Quality Assurance Project Plan

for the

Cooperative Lakes Monitoring Program

Supported By:

Michigan Department of Environmental Quality
Water Resources Division

and

The Michigan Clean Water Corps Partnership

Great Lakes Commission
Huron River Watershed Council
Michigan Lake and Stream Associations, Inc.
Michigan State University

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This Quality Assurance Project Plan (QAPP) for the Cooperative Lakes Monitoring Program (CLMP) was originally written by Howard Wandell, Michigan State University, Department of Fisheries and Wildlife and Ralph Bednarz of the Water Bureau, Michigan Department of Environmental Quality. It is intended to be a comprehensive documentation of the program's planning, implementation and assessment including the elements of program management, data generation and acquisition, assessment and oversight as well as data validation and usability. The original QAPP was developed over a six month time period in 2001, during which numerous meetings were held by the involved organizations and input was secured from volunteers, environmental managers, researchers and other interested parties. The QAPP was organized following *The Volunteer Monitor's Guide to Quality Assurance Project Plans* (U.S. EPA 1996). The QAPP was updated in August 2004, January 2007, July 2009, October 2013, March 2015, July 2018. Since the CLMP is a long-term, ongoing program the QAPP is intended to be a living document, reviewed and updated periodically.

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A. Program/Task Organization

As a Michigan Clean Water Corps (MiCorps) program, the Cooperative Lakes Monitoring Program (CLMP) is a partnership between the Michigan Department of Environmental Quality (MDEQ), the Great Lakes Commission (GLC), the Huron River Watershed Council (HRWC), Michigan Lake & Stream Associations, Inc. (MLSA), Michigan State University (MSU) and Michigan citizen volunteer samplers.

- MDEQ Water Resources Division - Coordinate and oversee MiCorps, including the CLMP. Coordinate laboratory support, data evaluation and quality assurance and quality control (QA/QC).
- Great Lakes Commission – Primary contractor for MiCorps. Oversee MiCorps contract for development and implementation of all MiCorps programs, including the CLMP and the MiCorps Data Exchange (MDE).
- Huron River Watershed Council – MiCorps partner under contract with GLC. Oversee development and implementation of MiCorps programs, including all CLMP operations.
- Michigan Lake and Stream Associations, Inc. – Administer CLMP operations including administrative logistics, enrollment targets, volunteer training, sampling logistics, sample handling and delivery, data management, and annual report printing and distribution. Assist with program coordination, pilot study development and implementation, and quality control activities.
- Michigan State University– Support MLSA in administering CLMP operations. Assist with volunteer training, sampling logistics, sample handling and delivery, data management and reporting, pilot study development and implementation, and quality control activities. Provide technical and scientific expertise and program outreach.
- MDEQ Environmental Laboratory and its overflow laboratories - Perform all specified analyses on lake water quality samples collected for the CLMP.

Table 1 provides specific names and contact information for each participating agency.

Table 1. Contact Information for CLMP Partners			
Name	**Agency**	**Contact Information**	**Role**
Marcy Knoll Wilmes	MDEQ	517- 284-5544 KnollM@michigan.gov	DEQ Contract Administrator
Laura Kaminski	GLC	734-971-9135 laurak@glc.org	Contract Manager
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Melissa Smith	MDEQ Lab	517- 335-9800 smithm36@michigan.gov	Laboratory Sample Coordinator

B. Problem Definition/Program Goal

Effective environmental monitoring is an essential component of the MDEQ mission. The MDEQ and the MiCorps partners recognize that comprehensive water quality monitoring is necessary to improve natural resource management, maintain sustainable ecosystems, and protect public health. The MDEQ and the MiCorps partners have certain responsibilities and interests in the management and protection of Michigan's inland lake resources.

Michigan has nearly 3500 lakes over 25 acres in size and many thousand smaller lakes and ponds. The state has made a substantial effort to monitor the major inland lakes and has supported a citizen volunteer lakes monitoring program since 1974. However, non-stable funding in the past has limited the scope of these water quality monitoring and lake water quality assessment programs.

