONS BY DIONEX V						
Chloride	10%	10%	10%	Day	Yes	No
Nitrate	10%	10%	10%	Day	Yes	No
Sulfate	10%	10%	10%	Day	Yes	No
Fluoride	10%	10%	10%	Day	Yes	No
ORGANICS VI						
BOD	N/A	*Batch	N/A	Quarter	Yes	No
SOD	N/A	*Batch	N/A	N/A	Yes	No
BIOLOGICAL VII						
Chlorophyll	N/A	*Batch	N/A	Quarter	Yes	No

* Dependent on Amount of Material Available.

APPENDIX B
YSI Multi-parameter Meter Calibration and Maintenance Procedures

✓ When using the Calibration Cup for dissolved oxygen calibration, make certain that the vessel is vented to the atmosphere by loosening the bottom cap or cup assembly, depending on orientation, and that approximately 1/8" of water is present in the cup.

Table 1 6820 and 6920 Sondes

Probe to Calibrate	Upright	Upside Down
Conductivity	200ml	200ml
pH/ORP	100ml	250ml
ISE	125ml	275ml
Turbidity or Chlorophyll	25ml	N/A

Table 2 600XL and 600XLM Sondes

Probe to Calibrate	Upright	Upside Down
Conductivity	50ml	50ml
pH/ORP	25ml	50ml

Table 3 6600 Sonde

Probe to Calibrate	Upright	Upside Down
Conductivity	425ml	225ml
pH/ORP	300ml	275ml
ISE	300ml	275ml
Turbidity or Chlorophyll	130ml	N/A

2.6.1 CALIBRATION PROCEDURES

The following calibration procedures are for the most commonly used sensors. For detailed information on all calibration procedures, refer to **Section 2.9.2, Calibrate.**

To ensure more accurate results, you can rinse the calibration cup with water, and then rinse with a small amount of the calibration solution for the sensor that you are going to calibrate. Discard the rinse solution and add fresh calibrator solution. Use tables 1, 2 and 3 to find the correct amount of calibrator solution.

1. Carefully immerse the probes into the solution and rotate the calibration cup to engage several threads. YSI recommends supporting the sonde with a ring stand and clamp to prevent the sonde from falling over.

2. With a field cable connecting the sonde to a PC, access EcoWatch for Windows and proceed to the Main menu (for information on how to run EcoWatch for Windows software, see **Section 2.4.2, Running EcoWatch Software**). From the sonde Main menu, select number **2-Calibrate.**

3. Note that the exact appearance of this menu will vary depending upon the sensors that are available and enabled on your sonde. To select any of the parameters from the Calibrate menu, input the number that is next to the parameter and press **Enter**. Once you have chosen a parameter, some of the parameters will have a number that appears in parentheses. These are the default values and will be used during calibration if you press **Enter** without inputting another value. If no default value appears, you must type a numerical value and press **Enter**.

```
---------------Calibrate--------------
1-Conductivity        5-ISE2 ORP
2-Dissolved Oxy       6-ISE3 NH4+
3-Pressure-Abs        7-ISE4 NO3-
4-ISE1 pH             8-Turbidity

Select option (0 for previous menu):
```

4. After you input the calibration value, or accept the default, press **Enter**. A real-time display will appear on the screen. Carefully observe the stabilization of the readings of the parameter that is being calibrated. When the readings have been stable for approximately 30 seconds, press **Enter** to accept the calibration. The calibrated value is bolded on the example screen on the following page.

5. Press **Enter** to return to the Calibrate menu, and proceed to the next calibration.

NOTE: If an ERROR message appears, begin the calibration procedure again. Be certain that the value you enter for the calibration standard is correct. Also see **Section 6, Troubleshooting** for more information on error messages. If you continue to observe error messages during calibration, contact YSI Customer Service. See **Section 8, Warranty and Service Information**.

```
=============================================================================
 Temp SpCond     Sal DOsat      DO    Depth      pH NH4+ N NO3- N Turbid
    C  mS/cm     ppt      %   mg/L     feet            mg/L   mg/L     NTU
-----------------------------------------------------------------------------
To calibrate, press <Enter> when the readings are stable.
23.52  7.496    4.13  98.4    8.36    0.310   7.15  11.03  0.000      0.9
```

You will find specific start-up calibration procedures for all sensors that commonly require calibration in the following sections. If a sensor listed is not installed in your sonde, skip that section and proceed to the next sensor until the calibration protocol is complete. Before you use the sonde in the laboratory or field, read and study the more-detailed information on calibration in **Section 2.9.2, Calibrate**.

Temperature does not require calibration, and is therefore not included in the Calibrate menu. ORP calibration is required only infrequently and is only discussed in **Section 2.9.2, Calibrate.**

CONDUCTIVITY

This procedure calibrates conductivity, specific conductance, salinity, and total dissolved solids.

Place approximately the correct amount (by using tables 1, 2 and 3) of conductivity standard into a clean, dry or pre-rinsed calibration cup.

For maximum accuracy, the conductivity standard you choose should be within the same conductivity range as the water you are preparing to sample. However, we do not recommend using standards less than 1 mS/cm. For example:

- ✓ For fresh water use a 1 mS/cm conductivity standard.
- ✓ For brackish water use a 10 mS/cm conductivity standard.
- ✓ For seawater use a 50 mS/cm conductivity standard.

Before proceeding insure that the sensor is as dry as possible. Ideally, rinse the conductivity sensor with a small amount of standard that can be discarded. Be certain that you avoid cross-contamination of standard solutions with other solutions. Make certain that there are no salt deposits around the oxygen and pH/ORP probes, particularly if you are employing standards of low conductivity.

Carefully immerse the probe end of the sonde into the solution. Gently rotate and/or move the sonde up and down to remove any bubbles from the conductivity cell. The probe must be completely immersed past its vent hole. Using the recommended volumes from the table in the previous subsection should insure that the vent hole is covered.

Allow at least one minute for temperature equilibration before proceeding.

From the Calibrate menu, select number **1-Conductivity** to access the Conductivity calibration procedure and then number **1-SpCond** to access the specific conductance calibration procedure. Enter the calibration value of the standard you are using (mS/cm at 25°C) and press **Enter**. The current values of all enabled sensors will appear on the screen and will change with time as they stabilize.

Observe the readings under Specific Conductance or Conductivity and when they show no significant change for approximately 30 seconds, press **Enter**. The screen will indicate that the calibration has been accepted and prompt you to press **Enter** again to return to the Calibrate menu.

Rinse the sonde in tap or purified water and dry the sonde.

DISSOLVED OXYGEN

Place approximately 3 mm (1/8 inch) of water in the bottom of the calibration cup. Place the probe end of the sonde into the cup. Make certain that the DO and temperature probes are not immersed in the water. Engage only 1 or 2 threads of the calibration cup to insure the DO probe

is vented to the atmosphere. Wait approximately 10 minutes for the air in the calibration cup to become water saturated and for the temperature to equilibrate.

Two calibration protocols are provided below for dissolved oxygen, one for sampling applications and one for long-term monitoring applications.

Sampling Applications

If your instrument will be used in sampling applications where the dissolved oxygen is pulsing continuously, deactivate "Autosleep RS232" as described in **Section 2.5, Sonde Software Setup**.

From the Calibrate menu, select number **2-Dissolved Oxy,** then number **1-DO %** to access the DO percent calibration procedure. Calibration of dissolved oxygen in the DO % procedure also results in calibration of the DO mg/L mode and vice versa.

Enter the current barometric pressure in mm of Hg. (Inches of Hg x 25.4 = mm Hg).
Caution: Barometer readings that appear in meteorological reports are generally corrected to sea level and are not useful for your calibration procedure unless they are uncorrected.

Press **Enter** and the current values of all enabled sensors will appear on the screen and change with time as they stabilize. Observe the readings under DO %. When they show no significant change for approximately 30 seconds, press **Enter**. The screen will indicate that the calibration has been accepted and prompt you to press **Enter** again to return to the Calibrate menu.

Rinse the sonde in water and dry the sonde.

Monitoring Applications

If your instrument will be used in monitoring applications where data is being captured at a longer interval (e.g. 15 – 60 minutes) to internal sonde memory, a data collection platform or a computer, you need to activate "Autosleep RS232" as described in **Section 2.5, Sonde Software Setup**. Then follow the instructions detailed above for the Sampling Application calibration. With Autosleep active, the calibration will occur automatically with a display similar to that shown below.

```
=============================================================================
 Temp  SpCond     Sal  DOsat      DO     Depth      pH  NH4+ N  NO3- N  Turbid
    C   mS/cm     ppt       %   mg/L      feet             mg/L    mg/L     NTU
-----------------------------------------------------------------------------
Stabilizing: 38
```

After the warm-up time is complete, the readings just before and just after calibration are displayed. When you press **Enter**, the screen returns to the DO Calibration menu.

DEPTH AND LEVEL

For the depth and level calibration, you can leave the sonde set up the same way as for dissolved oxygen, in water-saturated air.

From the Calibrate menu, select number **3-Pressure-Abs** (or number **3-Pressure-Gage** if you have a vented level sensor) to access the depth calibration procedure. Input 0.00 or some known sensor offset in feet. Press **Enter** and monitor the stabilization of the depth readings with time. When no significant change occurs for approximately 30 seconds, press **Enter** to confirm the calibration. This zeros the sensor with regard to current barometric pressure. Then press **Enter** again to return to the Calibrate menu.

For best performance of depth measurements, users should ensure that the sonde's orientation remains constant while taking readings. This is especially important for vented level measurements and for sondes with side mounted pressure sensors.

pH 2-POINT

Using the correct amount of pH 7 buffer standard (from tables 1, 2 and 3) in a clean, dry or pre-rinsed calibration cup, carefully immerse the probe end of the sonde into the solution. Allow at least 1 minute for temperature equilibration before proceeding.

From the Calibrate menu, select number **4-ISE1 pH** to access the pH calibration choices and then press number **2- 2-Point.** Press **Enter** and input the value of the buffer (7 in this case) at the prompt. Press **Enter** and the current values of all enabled sensors will appear on the screen and change with time as they stabilize in the solution. Observe the readings under pH and when they show no significant change for approximately 30 seconds, press **Enter**. The display will indicate that the calibration is accepted.

After the pH 7 calibration is complete, press **Enter** again, as instructed on the screen, to continue. Rinse the sonde in water and dry the sonde before proceeding to the next step.

Using the correct amount (from tables 1, 2 and 3) of an additional pH buffer standard into a clean, dry or pre-rinsed calibration cup, carefully immerse the probe end of the sonde into the solution. Allow at least 1 minute for temperature equilibration before proceeding.

Press **Enter** and input the value of the second buffer at the prompt. Press **Enter** and the current values of all enabled sensors will appear on the screen and will change with time as they stabilize in the solution. Observe the readings under pH and when they show no significant change for approximately 30 seconds, press **Enter**. After the second calibration point is complete, press **Enter** again, as instructed on the screen, to return to the Calibrate menu.

Rinse the sonde in water and dry. Thoroughly rinse and dry the calibration containers for future use.