In 1998 the citizens of Michigan passed a general obligation bond, the Clean Michigan Initiative (CMI), to protect and enhance Michigan's environmental quality, natural resources, and infrastructure. The Governor and Legislature supported this initiative. The bond legislation called for a portion of the CMI funds, known as the Clean Water Fund (CWF) to implement the "Strategic Environmental Quality Monitoring Program for Michigan's Surface Waters" (Strategy), which was developed by the MDEQ in January 1997 (MDEQ 1997). This Strategy identifies a number of monitoring activities necessary for a comprehensive assessment of water quality in Michigan surface waters. One component of the Strategy is to expand the citizen volunteer lakes monitoring program.

With CMI-CWF support a cooperative project was undertaken in September 2000 by the MDEQ and MLSA in partnership with MSU to expand and enhance the CLMP volunteer monitoring network in terms of lakes enrolled and water-quality indicators monitored. A five-year program expansion plan was developed and the first year of the plan was implemented during the spring of 2001.

In September 2003 the Michigan Clean Water Corps (MiCorps) was created as a statewide network of volunteer monitoring programs to assist the MDEQ in collecting and sharing water quality data for use in water resources management and protection programs (www.micorps.net). The GLC in partnership with the HRWC was retained under contract to assist the MDEQ in developing and implementing MiCorps. The CLMP is a core MiCorps program. MLSA and MSU continue to provide administrative and technical support to the CLMP as MiCorps partners.

The CLMP goals are both data and education oriented including:

- Provide baseline information and document trends in water quality for individual lakes.
- Provide a cost-effective process for the MDEQ to increase baseline data for lakes statewide.
- Make volunteer lake monitoring data electronically available on the MiCorps web-site.
- Educate lake residents, users, and interested citizens in the collection of water quality data, lake ecology, and lake management practices.
- Build a constituency of citizens to practice sound lake management at the local level and to build public support for lake quality protection.

Data collected as part of the CLMP are incorporated into Michigan’s lake water quality assessment process for classifying lakes by their water quality trophic state, identifying possible conflicts with water quality standards (screening tool assessment), documenting trends in lake eutrophication indicators, and supporting lake management activities. The CLMP is a significant source of consistent long-term eutrophication data for Michigan’s inland lakes.

Besides the MDEQ, CLMP data may be used by other state and local agencies and groups including: the Department of Natural Resources (MDNR), lake boards, watershed councils, local government public works boards, lake and stream associations, conservation groups and others interested in water resource management.

CLMP records are often the only current lake water quality data available to state and local agencies and organizations. These groups may use CLMP data to make initial assessments of water resource conditions and management needs. From these initial assessments, planning activities may be set in motion leading to comprehensive resource/watershed management projects.

C. General Program/Task Description

Originally known as the Self-Help Program, the CLMP continues a long tradition of citizen volunteer monitoring of Michigan's inland lakes. Michigan has maintained a volunteer lakes monitoring program since 1974, making it the second oldest volunteer monitoring program for lakes in the nation.

The original program was designed for lake property owners to monitor water quality by measuring water clarity with a Secchi disk. In 1992, the MDEQ (then part of the MDNR) and MLSA entered into a cooperative agreement to expand the basic program. An advanced Self-Help program was initiated in 1993 that included a monitoring component for total phosphorus during spring lake turnover. In 1998, the program was further enhanced to include chlorophyll *a* and late-summer total phosphorus sampling. At that time the program was re-named the CLMP. In 2001, dissolved oxygen and temperature profile monitoring was added to the CLMP and an aquatic plant identification and mapping component was pilot tested and then added to the CLMP in 2002. An exotic plant watch component was pilot tested and then added as a full project parameter to the CLMP in 2011. A shoreline health parameter, called "Score the Shore" was pilot tested in 2015 and then added as a full project parameter to the CLMP in 2016.