The next calibration instructions are only for the 6820, 6600 and 6920 sondes. If you do not have one of these sondes, you may skip to 2.7, Taking Readings.

AMMONIUM (NH_4^+) , CHLORIDE Cl^- AND NITRATE (NO_3^-) 3-POINT

WARNING: AMMONIUM AND NITRATE SENSORS CAN ONLY BE USED AT DEPTHS OF LESS THAN 50 FEET (15 METERS). USE OF THE SENSORS AT GREATER DEPTHS IS LIKELY TO PERMANENTLY DAMAGE THE SENSOR MEMBRANE.

The calibration procedures for ammonium, nitrate or chloride are similar to pH except for the reagents in the calibration solutions. Suggested values for calibrants are 1 and 100 mg/L of either ammonium-nitrogen (NH_4-N) or nitrate-nitrogen (NO_3-N). Suggested values for calibrants are 10 and 1000 mg/L of Chloride (Cl^-).

NOTE: The following procedure requires one portion of the high concentration calibrant and two portions of the low concentration calibrant. The high concentration solution and one of the low concentration solutions should be at ambient temperature. The other low concentration solution should be chilled to less than 10°C prior to beginning the procedure.

Place the proper amount of 100 mg/L standard (1000mg/l for chloride) into a clean, dry or pre-rinsed transport cup. Carefully immerse the probe end of the sonde into the solution. Allow at least 1 minute for temperature equilibration before proceeding.

Select number **6-Ammonium, 7-Nitrate** or number **8- Chloride** to access the appropriate calibration choices. Then select number **3-3-Point**. Press **Enter** and input the concentration value of the standard as requested. Press **Enter** and the current values of all enabled sensors will appear on the screen and will change with time as they stabilize in the solution. Observe the readings under $NH4^+$, $NO3^-$, or Cl^-. When they show no significant change for approximately 30 seconds, press **Enter**.

After the first calibration point is complete, proceed as instructed on the screen, to continue. Rinse the sonde in water and dry the sonde prior to the next step.

Place the proper amount of 1 mg/L standard for Ammonium or Nitrate (10 mg/l for Chloride) into a clean, dry or pre-rinsed transport cup. Carefully immerse the probe end of the sonde into the solution. Allow at least 1 minute for temperature equilibration before proceeding.

Press **Enter** and input the concentration value of the standard as requested.

Press **Enter** and the current values of all enabled sensors will appear on the screen and will change with time as they stabilize in the solution. Observe the readings under $NH4^+$, $NO3^-$, or Cl^- .and when they have show no significant change for approximately 30 seconds, press **Enter**.

After the second value calibration is complete, press **Enter** to continue. Place the proper amount of chilled 1 mg/L standard (10 mg/L for the chloride) into a clean, dry or pre-rinsed calibration cup. Carefully immerse the probe end of the sonde into the solution. Allow at least 5 minutes for temperature equilibration before proceeding.

Press **Enter** and input the concentration value of the standard as requested.

Press **Enter** and the current values of all enabled sensors will appear on the screen and will change with time as they stabilize in the solution. Observe the readings under $NH4^+$, $NO3^-$ or Cl^- and when they show no significant change for approximately 30 seconds, press **Enter.** After the third value calibration is complete, press **Enter** to return to the Calibrate menu.

Thoroughly rinse and dry the calibration cups for future use.

CALIBRATION TIP: HOW TO AVOID DRIFT DURING CALIBRATION OF THE NH4+, NO3- AND Cl- PROBES AFTER pH CALIBRATION. Exposure to the high ionic content of pH buffers can cause a significant, but temporary, drift in these ISE probes (ammonium, nitrate and chloride probes). Therefore, when calibrating the pH probe, YSI recommends that you use one of the following methods to minimize errors in the subsequent readings:

- Calibrate pH first, immersing all of the probes in the pH buffers. After calibrating pH, place the probes in 100 mg/L nitrate or ammonium standard (1000 mg/L chloride) and monitor the reading. Usually, the reading starts low and may take as long as 30 minutes to reach a stable value. When it does, proceed with the calibration.

- When calibrating pH, remove the probe guard and immerse only the pH and temperature probes in the buffers. You can then calibrate nitrate, ammonium or chloride immediately. This will be virtually impossible if a turbidity probe is installed.

TURBIDITY 2-POINT

Select **8-Turbidity** from the Calibrate Menu and then **2-2-Point.**

NOTE: One standard must be 0 NTU, and this standard must be calibrated first.

To begin the calibration, the correct amount (from tables 1, 2 and 3) of 0 NTU standard (clear deionized, distilled, or tap water) into the clear calibration cup (provided) or in a glass beaker. With the probe guard installed, immerse the sonde in the water. Input the value 0.00 NTU at the prompt, and press **Enter.** The screen will display real-time readings that will allow you to determine when the readings have stabilized. If you have a mechanically-cleaned turbidity probe installed, activate the wiper 1-2 times by pressing number **3-Clean Optics** as shown on the screen to remove any bubbles. If your probe is not mechanically cleaned, rotate the sonde back and forth in the water to facilitate removal of bubbles. After stabilization is complete, press **Enter** to "confirm" the first calibration and then, as instructed, press **Enter** to continue.

Dry the sonde carefully and then place the sonde in the second turbidity standard (100 NTU is suggested) using the same container as for the 0 NTU standard. Input the correct turbidity value in NTU, press **Enter,** and view the stabilization of the values on the screen in real-time. As above, activate the wiper with the "3" key or manually rotate the sonde to remove bubbles. After the readings have stabilized, press **Enter** to confirm the calibration and then press **Enter** to return to the Calibrate menu.

Thoroughly rinse and dry the calibration cups for future use. For additional information related to calibrating the turbidity sensor, see **Appendix E, Turbidity Measurements.**

Select **Optic Chlorophyll** from the Calibrate Menu and then select **Chl µg/L**. Then select **1-1 point.**

NOTE: This procedure will zero your fluorescence sensor and use the default sensitivity for calculation of chlorophyll concentration in µg/L. The default sensitivity is usually within 25 % for any probe. The 1-point calibration will therefore allow quick and easy fluorescence measurements that are only semi-quantitative with regard to chlorophyll. However, the readings will reflect changes in chlorophyll from site to site, or over time at a single site.

To increase the accuracy of your chlorophyll measurements, follow the 2-point or 3-point calibration protocols outlined in **Section 2.9, Sonde Menu.**

Before making any field readings, carefully read Sections 5.12, **Chlorophyll** and **Appendix I, Chlorophyll** about chlorophyll that describe practical aspects of fluorescence measurements.

To begin the calibration, place the correct amount of clear deionized or distilled water, from Tables 1, 2 and 3, into the YSI clear calibration cup provided or in a glass beaker of an appropriate size (600 mL for 6820 and 6920 sondes; 800 mL for the 6600 sonde). With the probe guard installed, immerse the sonde in the water. Input the value 0 µg/L at the prompt, and press **Enter**. The screen will display real-time readings that will allow you to determine when the readings have stabilized. Activate the wiper 1-2 times by pressing number **3-Clean Optics** as shown on the screen to remove any bubbles from the sensor. After stabilization is complete, press **Enter** to "confirm" the calibration and then, as instructed, press **Enter** to return to the Calibrate menu.

Thoroughly rinse and dry the calibration cups for future use. For additional information related to calibrating the chlorophyll sensor, see Sections 5.12, **Chlorophyll** and **Appendix I, Chlorophyll**.

HydroLab Multi-Parameter Meter Calibration and Maintenance Procedures

CHAPTER 3: HydroLab Sonde MAINTENANCE AND CALIBRATION

1. Maintenance

For multiprobe and sensor maintenance, we recommend that you refer to the corresponding chapter in your multiprobe user's or operating manual.

When Do I Need to Service or Maintain my Surveyor 4?

- When returning from deployment and you notice that your unit is dirty (case, screen, and other components)
- When you notice that your batteries need to be replaced

How Do I Clean my Surveyor 4?

You will need to prepare the following items:

- Tap water
- Soap
- Very clean, soft, *nonabrasive* cloths
- Cotton swabs

Clean the case, screen, and other components (except for connectors and plugs!) with a slightly wet cloth. Use soap if you notice grease spots. Use a wet cotton swab for the areas you cannot reach with the cloth.

Surveyor 4 Internal Battery Recharging

NOTE:

- **The Surveyor 4 must be turned on (with a charger cable and a power adapter properly connected) and left on in order to charge.**

You will need the following items to recharge your Surveyor 4 internal battery (IBP):

- Surveyor 4
- Surveyor 4 charger cable (013160)
- 110 or 220* power adapter (013450 or 013460*). * For the 220 power adapter, you need to connect your country's corresponding power cord to the IEC 320 connector.

NOTES:

- We recommend recharging your Surveyor 4 when your instrument internal battery

voltage (IBV) reaches 6.5 volts.

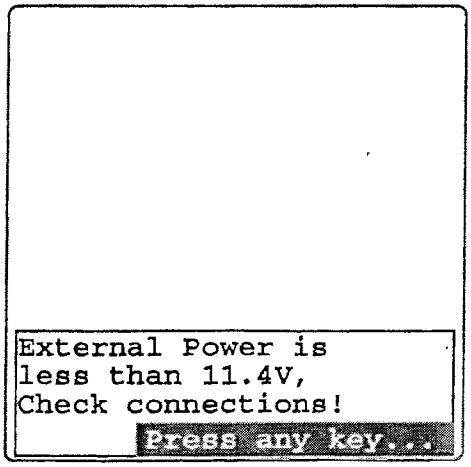
- The recharge time depends on the percent left (IB%) in your battery. Charging is complete in three and a half hours.
- When you first receive your Surveyor 4, we recommend that you go through a complete discharge cycle and become familiar with the instrument. Then, recharge your Surveyor 4 following the next steps.

Before starting the recharge process, carefully read the following warnings.

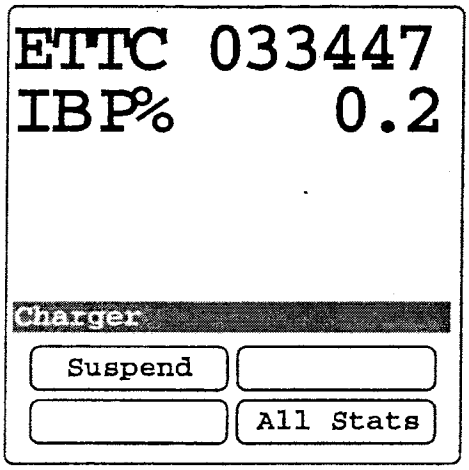
⚠ WARNING: **To avoid potentially fatal electrical shock, never connect your Surveyor 4 to a power source which exceeds 15 volts.**

⚠ WARNING: **To avoid potentially fatal electrical shock, we suggest that you avoid using AC (110 and 220 VAC 12VDC power adapters) to power your multiprobe. When deploying your multiprobe outdoors, you should only use battery power. If you elect to deploy your multiprobe outdoors using any power supply that is in any way connected to the AC mains (110 or 220 VAC), your AC power supply cable MUST be protected by a Ground Fault Interrupt (GFI) device. The installation of the GFI device MUST be done by a licensed electrician. This device may save your life!**

STEP 1: Connect the Surveyor 4 charger cable to your instrument. Attach the 110 or 220 power adapter to the other end of the charger cable. For the 220 power adapter, you also need to connect your country's corresponding power cord to the IEC 320 connector. Turn your Surveyor 4 on. If the following - or similar - screen appears on your display, it means that our instrument is connected to an external power source providing insufficient voltage or you have poor connections. Recheck all connections and try again. Insert the loose end of the power adapter or your country's corresponding power cord into the wall plug. Press any key on your Surveyor 4, and then move to step 2.