C1. CLMP Parameters Measured

The CLMP is a volunteer-based program for monitoring trophic state indicators in lakes. The focus of the CLMP is on the primary indicators Secchi disk transparency, total phosphorus and chlorophyll *a*. However, with CMI-CWF support additional parameters have been added to the CLMP including water-column dissolved oxygen and temperature, aquatic plant identification and mapping, a specialized exotic plant program, and shoreline habitat (Score the Shore). Volunteer participation determines which lakes will be monitored for these parameters.

Table 2 provides a summary of the parameters currently being monitored in the CLMP. A general description of each CLMP sampling component follows.

Table 2. Parameters Measured as Part of the CLMP

Parameter	Sample matrix	Measures
Secchi disk transparency	physical	clarity, trophic state
Spring phosphorus	water chemistry	water chemistry, nutrient enrichment

Summer phosphorus	water chemistry	water chemistry, trophic state
Chlorophyll *a*	biological	algal productivity, trophic state
Dissolved oxygen and temperature	water chemistry and physical	hypolimnetic oxygen depletion and thermal stratification
Aquatic plants ID and mapping	biological	species present, relative abundance, exotic species, trophic state
Exotic plant watch	biological	species present, relative abundance
Score the Shore	Physical, biological	Shoreline and riparian ecological health

C2. Secchi disk transparency component:

Clear lakes are universally valued as resources with exceptional quality. For almost 150 years a lake's clarity or transparency has been used to appraise its quality. The Secchi disk has become a standard tool used by scientists around the world to generally assess lakes. It has been standardized as an eight-inch (20-centimeter) disk, with four alternating black and white quadrants painted on the surface.

To make a transparency measurement the disk is attached to a measured line and lowered into the lake until it disappears. The water depth at which the disk disappears is the Secchi disk depth or value for the lake. Obviously the deeper the disk is seen the clearer the water or the greater the transparency of the lake. A lake's clarity or transparency is influenced by several factors, but for most lakes the amount of algae in the water is a major cause for changes in transparency. As more nutrients like phosphorus enter the lake from the watershed more algae is produced. As more algae is produced the clarity of the water decreases. In very clear lakes, Secchi disk values greater than 30 feet can be measured. On the other hand, in lakes with high nutrient supplies and algae production the disk can disappear in two to three feet.

CLMP volunteers measure Secchi disk transparency weekly or every other week through out the summer growing season from mid-May through mid-September.

The Secchi disk transparency along with total phosphorus and chlorophyll *a* results provide an estimate of the level of biological productivity, or trophic state, of lakes. These results are used to calculate a set of trophic state indices (i.e. Carlson TSI_{SD}, TSI_{TP}, and TSI_{CHL}) for the lake (Carlson 1977). These indices provide a quantitative means of describing the stage of lake aging, or eutrophication. Using the Carlson's TSI approach, lakes are classified according to their trophic status (i.e. oligotrophic, mesotrophic, eutrophic, hypereutrophic, etc.).

The summer season average of the weekly summer Secchi disk transparency measurements is used to calculate the Carlson TSI_{SD} for the lake which is compared with the TSI_{TP} and TSI_{CHL} for the trophic status determination.

C3. Total phosphorus component:

In the CLMP, total phosphorus is sampled once just below the water surface (1-2 feet depth) in the spring and in late summer. Phosphorus is one of several essential nutrients that algae and rooted aquatic plants need to grow and reproduce. For most lakes in Michigan, phosphorus is the limiting factor for algae growth. The total amount of phosphorus in the water is used to predict the level of biological productivity and eutrophication in a lake. An increase in phosphorus over time is an indication of nutrient enrichment.

Phosphorus is found in lakes in several forms that are in a constant state of flux as environmental conditions change and plants and animals live, die, and decompose in the lake. Because the forms of phosphorus are continuously changing and recycling, it is convenient to measure all of the forms of phosphorus together as total phosphorus.