STEP 2: After the welcome screen briefly appears, this screen comes up:

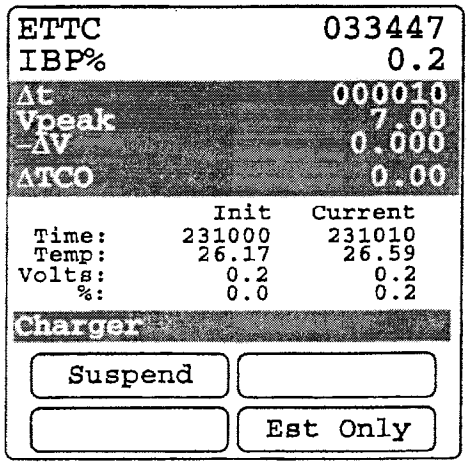


ETTC stands for estimated time to charge, which for our example above is 033447 (3 hours, 34 minutes and 47 seconds). This number will decrease as the full recharge time approaches. IBP% represents the estimated current charge level of the internal battery pack in percent. In our example above, the IBP is only 0.2% charged. This number will change until it reaches full recharge capacity.

NOTE:

- IB% is an estimate. Do not disconnect the Surveyor 4 from charging until prompted to do so. Early disconnect can severely reduce the field operating time.

The history line tells us that we are currently connected to a charger. The Suspend key will pause the recharge process until you decide to start by pressing the Resume key. After you resume the charging process, you will notice that some of your original numbers have been reset. The All Stats key, when pressed, gives you a more detailed account of the recharge process, and is similar to the next screen.



The Suspend function key is available for this screen and All Stats has been replaced with Est Only which, if pressed, brings you back to the first charge mode menu. To return to the first screen, press the Est Only key.

Let's see what the previous screen tells us about the charging process.

First, ETTC and IBP% are the same as for the initial screen. The numbers might have changed while you were following our directions to get to the All Stats screen.

Δt is the elapsed time from the beginning of the charging event. Charging stops when Δt exceeds approximately three and a half hours.

Next, Vpeak is the maximum voltage at any time during the charging event.

Below that is $-\Delta V$ which refers to the negative change of voltage (Vpeak minus current voltage reading). Charging stops when $-\Delta V$ exceeds 60 mV.

Next, comes ΔTCO which stands for the change in temperature from the beginning of the charging event to the current time. Charging stops when ΔTCO exceeds 15 °C.

The next lines display a table with the initial reading (Init) when you started the charge and the current reading (Current). The parameters displayed are time, temperature, voltage (Volts), and battery percentage capacity (%).

You can now monitor your Surveyor 4 charging process. You need to leave the instrument on to complete the charging process.

Your instrument will let you know when the charge is complete by displaying the following, or similar, message at the bottom of your screen: `Charging complete! Disconnect charger cable for normal operation. Press any key ...`

NOTE:

- Charging is not necessarily done when ETTC=0 or IB%=100. Charging is done when Δt equals or exceeds three and a half hours, $-\Delta V$ equals or exceeds 60 mV, or ΔTCO equals or exceeds 15 °C.

STEP 3: Once the IBP is fully recharged, disconnect the Surveyor 4 charger cable from your instrument. The Surveyor 4's screen will display the NoConn message, to let you know that your instrument is not connected to any instrument or external power source. If you decide to turn the Surveyor off, press the Off/On key once. If you decide to proceed with a calibration, setup, or another procedure, such as data transfer to a PC, connect the appropriate cable and go to the corresponding chapter in this manual.

Surveyor 4 Internal Battery Replacement

You will need the following items to replace your instrument's internal battery (IBP):

- Silicone grease
- A replacement battery (Duracell® DR30 7.2 volt nickel metal hydride or equivalent) (HL No. 013230)
- 1 standard screwdriver

⚠ **CAUTION: To avoid water contacts with the Surveyor 4's internal components during battery replacement, we recommend that you avoid replacing the battery close to a water source.**

Follow the next steps with the corresponding illustrations (figures 3-6) on the following pages to replace your Surveyor 4 internal battery.

STEP 1: Make sure that your working surface is clean and dry. Disconnect any cable connected to your Surveyor 4. Turn your Surveyor 4 upside down on the working surface (see figure 3 on the next page). Unscrew the four retaining screws with the standard screwdriver. To facilitate reassembly, do not pull the screws completely out.

STEP 2: Lift the back panel from the bottom part of the Surveyor 4 (see arrow on fig. 3). If you feel some resistance, unscrew the retaining screws some more and try again.

STEP 3: Put the back panel down on the work surface and remove the old battery from its compartment.

STEP 4: Insert the new battery in the battery compartment back panel, aligning the notches on the battery with the notches in the Surveyor 4 case (see figure 5).

STEP 5: Lightly coat the o-ring around the battery compartment with silicone grease. Do not use any other kind of grease and do not over-grease.

STEP 6: Place the back panel over the battery compartment that holds the new battery and screw the retaining screws. Do not overtighten the screws.

Your Surveyor 4 is now operational, if the new battery is charged.

For complete information on expected battery life, refer to chapter 6 under "Expected battery life."