During spring overturn most Michigan lakes are well mixed from top to bottom. This is an opportune time to sample just the surface of the lake to obtain a representative sample for estimating the total amount of phosphorus in the lake and for determining whole lake nutrient changes or trends over time. At other times of the year, more extensive water column sampling is needed to determine phosphorus levels in the lake. A surface sample taken during late summer stratification is a representative sample of the upper water layer of the lake, the epilimnion.

The late summer phosphorus results are used to calculate the Carlson TSI_{TP} for the lake which is compared with the TSI_{SD} and TSI_{CHL} for the trophic status determination.

C4. Chlorophyll *a* component:

The relative amount of algae in a lake can be estimated by measuring the chlorophyll *a* concentration in the water. The amount of chlorophyll in an algal cell varies among algae species as well as with changing light conditions at different depths within the lake. Changing seasons also create different light conditions that, in turn, affects chlorophyll production. To account for some of this variability, algal chlorophyll is monitored during five mid-month sampling events over the summer season (May through September) using a water column composite sampling technique. Samples are field filtered by the volunteer and frozen until delivered to the MDEQ laboratory for analysis.

The median value of the summer chlorophyll monitoring results is used to calculate the Carlson TSI_{CHL} for the lake which is compared with the TSI_{SD} and TSI_{TP} for the trophic status determination.

C5. Dissolved oxygen and temperature component:

In the CLMP, dissolved oxygen and temperature are measured from the water surface to within three feet of the bottom in the deepest basin of the lake. Measurements are taken twice per month from early spring to late summer. Dissolved oxygen and temperature profiles are plotted for each sampling event.

Dissolved oxygen and temperature are two of the fundamental variables in lake ecology. Measuring these parameters together provides valuable information for assessing the condition of a lake. The amount of dissolved oxygen in the water is an important indicator of overall lake health. Water temperature serves as a driving force for many important lake processes. The temperature controls the length of the growing season in lakes, which influences the type and amount of biological activity.

During the summer growing season, most lakes with sufficient depth (greater than 30 feet) are thermally stratified forming distinct layers of differing temperature and density. These layers are referred to as the epilimnion (warm surface layer) and hypolimnion (cold bottom layer) separated by a metalimnion or thermocline (middle layer with decreasing temperature). The greatest changes in temperature occur at the thermocline.

Physical and chemical changes within these layers influence the cycling of nutrients and other elements within the lake system. Temperature also affects the level of dissolved oxygen in the water. As temperature increases, the amount of atmospheric oxygen that can be dissolved in water decreases. Dissolved oxygen levels also are influenced by the time of day and by oxygen requirements of bacteria and other aquatic organisms. Photosynthesis during the daylight hours increases dissolved oxygen levels in the lake while dissolved oxygen is consumed by respiration at night.

The bottom waters of many stratified lakes are susceptible to oxygen depletion, since atmospheric replenishment and photosynthetic production of oxygen are decreased at greater water depth and decomposition of organic matter in the bottom waters and sediment utilizes available oxygen. Low dissolved oxygen levels can result in the loss of susceptible organisms, such as trout and other cold water fish, and the plant nutrient phosphorus can be released from the sediments when dissolved oxygen is depleted in the bottom waters. Hypolimnetic dissolved oxygen decline during summer stratification is used as an early warning indicator of eutrophication in oligotrophic lakes.

C6. Aquatic plant identification and mapping component:

Rooted aquatic plants are a natural and essential part of the lake, just as grasses, shrubs and trees are a natural part of the land. Their roots are a fabric for holding sediments in place, reducing erosion and maintaining bottom stability. They provide habitat for fish, including structure for food organisms, nursery areas, foraging and predator avoidance. Waterfowl, shore birds and aquatic mammals use plants to forage on and within, and as nesting materials and cover. Though plants are important to the lake, nutrient enrichment and the spread of exotic species can cause overabundance of plants. Excessive plant populations can negatively affect fish populations, fishing and the recreational activities of property owners. In this situation, it is advantageous to manage the lake and its aquatic plants for the maximum benefit of all users. To be able to do this effectively it is necessary to know the plant species present in the lake and their relative abundance and location. A map of the lake showing the plant population locations and densities will greatly aid management projects.