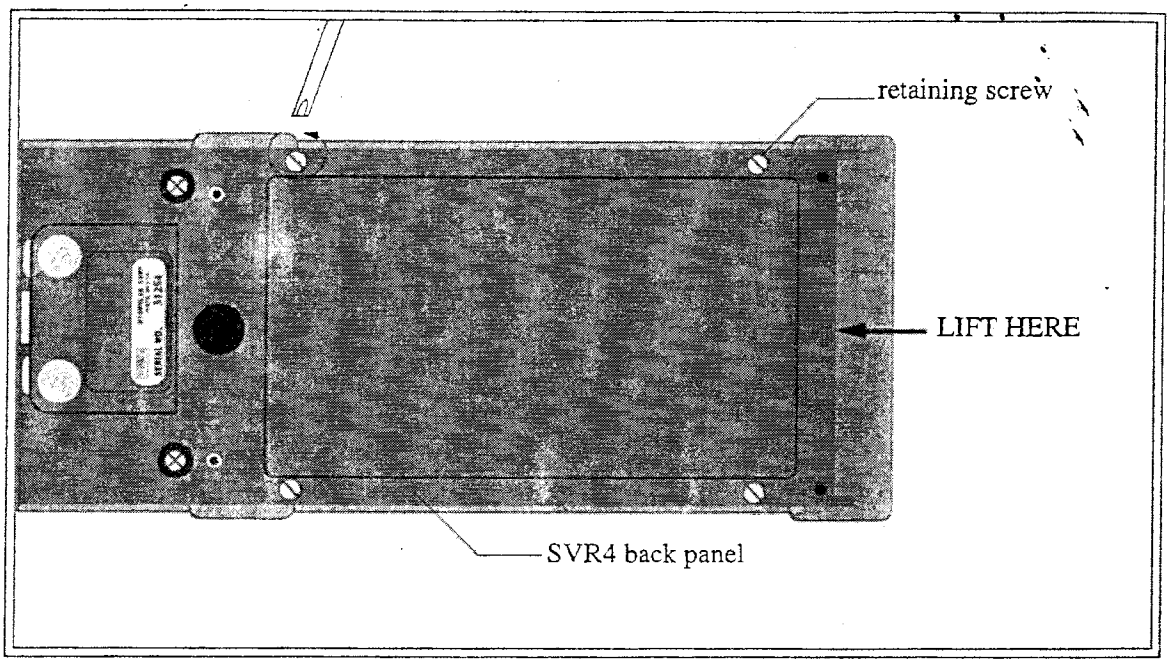


FIGURE 3: OPENING THE SURVEYOR 4 BACK PANEL

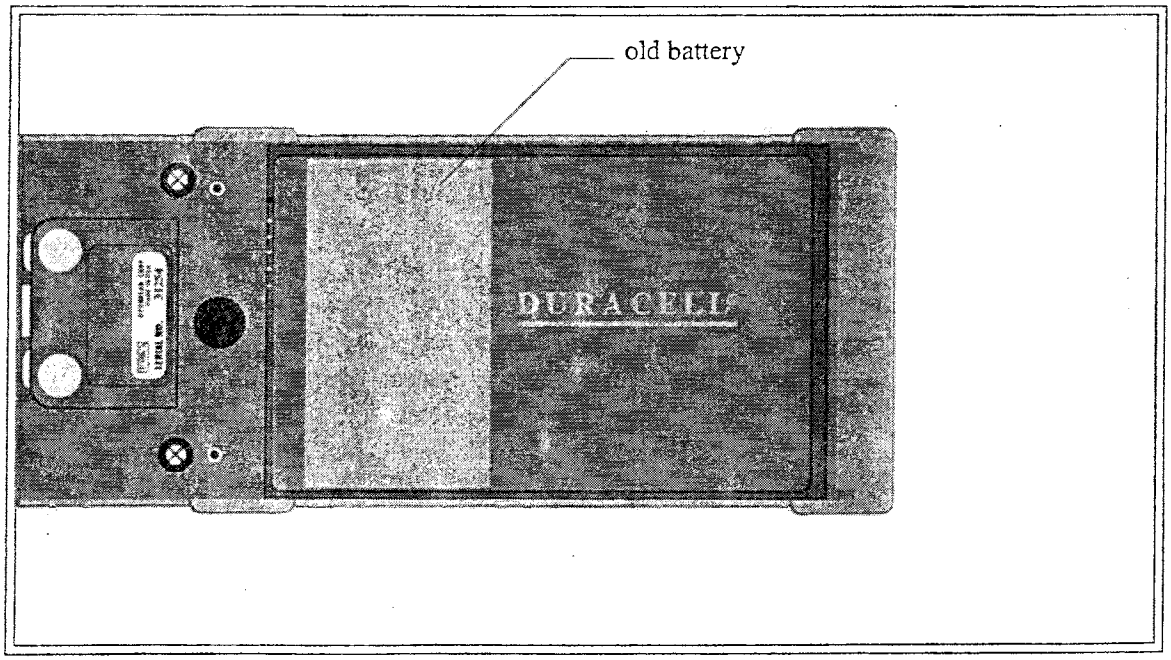


FIGURE 4: REMOVING THE OLD BATTERY

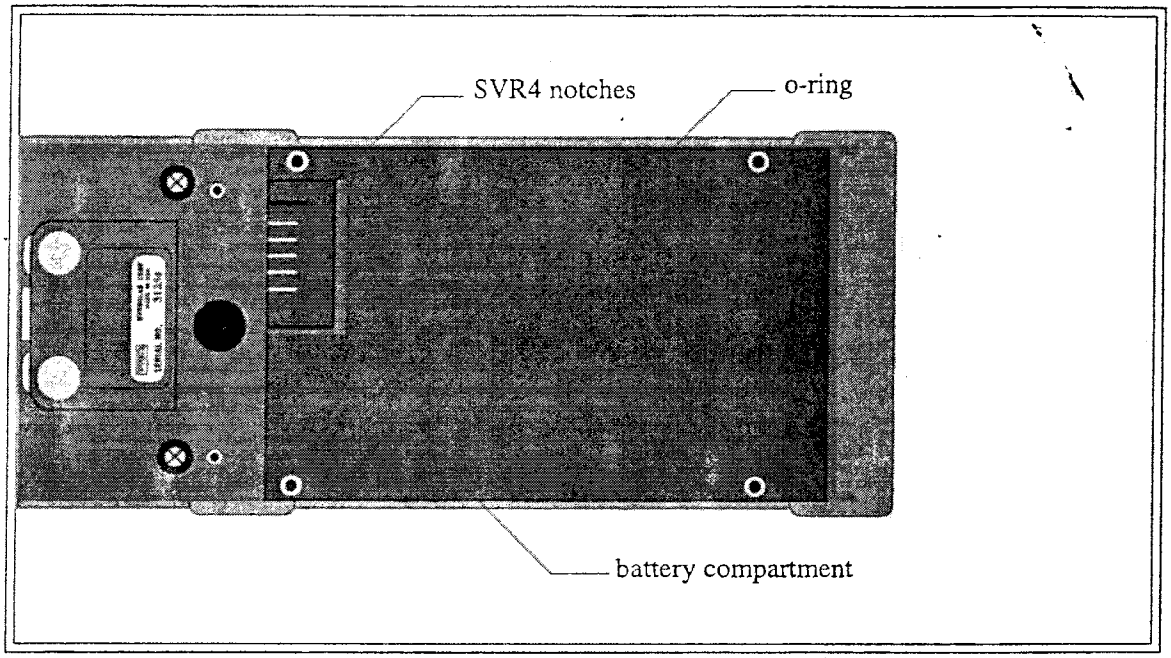


FIGURE 5: IDENTIFYING THE COMPONENTS

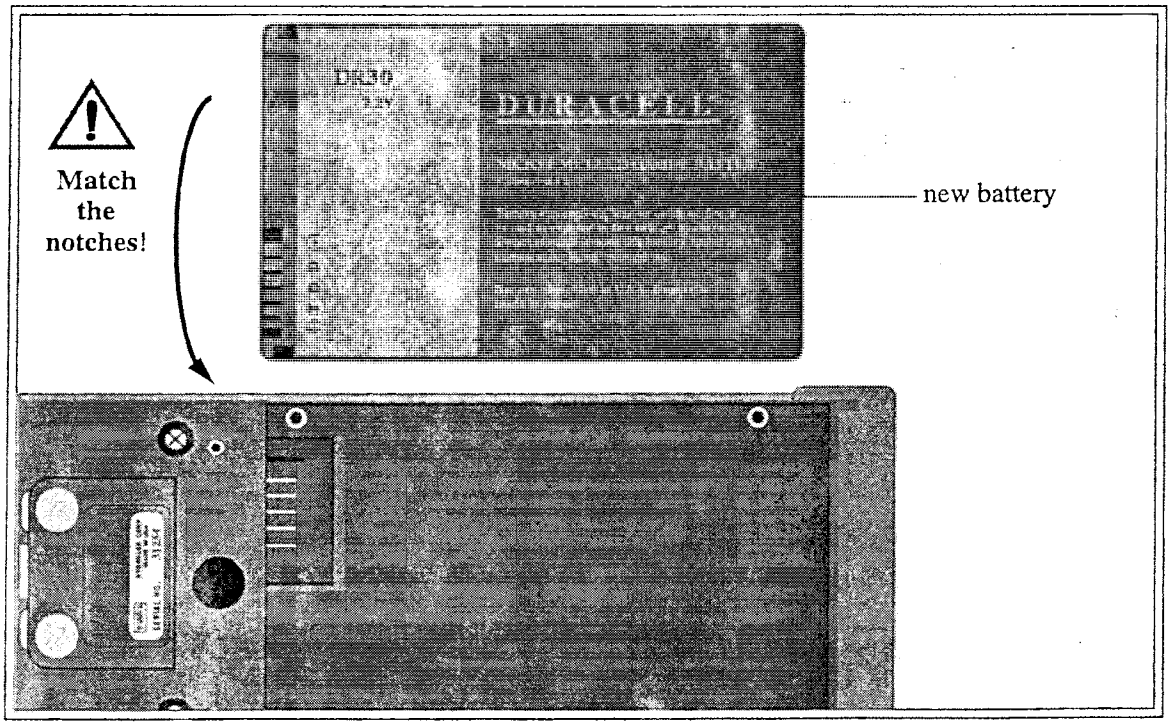


FIGURE 6: INSTALLING THE NEW BATTERY

Duracell Rechargeable Battery Quick Consumer Guide

This quick guide will give you information about performance, care, operation, and other Duracell battery-related information. It was reproduced, in part, by permission of Duracell USA.

Optimum Performance Recommendations

When you charge your battery for the first time, your charge (or ETTC for your Surveyor 4) may indicate that charging is complete after just 10 to 15 minutes. This is normal and can happen with all rechargeable batteries when first charged. You need to remove the battery, reinstall it, and then repeat the charging process. (For Surveyor 4, let the normal charge termination methods work as described on page 3-4.)

Upon first use, or after prolonged periods of storage, you may need to charge and discharge your battery two or three times before obtaining optimum performance.

It is recommended to charge the battery at room temperatures ranging between 15 °C (59 °F) and 30 °C (86 °F).

It is normal for the battery to become warm during charging or after use.

It is not necessary to fully discharge your Duracell battery before charging. You can "top-off" the charge (charge your battery when it is only partly discharged) at any time.

A charged battery will gradually lose its charge if left in storage. We suggest that you "top-off" the charge before use.

It is recommended to fully charge the battery once a month, and then fully discharge it until your instrument shuts off automatically.

If the metal terminals become dirty, wipe them off with a soft, dry cloth.

It is recommended to remove the battery from the equipment when not in use. Store at room temperature in a dry place.

It is recommended not to leave the battery in the charger (in an external charger for the Surveyor 4) for an extended period of time.

Safety Precautions and Battery Protection Information

Do not disassemble or attempt to open the battery under any circumstances.

Do not drop the battery or subject it to mechanical shock.

Do not short circuit the battery by directly connecting the metal terminals (+ and -), make sure that no metal objects such as coins, paper clips, etc., touch the terminals.

Do not heat or expose the battery to fire or high temperature. The battery can explode, leak or catch on fire.

Only use the charger recommended by the instrument manufacturer (in this case Hydrolab).

Use the battery only with equipment that specifies its use.

Benefits of Having a Spare Battery

Having a spare battery will allow you to use your instrument for twice as long as with one battery. Often long flights, meetings, or field work where power is not readily available force you to operate your instrument on battery power for extended periods of time. With one battery, you may run the risk of losing power before desired. Carrying a spare battery allows you to continue your work in these situations.

Nickel Metal Hydride Rechargeable Recycling Program

Duracell is committed to environmental responsibility and has a program in place for consumers to dispose of their spent nickel metal hydride (NiMH) rechargeable batteries. When you call your local Duracell customer service representative, Duracell will send you a special postage-paid mailer for returning the spent battery. Approximately 80% of the metals in the Duracell battery can be recovered for use in the production of stainless steel. This program is designed for Duracell NiMH batteries *only* and *under no circumstances* should other batteries be included in the program.

The Duracell Quality Guarantee

Duracell Inc. guarantees their NiMH batteries against defects in material and workmanship. If not completely satisfied with a Duracell NiMH battery, call: 800-551-2355* (9:00 am - 5:00 pm E.S.T.) or contact your nearest Duracell business office. Should any instrument be damaged by a Duracell NiMH battery due to a defect in material or workmanship, Duracell will repair or replace it (at Duracell's option), providing that you have followed both equipment and battery usage instructions. Send the instrument with the battery and prepaid postage to: Duracell USA, Berkshire Corporate Park, Bethel, CT 06801, USA. Attention: Consumer Relations Department.

(*) Number valid in the United States of America and Canada only.

Surveyor 4 Lithium Battery Replacement

Your Surveyor 4 is equipped with a lithium battery which powers the internal clock. The expected life for this battery is 2 years. We recommend replacing the lithium battery before the end of this two-year period. There is no loss of data if the battery "dies," but the internal clock will become inaccurate and time-triggered logging will not operate correctly.

⚠ WARNING: **To avoid damage to the internal components when opening the Surveyor 4, make sure that the instrument is clean and dry and that you have disconnected any cable attached to the unit.**

What Do I Need to Replace the Lithium Battery?

- 1 lithium battery (Panasonic reference: CR 2032, or equivalent)
- 1 Phillips screwdriver

Steps to follow

⚠ CAUTION: **To avoid water contacts with the Surveyor 4's internal components during battery replacement, we recommend that you avoid replacing the battery close to a water source.**

Refer to the figures 7-12 on the following pages, when replacing the lithium battery.

STEP 1: Turn the Surveyor 4 face down, so that the front panel faces the work surface.

STEP 2: Using the Phillips screwdriver, unscrew the retaining screws on the top cover of your instrument's back panel.

STEP 3: Slowly pull the cover, and flip it back on the bottom part of the back panel. The lithium battery is located on the top left-hand corner of the printed circuit board (PCB).

STEP 4: Place one of your hands over the loose top cover and the bottom part of the PCB. Lift the Surveyor 4 to a vertical position over the work surface, lithium battery facing down.

STEP 5: To remove the battery, slide your thumbnail under the battery clip. Pull the clip away from the battery and let the battery slide out of the clip and fall on the work surface.

STEP 6: Insert the new battery. Observe the polarity: match the "+" on the battery with the "+" on the battery clip.

STEP 7: Replace the top cover over the PCB, insert and tighten the four retaining screws.

STEP 8: Reset the time and date after replacing the lithium battery. To do so, press the `Setup/Cal`, and `Setup`, then `Clock`, and finally enter the correct date and time.