Quantifying the aquatic plant populations of a lake is not an easy task. Additionally, sampling procedures used to collect aquatic plant data that can be statistically analyzed are complicated and time and cost intensive. Consequently, the CLMP is using qualitative techniques that allow volunteer monitors to generally assess the aquatic plants in their lake. This assessment may be viewed as a “snapshot” of the species of plants in the lake, their general location and relative abundance. Although not quantitative, this CLMP component provides valuable information about a lake’s aquatic plants that is often missing in many lake and aquatic plant management programs.

C7. Exotic plant watch component:

Exotic plants are a significant threat to the health of Michigan lakes. Species such as Eurasian milfoil, curly-leaf pondweed, European frog-bit, and hydrilla can quickly spread across a lake and impair human, fish, and wildlife use of the resource. However, exotic species can be managed effectively through early detection and rapid response.

This component trains volunteers how to recognize and effectively sample selected exotic plants. It is intended for lake communities that currently do not have exotic species or are managing existing populations and have them under good control. The program will have less value for lake communities that currently have exotic species covering large areas. However, it can help these lake communities identify new exotics that may invade the lake. Upon discovering exotic plants in a lake, the lake community has the option of pursuing outside assistance in proper control and eradication.

C8. Score the Shore component: Healthy shorelines are an important and valuable component of the lake ecosystem. The shoreline area is a transition zone between water and land, and is a very diverse environment that provides habitat for a great variety of fish, plants, birds, and other animals. A healthy shoreline area is also essential for maintaining water quality, slowing runoff, and limiting erosion. However, Michigan's inland lake shorelines are threatened. Extensive development, often combined with poor shoreline management practices, can reduce or eliminate natural shoreline habitat and replace it with lawn and artificial erosion control such as sea walls and rock. As a result, shoreline vegetation is dramatically altered, habitat is lost, and water quality declines.

The goal of this component of the program is to train volunteers on the procedures and then have them conduct an assessment of the quality of a lake's shoreline on three primary categories: Littoral Zone Characteristics, Riparian Zone Characteristics, and Shoreline Erosion Control Practices. Volunteers motor around the lake, scoring aspects of each of the characteristics on a data sheet per every 1000 foot shoreline section.

C9. How Results are Evaluated

Data collected in the CLMP are used to assess water quality/trophic status conditions, nutrient enrichment, and water quality changes and trends in lakes enrolled in the program. Volunteer collected CLMP data are evaluated with professionally collected side-by-side data, other quality control data and data from other state agency monitoring programs. These data are collectively utilized to assess the water quality status and update the trophic status classification of Michigan's inland lakes.

The Carlson TSI approach is used for updating trophic status classification of Michigan's inland lakes (Carlson 1977). The TSI equations for calculating the individual trophic state indicators are listed in Table 3.

Table 3. Carlson TSI Equations

$TSI_{SD} = 60 – 33.2 \log_{10}SD$	where, SD = Secchi depth transparency (m)
$TSI_{TP} = 4.2 + 33.2 \log_{10}TP$	TP = total phosphorus concentration (ug/l)
$TSI_{CHL} = 30.6 + 22.6 \log_{10}CHL$	CHL = chlorophyll *a* concentration (ug/l)

Individual TSI values are calculated for each trophic state indicator. An overall TSI is determined from the mean of the individual TSI values and the trophic status classification is determined based on the criteria listed in Table 4.

Table 4. Michigan Inland Lakes Trophic Status Classification Criteria

Trophic State	Carlson TSI	TP (ug/l)	SD-Trans. (ft)	SD-Trans. (m)	Chl-a (ug/l)
Oligotrophic	<38	<10	>15	>4.6	<2.2

Meotrophic	38-48	10-20	7.5-15	2.3-4.6	2.2-6
Eutrophic	48-61	20-50	3-7.5	0.9-2.3	6-22
Hypereutrophic	>61	>50	<3	<0.9	>22

A trend analysis is done for lakes that have eight or more years of Secchi disk transparency or total phosphorus data. A regression analysis is done and an apparent trend line fitted to the data. Figure 1 illustrates the annual mean transparency results over time with the apparent trend line for Corey Lake, St. Joseph Co. It should be noted that Corey Lake has been in the volunteer monitoring program continuously from the beginning in 1974 to the present and most of the measurements have been taken by the same volunteer over the this time span. This is a tremendous set of long-term data for this lake.

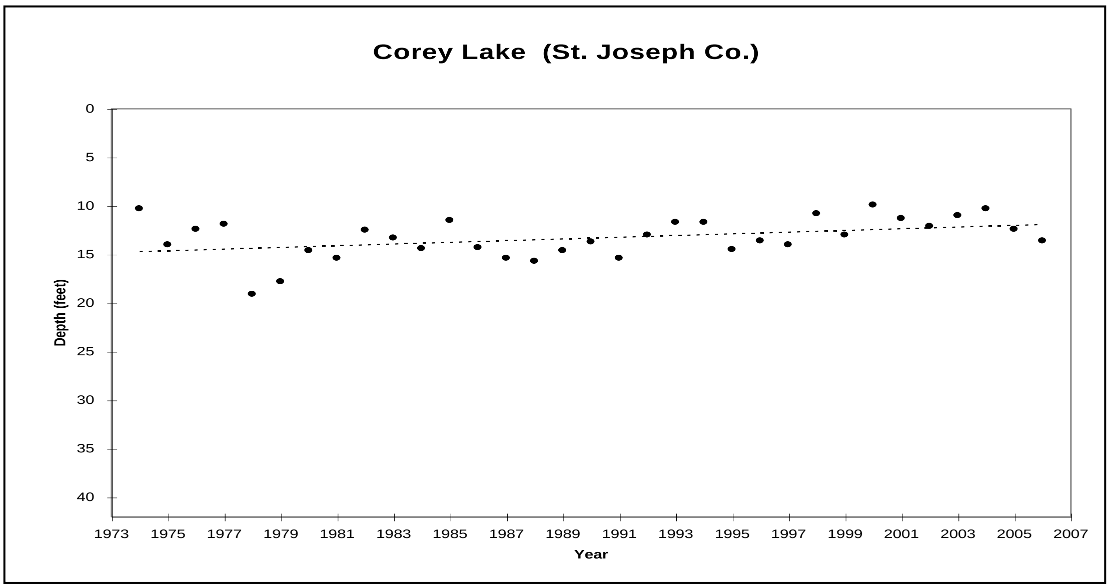

Figure 1. CLMP Annual Mean Transparency – Corey Lake, St. Joseph Co.

Figure 2 illustrates the spring total phosphorus concentration over time with the apparent trend line for Long Lake, Iosco Co. This is another lake with a long-term history of volunteer monitoring.