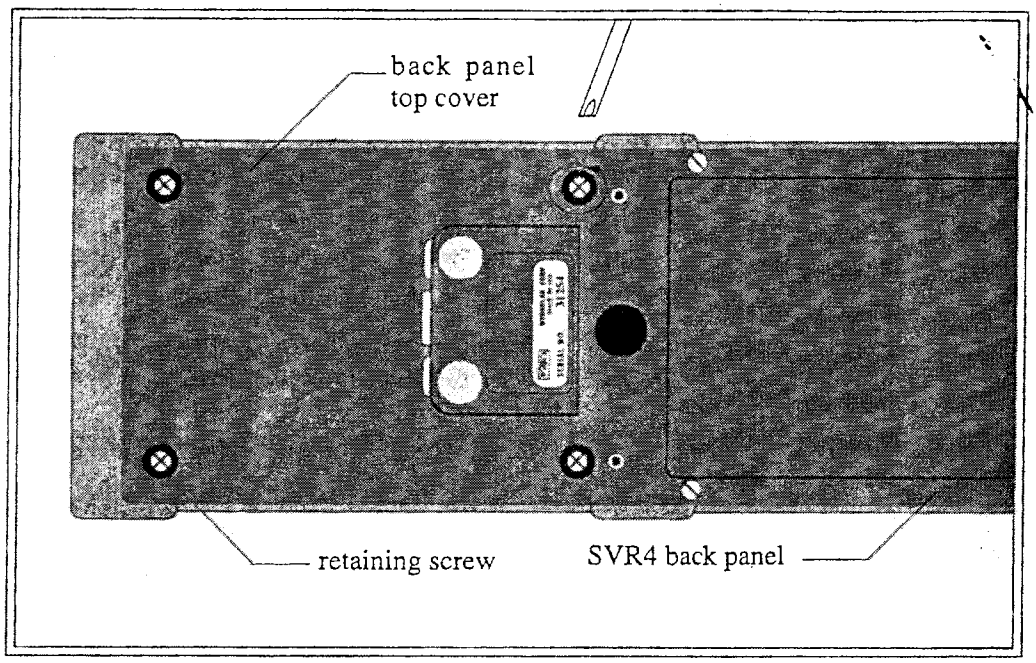


FIGURE 7: OPENING THE TOP COVER

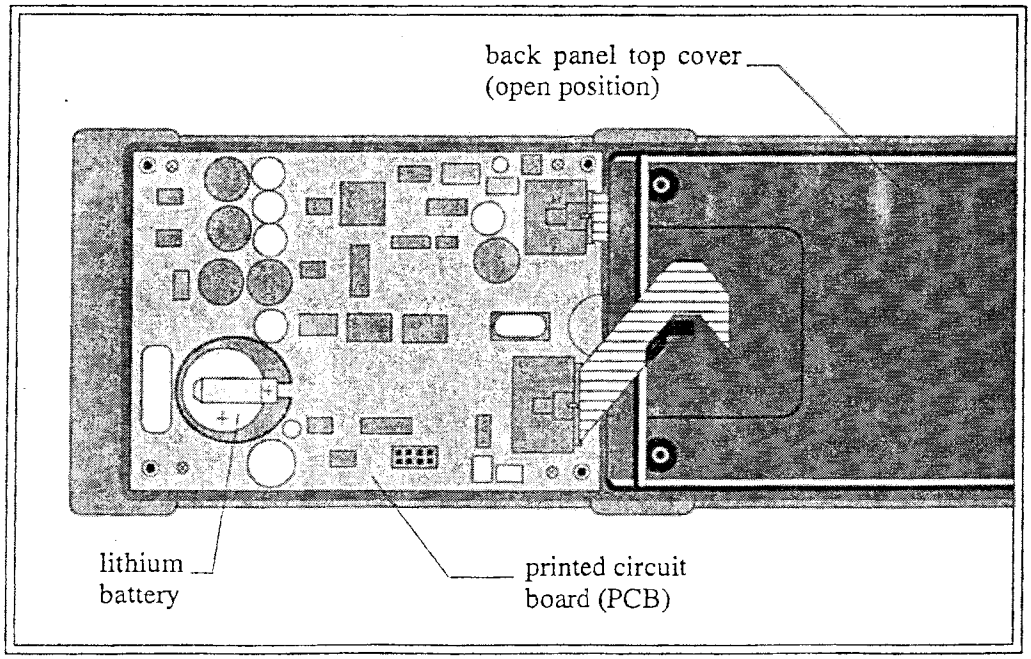


FIGURE 8: LOCATING THE COMPONENTS

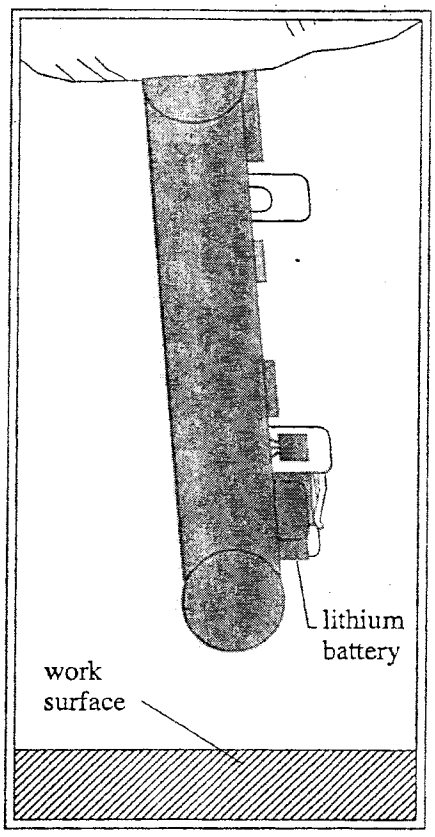


FIG. 9: VERTICAL POSITION

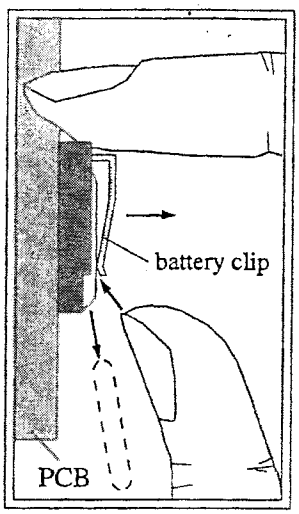


FIG. 10: REMOVAL (CLOSE UP VIEW)

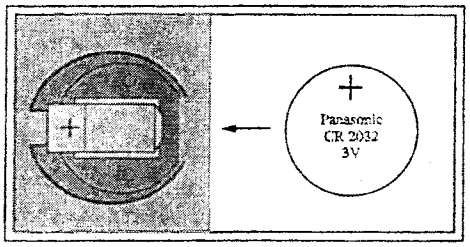


FIG. 11: INSTALLATION (CLOSE UP VIEW)

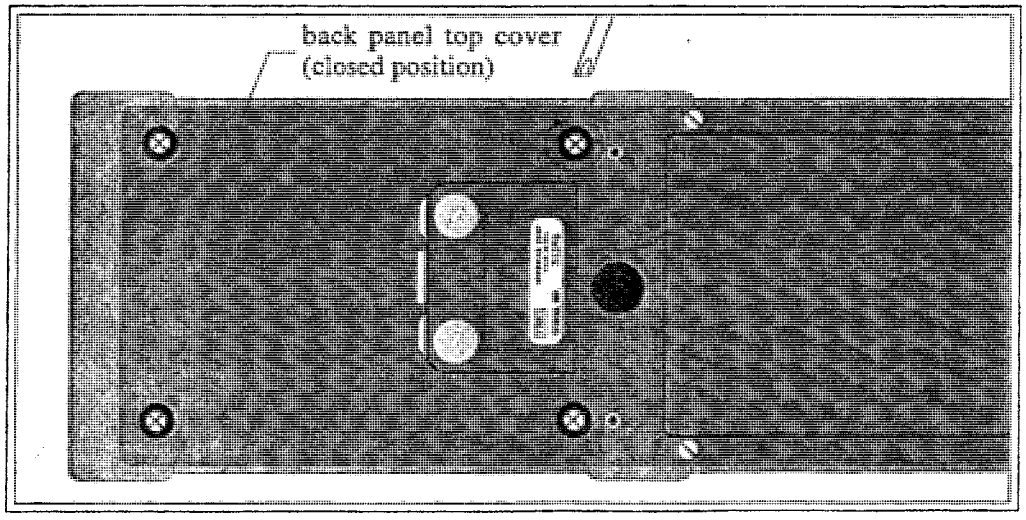


FIGURE 12: CLOSING THE TOP COVER

2. Calibration

Surveyor 4 calibration is not necessary, unless you have an option that requires calibration (e.g. the internal barometer). If this is the case, refer to the corresponding appendix at the end of this manual. Otherwise, if you go to the Surveyor 4 calibration submenu, you will be greeted by the following message: `No Svr4 parameters require calibration! Press any key....`

Your Surveyor 4 allows you to calibrate a multiprobe, just like you would with a computer. In this section we are going to show you how you access the multiprobe calibration submenu.

⚠ WARNING: **When loosening removable parts from a multiprobe or any instrument, always point those parts away from your body and other people. In extreme conditions, excess pressure may build up inside a housing, causing the caps, sensors, or other removable parts to disengage with force sufficient to cause serious injury.**

Proper maintenance of all sensors should precede calibration. Please refer to your multiprobe user's or operating manual for detailed sensor maintenance procedures.

Calibrating your multiprobe with a Surveyor 4 is quick and easy. We are going to take you to the multiprobe (Sonde) parameter submenu, then you can refer to the multiprobe User's Manual for parameter calibration procedures or to the corresponding operating manual chapters.

Your Surveyor 4 displays a certain character instead of or after a reading to let you know that something is not functioning properly or that it does not have the requested information available yet. Review the table on the next page to locate any visual prompts which will appear on your instrument's screen.

TABLE 3: SURVEYOR 4 SOFTWARE SYMBOLS

Symbols	What does this mean? What should you do?
(Blank)	It indicates that this reading is within expected range and does not present any anomalies. No service is required.
#	It indicates that the reading cannot be taken for this parameter, it is out of range (above or below the multiprobe's measurement capability). For instance, if the Surveyor 4 battery voltage is out of range, your instrument will display # signs on your screen where the reading should be.
X	It indicates that the Surveyor 4 is interrogating the multiprobe for information, or that the parameter will keep a fixed value and will not update.
_____	It indicates that the Surveyor 4 is interrogating the multiprobe for information, or that the parameter is not available or is off-line (the reading will not update).
*	It is a reminder that you need to set the time after a clock battery change or a parmeter has never been calibrated after a reset.
&	After "D/T", it indicates that the Surveyor 4 clock is not functioning. Replace the lithium battery. After "IB% Svr4:%Left", it means that the Surveyor 4 battery was removed. You need to call Hydrolab at 800-949-3766 (In the USA and Canada only) or (512) 255-8841.
!	For versions before 1.10 only. When your Surveyor 4 is connected to an external power source, it indicates that your Surveyor 4 internal battery is "dead". You need to recharge the battery.
^	After "D/T", it indicates that the Surveyor 4 clock battery is low. You need to replace the battery. Only for versions < 1.10: after "IB% Svr4:%Left", it indicates that the Surveyor 4 battery was replaced. It can also indicate that your Surveyor 4 cannot detect the estimated battery status. You need to go through a new discharge and recharge cycle.

The software symbols used for your multiprobe parameters will also appear on your Surveyor 4 display. Please, refer to your multiprobe manual "Maintenance, calibration, and storage" chapter software symbols table for details. Note that "N/A" will be displayed as "N" on your Surveyor 4 screen.

You are now ready to start the calibration process. Follow the next steps to reach the multiprobe (Sonde) parameter submenu.

TABLE 3: SURVEYOR 4 SOFTWARE SYMBOLS

Symbols	What does this mean? What should you do?
(Blank)	It indicates that this reading is within expected range and does not present any anomalies. No service is required.
#	It indicates that the reading cannot be taken for this parameter, it is out of range (above or below the multiprobe's measurement capability). For instance, if the Surveyor 4 battery voltage is out of range, your instrument will display # signs on your screen where the reading should be.
X	It indicates that the Surveyor 4 is interrogating the multiprobe for information, or that the parameter will keep a fixed value and will not update.
-----	It indicates that the Surveyor 4 is interrogating the multiprobe for information, or that the parameter is not available or is off-line (the reading will not update).
*	It is a reminder that you need to set the time after a clock battery change or a parmeter has never been calibrated after a reset.
&	After "D/T", it indicates that the Surveyor 4 clock is not functioning. Replace the lithium battery. After "IB% Svr4:%Left", it means that the Surveyor 4 battery was removed. You need to call Hydrolab at 800-949-3766 (In the USA and Canada only) or (512) 255-8841.
!	For versions before 1.10 only. When your Surveyor 4 is connected to an external power source, it indicates that your Surveyor 4 internal battery is "dead". You need to recharge the battery.
^	After "D/T", it indicates that the Surveyor 4 clock battery is low. You need to replace the battery. Only for versions < 1.10: after "IB% Svr4:%Left", it indicates that the Surveyor 4 battery was replaced. It can also indicate that your Surveyor 4 cannot detect the estimated battery status. You need to go through a new discharge and recharge cycle.

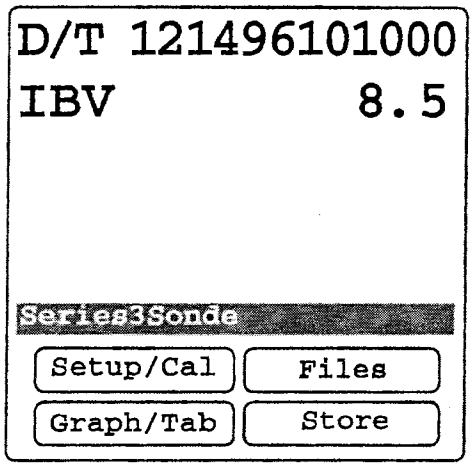
The software symbols used for your multiprobe parameters will also appear on your Surveyor 4 display. Please, refer to your multiprobe manual "Maintenance, calibration, and storage" chapter software symbols table for details. Note that "N/A" will be displayed as "N" on your Surveyor 4 screen.

You are now ready to start the calibration process. Follow the next steps to reach the multiprobe (Sonde) parameter submenu.

Series 3 Calibration

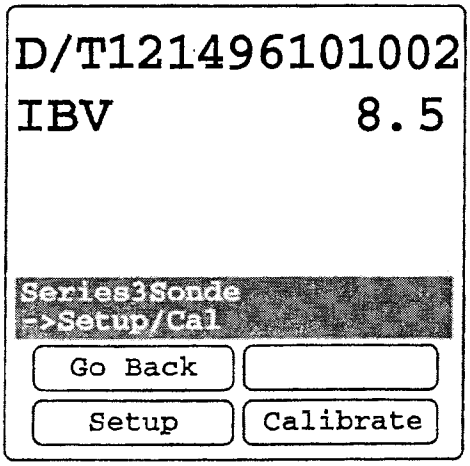
Series3Sonde SL2

After setting the I/F Mode to Series 3, your screen should be similar to this:

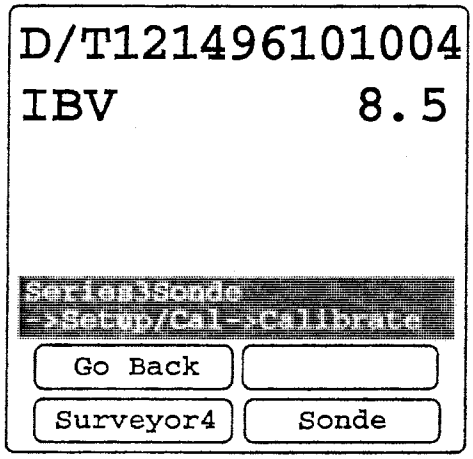


You will notice Series3Sonde on the history line which tells you that you are connected to a DataSonde 3, a Recorder, a Reporter, an H20, or an H20G.

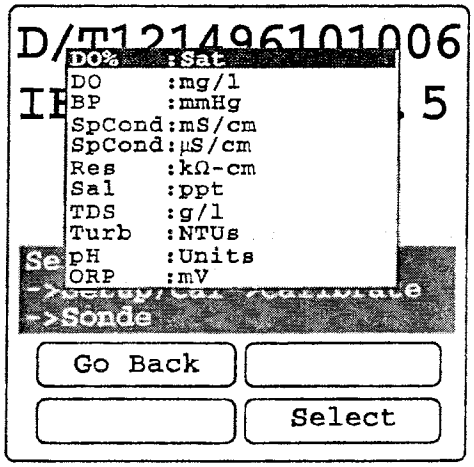
STEP 1: From the initial screen above, press the Setup/Cal key, to get:



STEP 2: Next, press the Calibrate key. Your Surveyor 4 will display the next screen:



STEP 3: Then, press the Sonde key and the next or similar screen will appear:



NOTE:

- Before calibrating your Series 3 multiprobe, you may want to go to the Setup->Sonde submenu and choose the appropriate setup for your parameters. For instance, if you have turbidity, you have the choice between "Nephelometric" (Neph) or "Ratio" (Rat) mode. Refer to section 2.4.

You are now in the Series3Sonde (multiprobe) calibration submenu. Your screen may differ (different parameters displayed) from the sample screen above, since your multiprobe configuration may be different from the one used for this sample screen. Move the cursor to the parameter you want to calibrate and press Select. Follow the Surveyor 4 prompts with the maintenance and calibration chapter of the appropriate Series 3 multiprobe Operating Manual.

NOTE:

- For calibration in Terminal mode, refer to the maintenance and calibration chapter of the corresponding Series 3 Operating Manual.

Series 4 Calibration

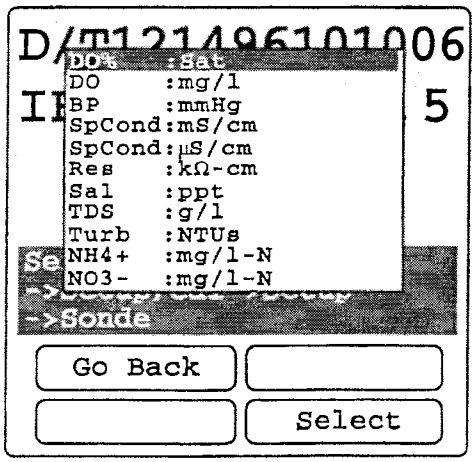
Series4Sonde SL2

To calibrate a Series 4 multiprobe (DataSonde 4 or MiniSonde), follow the next steps:

STEP 1: From the initial Series4Sonde screen, press the Setup/Cal key.

STEP 2: Next, press the Calibrate key.

STEP 3: Then, press the Sonde key and the next screen, or similar, will appear:



You are now in the Series4Sonde (multiprobe) calibration submenu. Your screen may differ (different parameters displayed) from the sample screen above, since your multiprobe configuration may be different from the one used for this sample screen. Move the cursor to the parameter you want to calibrate and press Select. Follow the Surveyor 4 prompts with the calibration sections of the multiprobe user's manual.

APPENDIX C
Cyanotoxin Microcystin ELISA Method

ESS BIO GENOP 2100.1

ANALYSIS OF THE CYANOTOXIN MICROCYSTIN BY ELISA

1. Description and Applicable Matrix

Microcystin is a potent toxin that can be produced by some freshwater cyanobacteria (also known as blue-green algae). This method quantitatively determines total microcystin (cell bound toxin plus dissolved toxin) residues in water using an enzyme-linked immunosorbent assay (ELISA). Microcystins in the sample compete with the microcystin-enzyme conjugate for a limited number of antibody binding sites. The resulting yellow endpoint is read on a microtiter plate reader.

This method outlines how to run the assay using the EnviroGard® Microcystins 96-Well Plate Kit, Strategic Diagnostics Inc., using non-toxic microcystin-LR standards equivalent to 0.1, 0.4 and 1.6 ppb microcystin-LR. There are many comparable ELISA kits that may be substituted. If using another ELISA kit, follow the manufacture's instructions.

2. Safety and Pollution Prevention

A. General safety practices for all laboratory operations are outlined in the Wisconsin State Laboratory of Hygiene's Chemical Hygiene Plan for Environmental Sciences (SOP EHD 4000).
B. As with any potentially toxic or dangerous substance, care should be taken when handling samples, acids, bases and solvents. Proper personal protection; gloves, apron or labcoat, and eye protection are suggested. Any further precautions are at the discretion of the laboratory personnel or the supervisor.
C. All laboratory waste, excess reagents and samples will be disposed of in a manner which is consistent with applicable rules and regulations. Waste disposal guidelines are described in the University of Wisconsin Chemical Safety and Disposal Guide.

3. Equipment

A. **Microtiter plate reader**
B. **Orbital shaker table**
C. **500mL glass or polypropylene bottles**

D. **20mL glass scintillation vials**
E. **10cc syringes**
F. **0.45µm 13mm Millex® HV_{13} non-sterile filter units**
G. **100µL pipet, single and/or multi-channel**
H. **100µL pipet tips**
I. **Eppendorf Repeating Pipette**
J. **50µL Eppendorf tips**
K. **Microtiter plate cover or Parafilm®**
L. **Timer**

4. **Reagents and Consumables**

A. **EnviroGard® Microcystins 96-Well Plate Kit, Strategic Diagnostics Inc. or other manufacture's kit**
B. **Type I water**

5. **Procedure**

A. Sampling and Storage
   1) Collect a minimum of 250mL of sample in glass (preferable) or polypropylene bottles.
   2) If samples are not to be analyzed within 8 hours of collection, freeze sample to analyze for total microcystin. Leave enough head-space in bottle to accommodate freezing. Thaw sample prior to processing. Note: This freeze-thaw cycle will count towards one of the three cycles the sample will undergo (see 5.B.1 below).

B. Sample Preparation for Total Microcystin (cell bound toxin plus dissolved toxin)
   1) To release any toxin associated with the cells, the sample will undergo a freeze-thaw cycle at least three times. If preferred, may use the original sample bottle for the freeze-thaw cycles as long as there is enough head-space in the bottle to accommodate freezing.
      (a) Freeze sample at temperatures $\leq$ -20°C.
      (b) Once frozen, thaw sample.
      (c) Repeat freeze-thaw cycle two additional times for a total of at least three times.
   2) If low sensitivity is required (< 0.1 ppb), the sample may be concentrated following completion of the freeze-thaw cycles. (See ESS BIO GENOP 2110 or follow WLSH's Organic SOP entitled "Determination of Microcystin-LR in Water by HPLC" for concentration procedure.)
   3) If manufacture recommends particulates be removed prior to ELISA, filter

10mL of thawed sample into a labeled 20mL glass scintillation vial using a 10cc syringe and 0.45µm Millex®syringe filter unit.

C. ELISA Procedure

Follow manufacture's directions to perform ELISA. The following directions are based on Strategic Diagnostic's 96-well plate kit:

- All reagents and samples must be at room temperature before using (do not leave out for more than 8 hours).
- Two plate strips from the ELISA kit can be used to run the controls and seven samples in duplicate.
- When using fewer than eight strips, remove and store the remaining strips at 4°C.
- If running more than three strips, it's recommended to use a multi-channel pipet or a repeating pipet to deliver the conjugate, substrate and stop solutions.

1) Fill out plate template worksheet with location of controls, standards and samples.
2) Add 100µL of negative control, 0.1, 0.4 and 1.6 ppb non-toxic microcystin-LR standards and 100µL of each sample to their respective wells in duplicate.
3) Cover wells with plate cover or Parafilm® to prevent evaporation.
4) Place plate on orbital shaker table (120 RPMs) and incubate for 30 minutes at room temperature.
5) After 30 minutes, carefully remove cover and add 100µL of Microcystin-enzyme Conjugate to each well. Mix thoroughly by gently moving in a circular pattern on benchtop.
6) Cover wells with plate cover or Parafilm® and incubate for another 30 minutes at room temperature.
7) After incubation, remove cover carefully and shake out contents into sink. Flood wells completely with Type I water, shake to empty. Repeat wash step four times. Alternatively, use a microtiter plate washer for the wash steps.
8) Add 100µL of Substrate to each well.
9) Carefully mix contents. Cover wells again and incubate for 30 minutes at room temperature.
10) Add 100µL of Stop Solution to each well and mix thoroughly (Caution: Stop Solution is 1.0N HCl). The well solutions will turn yellow.
11) Read plate on microtiter plate reader within 30 minutes of adding Stop Solution.
    (a) Set reader's wavelength to read 450nm. If reader has dual wavelength capabilities, set reference wavelength to 650nm.
    (b) If necessary, zero plate reader on air.

(c) Read plate by hitting the run button.
(d) Set data reduction program to use a semi-log curve to fit the standard curve.

6. **Quality Assurance – Follow manufacture's recommendations. The following are based on Strategic Diagnostics' 96-well ELISA kit.**

A. Samples
1) All samples, at a minimum, are placed in duplicate on the ELISA plate.
2) Coefficient of Variation (CV) on sample replicates need to be ≤ 15%. If CV's > 15%, then sample is re-tested as soon as possible on a separate ELISA run.

B. ELISA Standard Curve
1) A standard curve consisting of negative controls, 0.1, 0.4, 1.6 ppb non-toxic microcystin-LR standards, all provided with Strategic Diagnostic's kit, will be run on each ELISA plate.
2) All standard curve controls, at a minimum, are place in duplicate on the ELISA plate.
3) CV's need to be ≤ 15% on controls.

C. Method Blank
1) A method blank consisting of Type I water may be run on each ELISA plate (in duplicate).
2) If contamination is evident in the method blank, steps will be taken to reduce or eliminate the interference(s).

D. Out of range samples

Samples reported on data reduction program as "R" are outside the standard curve and must be reported as such. If values are desired, samples may be concentrated or diluted as appropriate, so that they fall on the standard curve when re-tested. Follow manufacture's recommendations for concentration or dilution.
1) Per Strategic Diagnostic's recommendation, dilute samples that are higher than the highest calibrator using Type I water. Multiply result by the dilution factor.
2) Concentrate samples that are lower than the lowest calibrator (see ESS BIO GENOP 2110 or follow WLSH's Organic SOP entitled "Determination of Microcystin-LR in Water by HPLC" for concentration procedure). Divide result by the concentration factor.

7. **References**

A. Strategic Diagnostics Incorporated, 1997. Enviro®Gard Microcystins Plate Kit

Instructions 75400.

B. Chu, F.S., Xuan Huang and R.D. Wei. 1990. Enzyme-Linked Immunosorbent Assay for Microcystins in Blue-Green Algal blooms. J. Assoc. Off. Anal. Chem. 73:451-456.

C. Environmental Health Division Quality Assurance Manual, Wisconsin State Laboratory of Hygiene.

8. Signature Page

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Dept: Environmental Toxicology

Sediment/Diatom Methods

APPENDIX D
Sediment Diatom Methods

2.0 SEDIMENT DIATOM METHODS

This method, adapted from *Protocols for the analysis of algal samples collected as part of the U.S. Geological Survey National Water-Quality Assessment (NAQWA) program* (Charles et al. 2002), is used to process sediment core samples and identify and enumerate diatoms. The method involves digestion of core samples, coverslip preparation, slide mounting, and microscopic examination of mounted diatoms.

2.1 Responsibility and Personnel Qualifications

A qualified lab that has the appropriate training and experience in sediment diatom analysis may use this protocol to identify sediment diatoms. It is also important that the taxonomist maintains contact with other taxonomists through professional societies and other interactions, and keeps up with the pertinent literature, since taxonomic groupings and nomenclatural basis for species identifications are frequently updated over time. A second taxonomist will re-identify a randomly-selected 10% of the samples for quality control (QC), as noted below, to quantify taxonomic precision, or consistency, as rates of error (=percent disagreement), help target corrective actions, and ultimately help minimize problems during data analysis. Samples will be sent to the laboratory on a regular basis during the project as collection of the field samples is completed to avoid delays in processing and identifying samples.

Labs must track sample shipment by field crews using the Surface Water Information Management System (SWIMS). Participating laboratories will be given access to the SWIMS system, where they can acquire tracking numbers, and information on samples that have been batch shipped by field crews. Upon samples receipt, the laboratory must contact Marlys Cappeart at the Information Management Center by phone (541- 754-4467) or fax to confirm samples have arrived. If expected samples do not arrive, labs must notify Ellen Tarquinio at EPA (202-566-2267).

2.2 Precautions

- Wear appropriate clothing for safety precautions, such as safety glasses, nitrile gloves, rubber apron, long pants, etc.
- Use caution when working with acids. Always add acid very slowly and with great caution to avoid any unexpected reactions.

2.3 Equipment/Materials

- Laboratory coat, gloves, and goggles
- Fume hood
- Micropipette (100µg and 1000 µg)
- Pipette tips (100 µg and 1000 µg)
- 100-ml beaker
- Hot plate
- Nitric acid (or hydrogen peroxide)
- De-ionized water
- Potassium dichromate
- Fine-tipped vacuum hose
- 20-ml glass sample vials
- Cover slips, 18 x 18 mm, or 22 x 22
- Compound microscope
- Ceramic tiles
- 10% buffered formalin
- Wax
- Naphrax™
- Wooden toothpicks
- Forceps
- Single-edge razor blade
- Acetone
- 95% Ethanol
- Kimwipe® tissue
- Microscope
- pH test paper or Litmus paper
- Sediment Diatom Sample Log-In Form (TBD)
- Labels (TBD)

2.4 Procedure

2.4.1 Sediment (Sediment Core Sample) Digestion

~~1.~~ Transfer[PG1] approximately 0.5 to 1.0 cc of either moist or dry sediment to a 100-ml beaker. If dry, a small amount of water may be added to the sample (approximately 10 ml) to hasten disaggregation. ~~If the sample is to be analyzed quantitatively, record the wet weight, volume, or dry weight of the sample to be processed.~~

1.

2. Set the hot plate dial to 200° C. Put on laboratory coat, gloves, and goggles. Place tray containing all subsample beakers under the fume hood.

3. Add enough nitric acid to each beaker to increase the volume to 50 mL. Initially, add acid very slowly and with great caution, anticipating that an unexpected reaction may take place. After determining that there is no possibility of a violent reaction, slowly and cautiously add the remainder of the acid to the samples. As a rule, the minimum should be a 1:2 sample to acid ratio. A hydrogen peroxide method may also be used. **(Need 2-3 sentences describing approach)**

4. This procedure should be done in a fume hood using appropriate laboratory clothing. Tall 1000ml beakers should be used as the process can react vigorously. Add about 5 ml of H_2O_2 to the sample and allow to sit for 10-15 minutes. Add a small amount of potassium dichromate to the sample. If a reaction doesn't occur place the sample on a hot plate on low heat to start the reaction. When the reaction is finished the color should be yellow or light orange.

5. After the samples have cooled somewhat (a few minutes) the samples should be washed much as is done with the nitric acid treatment[PG2].

6. Heat - Transfer the beakers to the hotplate and heat for 2 hours. Pay careful attention to samples while heating. If the volume drops too low, add deionized water. When finished heating, add a dash of potassium dichromate to each beaker to catalyze the reaction. Keep adding small amounts until further reactions cease.

7. Cool and dilute - After the beakers have cooled somewhat, transfer them back to the tray. Top off the bakers with deionized water and allow diatom frustules to settle for 12 hours.

8. Siphon and add water - Using a fine-tipped vacuum hose, draw down the samples to approximately 50 mL. Siphon the water from the center of the water column under the surface. Make sure not to siphon the diatom layer off the bottom of the beaker. After siphoning, add deionized water to replace the supernatant drawn off and wash the sides of the beaker to remove diatoms adsorbed to the sides and top of the beaker. Let settle again for at least 9 hours. (As a rule, let settle 1 hour per 1 centimeter so the smallest diatoms can settle out).

9. Repeat siphoning - Repeat siphoning and addition step another 5 or 6 times and test the pH with pH test paper (or Litmus paper). When the samples are within the range of 6.5-7.5, the samples are ready for slide mounting.

10. Reduce volume - Draw the sample volumes down to between 25-50 mL, making sure not to remove diatoms.

11. Transfer and record volume - Transfer the remaining volume to labeled vials and record diatom volume after digestion on the laboratory processing sheet. Make sure to rinse all diatoms clinging to the beaker into the sample vial with deionized water. If the full volume does not fit into the vial, allow the vial contents to settle for at least 12 hours and siphon off some of the supernatant. Transfer the remaining contents of the beaker into the vial, again making sure to rinse all remaining diatoms into the sample vial.

2.4.2 Preparing Cover Slips

1. Estimate volume to be placed on the coverslips - Starting with cleaned material contained within 20-ml glass vials, estimate the volume of suspended material that will need to be deposited ("dripped") on a cover slip to produce a slide of the appropriate cell density. Generally, between 5 and 10 diatom specimens should be present in a single high power microscope field (1000X). To make the estimate, shake the cleaned material to ensure a homogeneous dispersion of cells within the 20-ml vial. Immediately open the vial and withdraw either a 25- or 50-µl sub-sample using the 0- to 100 µl adjustable

pipettor. Place the subsample on a slide and cover it with a cover slip. Then observe this preparation under a compound microscope at 50X magnification. Look at a number of fields and observe the density of cells. Then calculate the amount of material that would need to be dripped so that the density of cells seen at this magnification would be approximately 30 to 40 per field.

2. Sparse diatom samples - If a satisfactory slide could be made by increasing the concentration of cleaned diatom material by two to five times, then do this by using a micropipette to remove the required amount water from the vial of material after it has been allowed to settle for at least eight hours. Record the concentration factor. If a concentration of cleaned material greater than five times is required, then re-subsample the original sample. Take a subsample of a size sufficient to prepare satisfactory slides. Use all remaining sample only if absolutely necessary. Digest the subsample and prepare a new vial of cleaned material. Repeat procedure above. If the concentration of cleaned material is still not sufficient, concentrate it, as described above. If still too dilute, combine the two vials of cleaned subsample materials. Record steps and volumes, and final concentration factor; if, after following the steps above to concentrate the cleaned material, the density of diatoms on a cover slip still does not meet the criteria of 30 to 40 cells per field at 400 - 450x magnification, then proceed to make the densest slide possible.

3. Deposit[PG3] cleaned material on cover slips - Use forceps to remove single cover slips. Place each cover slip on a marked space of the ceramic tile. Be sure the ceramic tile is clean and dry to avoid cross-contamination. If the intended drip count is less than 600 µl, drip a small amount of distilled water onto the cover slip with a disposable pipette, sufficient to form a thin layer of water over the entire cover slip. Agitate the sample vial to a uniform dispersion and use the adjustable pipette to quickly withdraw the required amount from near the central portion of the sample. Eject this material smoothly and carefully onto the layer of distilled water already on the slip. By alternately drawing material up into the pipette and ejecting it, a homogeneous suspension is achieved on the cover slip. In the case where more than ~600 µl of original sample is required, the addition of distilled water is not necessary, and the sample can be ejected and mixed directly on the cover slip. In both cases, take care to ensure that the suspension covers the entire surface of the cover slip, including the extreme edges of the corners. Should the cover slip overflow, discard the cover slip, and repeat the procedure with a freshly cleaned cover slip.

4. Drying samples - Discard the pipette tip when finished with each sample and make cover slips following the same procedure as in step 3. Once the ceramic tile is loaded with cover slip preparations, the tile should remain undisturbed until the cover slips are dry. At this point, drying of the slips can proceed at room temperature (a period of several hours will be required), or gentle heat (warm to the touch only) may be applied to hasten evaporation (a crook-neck lamp with incandescent light bulb placed 15 - 30 cm over the drying plate is one option). Once completely dry, put the aluminum plate with cover slips on the hot plate that has been preheated to 250 to 300°F. Leave for 3 to 5 minutes. This procedure ensures that nearly all water is driven from the material on the cover slips and helps assure that the diatom frustules will adhere to the surface of the glass.

5. Check the slides - Remove the ceramic tile from the hotplate and inspect the cover slips. If the pattern of diatoms distributed on any of the cover slips is not even and smooth,

they should be re-dripped. If cover slip distributions seem unsatisfactory after repeated attempts, consult an algal analyst.

6. Store samples - After a diatom slide is made and no more sample is needed from the diatom vial, add two - four drops of 10% buffered formalin to each vial while working under a fume hood. Tightly cap the vials and seal them by immersing the top 1/3 of the vial in melted wax.

2.4.3 Mount Cover Slip on Microscope Slide

1. In a positive-draw fume hood, transfer a small amount of Naphrax™ (volume equivalent to ~2 to 4 drops of water) to the central portion of the etched side of the microscope slide using a rounded wooden splint or disposable pipette. Using a rounded wooden toothpick, distribute the Naphrax™ over an area approximately equivalent to the size of the cover slip.

2. Remove the appropriate cover slip from the aluminum plate with forceps, being careful to handle the cover slip only at the extreme corners. Invert the slip and place it gently on the Naphrax™ covered portion of the slide.

3. Place the slide (cover slip up) on the hotplate and apply gentle heat until the evolution of bubbles resulting from the evaporation of the toluene solvent first occurs, and then significantly diminishes.

4. Remove the slide from the hot plate, and, using the rounded toothpicks, gently position the cover slip and press it to form a uniform, thin layer of Naphrax™ beneath the entire cover slip. Make sure that the edges of the cover slip are brought parallel to the edges of the microscope slide. Care must be taken at this stage not to press so hard as to damage or dislodge the diatoms or cause warping of the cover slip.

5. Set aside the mount to let the Naphrax™ become hard, use a single-edge razor blade to carefully trim any excess Naphrax™ which has been squeezed out from beneath the cover slip. Great care must be taken to avoid "lifting" the cover slip by inadvertently allowing the edge of the blade to move between the cover slip and the microscope slide.

~~6.Under the hood, place the mount in successive baths of acetone first and then ethanol for no more than 10 or 15 seconds each. Wipe the mount clean with a Kimwipe® tissue. Add paper label to slides before slides have been analyzed.~~Wipe the mount clean with a Kimwipe® tissue.

2.4.4 Diatom Counts

1. Scan slides at low to medium magnification (100x to 450x) to confirm that diatoms are evenly distributed on the cover slip, and are at a density appropriate for efficient counting. At high magnification (1000x), there should be between 5-10 diatoms per field. If there are problems with dispersion or density that would compromise the quality and accuracy of the analysis, discuss these and have new slides made. Avoid counting diatoms in any disrupted areas of the mount, particularly edges that have optical

aberrations. Always save any count data generated for a sample, even if the number of valves or frustules is low (e.g., <100).

2. Because slides may need to be recounted for QC purposes, it is very important to clearly demarcate the areas of a slide scanned during a count. After the preliminary slide examination, secure the slide in the mechanical stage and use the microscope's diamond scribe to etch a horizontal or vertical line on the cover slip to mark the edge of the first row to be counted. Rows are narrow rectangular areas (strips) of the slide adjacent to the scribed line, with width equal to the field of view. Start rows far enough from the cover slip edge to avoid optical distortion, and end them near the opposite cover slip edge where diatoms are no longer clearly visible. Locate a starting point near one end of the etched line and make a circle with the scribe. This denotes the starting point of the count. ~~During the count, etch a circle around the last field counted in the first row and at the beginning and end of all other rows.~~ Always check to make sure that etching is clearly visible so that circles and lines can be located easily by others[PG4].

3. When the line and first field are etched on the cover slip, and the first field is focused under oil immersion, begin to count 500 valves. Count all partial valves that are more than 50% of the valve or that contain unique features such as recognizable central areas or distinct ends. Count all valves and fragments that extend at least halfway into the field of view.

4. Stop counting when 500 valve count is reached. Clean the slide and store it properly.

5. For slides where valves are scarce, sequential parallel transects should be scanned and counted in an effort to attain the 500 valve count target. Counting should stop after 6 transects or 4 hours, regardless of whether 500 valves have been counted or not.

2.4.5 Taxonomic identifications

1. The classification/nomenclatural framework for taxonomic hierarchy above genus level will be based on Round et al. (1990).

2. Taxonomic target level with be variety, thus, an individual identification result will be trinomial (genus/species [specific epithet]/variety).

3. The availability of names will be determined by comparison to the 2004 list developed by the US Geological Survey's National Water Quality Assessment (NAWQA), available online at:

   http://diatom.acnatsci.org/nawqa/diatomlist04.asp

   Comparison of names to this list is needed to enhance consistency (harmonization).

4. Due to the fluidity of the nomenclatural system for diatoms, it is necessary to maintain continuous interaction among all taxonomists. For this project the interactions will take several forms:
   a. Exchanging digital images for among-taxonomist concurrence; a goal for the project is that images will be taken for all specimens that constitute greater than 2% of the sample. Images will be posted on a web-page to be hosted by the

Academy of Natural Sciences of Philadelphia, Patrick Center for Ecology, Phycology Department.

b. Email and conference calls, as necessary

c. Workshop (TBD)

2.4.6 Data Recording and Transmittal

1. Taxonomists should enter data into an Excel spreadsheet in the format provided. The data elements to be captured are:

SITE_ID	Site ID
DATE_COL	Sample Collection Date
VISIT_NO	Within Year Site Visit Number
SAMPTYPE	Sample fraction (top, bottom, ml counted)
SAMP_LOC	Sample Location
SAMP_ID	Sample Tracking Number from Jar Label
LAB_ID	Lab Sample ID Number
LAB_TAXON	Lab Taxa ID Number[PGS]
TAXANAME	Unique Taxon Name
~~CELLS OR NAT. UNITS~~	~~Number of Cells or Natural Units~~
~~ABUND~~PROP	Proportion of total count
DIVISION	Taxonomic Division
ORDER	Taxonomic Order
FAMILY	Taxonomic Family
GENUS	Taxonomic Genus
SPECIES	Taxonomic Species
VARIETY	Taxonomic Variety
DISTINCT	Distinct Taxon within Sample? (Y/N)
TAXONOMIST	Name
COM_LAB	Lab Personnel Comments

2. All data will be transmitted from the laboratory to the Project QA Officer.

2.5 Pertinent QC Procedures

1. The project QA officer will randomly select 10% of the samples for QC procedures. Following completion of identifications and counts, slides will be sent to a second taxonomist for reidentification and re-counts. A chain-of-custody form will be completed and sent with the samples.

2. The QC taxonomist will perform the counting and identification procedure as described above, completing another copy of the Taxonomic Bench Sheet for each sample. Each bench sheet should be labeled with the term "QC Re-ID." As each bench sheet is completed, it should be faxed to the QA project officer.

3. The QA officer will compare the taxonomic results generated by the primary and QC taxonomists for each sample and calculate percent similarity as follows:

Equation 1

$$PSC = 1 - 0.5\sum_{i=1}^{K}|a-b|$$

where *a* and *b* are, for a given species, the relative proportions of the total samples *A* and *B*, respectively, which that species represents.

4. It is expected that the two counts will have a similarity of ≥70%. If not, the reasons for the discrepancies between taxonomists will be discussed on a reconciliation call between the primary and secondary taxonomist. Results less than 70% will be investigated and logged for indication of error patterns or trends.

5. Corrective actions will include determining problem areas (taxa) and consistent disagreements, addressing problems through taxonomist interactions. Disagreements resulting from identification to a specific taxonomic level, creating the possibility to double-count "unique" or "distinct" taxa will also be rectified through corrective actions.

6. A report or technical memorandum will be prepared by the QA Officer. This document will quantify both aspects of taxonomic precision, assess data acceptability, highlight taxonomic problem areas, and provide recommendations for improving precision. This report will be submitted to the project manager, with copies sent to the primary and QC taxonomists and another copy maintained in the project file. Significant differences may result in the re-identification of samples by the primary taxonomist and a second QC check by the secondary taxonomist.

7. Reference/ voucher samples must be prepared by the laboratory. Diatom vouchers will be slide-mounted.

8. All samples must be stored at the laboratory until the project officer notifies the lab.

2.6 Literature cited

Charles, D.F., C. Knowles, and R.S. Davis (editors). 2002. Protocols for the analysis of algal samples collected as part of the U. S. Geological Survey National Water-Quality Assessment Program. Report No. 02-06.The Academy of Natural Sciences of Philadelphia, Patrick Center for Environmental Research-Phycology Section. Philadelphia, PA. www.acnatsci.org.

Round, F. E., R. M. Crawford, and D. G. Mann. 1990. Diatoms. Biology and Morphology of the Genera. Cambridge University Press. Cambridge, UK. 757pp