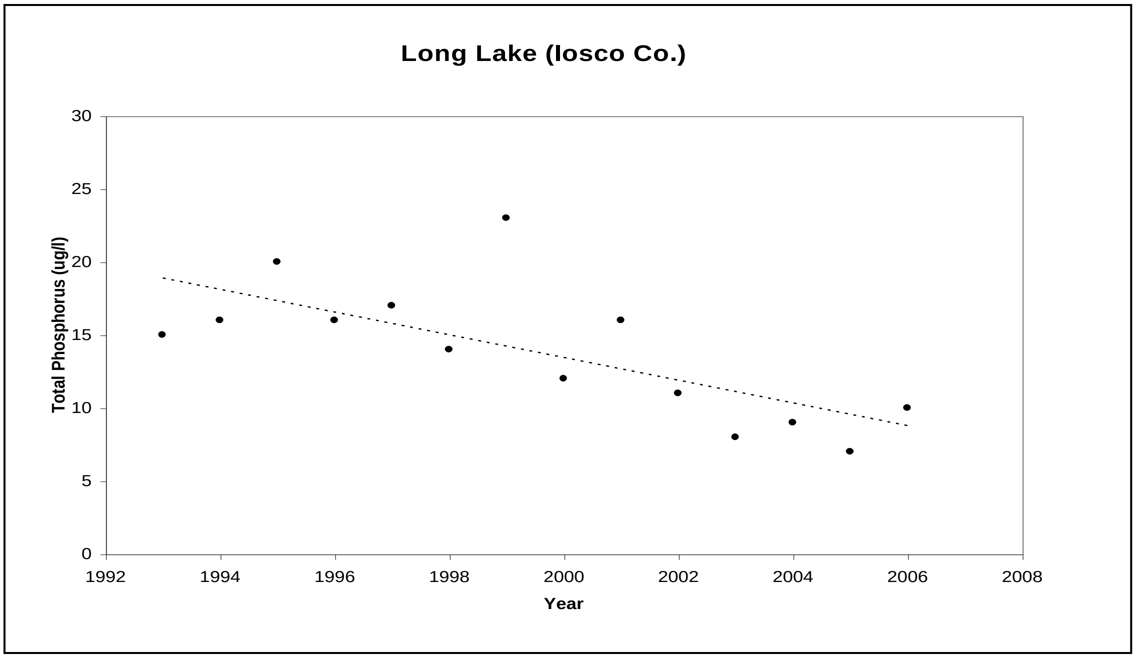

Figure 2. CLMP Annual Spring Total Phosphorus – Long Lake, Iosco Co.

These data are provided to the volunteer monitors to show apparent increasing, declining, or stable trends for these trophic state indicators in their lakes. The long-term data are tracked by the MDEQ to identify lakes that may need increased management activities. These data have also been evaluated to identify regional and state-wide trends (Bruhn and Soranno, 2005).

C10. Program Timetable

Table 5 is a general timetable for the CLMP. A complete and detailed monthly timetable is provided in Appendix 1.

Table 5. Monthly Work Task Within the CLMP Sampling Schedule

Date	Task
August	Review registration materials and revise as necessary
September	Distribute registration materials
Nov. – Dec.	Review sampling literature and revise as necessary; prepare equipment
Jan. – Mar.	Receive registration materials
March	Review training materials and revise as necessary
April	Give training, distribute sampling literature and equipment

April - Sept	Volunteer sampling, side-by-side sampling, laboratory analysis
October	Data recording
November-December	Data entry into the central database
January-February	Produce and distribute reports for each lake in the program
March	Produce a programmatic annual summary report.

D. Data Quality Objectives for Measured Parameters

D1. Precision, Accuracy, and Measurement Range

The precision, accuracy and measurement range for the CLMP parameters are listed in Table 6.

Table 6. CLMP Parameter Precision, Accuracy and Measurement Range

Matrix	Parameter	Precision	Accuracy	Measurement Range
Water	Secchi Disk Transparency	± 5%[a]	± 0.5 feet[a]	0.4 – 62 feet[b]
Water	Total Phosphorus (Spring)	± 14%[c]	± 11.5%[d]	<5 – 120 ug/l[b]
Water	Total Phosphorus (Late-Summer)	± 13%[c]	± 21%[d]	<5 – 470 ug/l[b]
Water	Chlorophyll *a*	± 25%[c]	± 33%[d]	<1 – 98 ug/l[b]
Water	Temperature	± 10%[a]	± 0.3 ^{o}C[e]	-5 – 45 ^{o}C[e]
Water (550A)	Dissolved Oxygen	± 10%[a]	± 0.3 mg/l[e]	0 – 20 mg/l[e]
Water (Pro20)	Dissolved Oxygen	± 10%[a]	± 0.3 mg/l[e]	0 – 50 mg/l[e]

a CLMP general observations
b CLMP data range
c CLMP volunteer replicate (QA/QC) data
d CLMP side-by-side (QA/QC) data
e YSI model 550A, Pro20 meters specifications

Secchi disk transparency, dissolved oxygen and temperature measurement precision are determined through field observations during side-by-side sampling events. Total phosphorus and chlorophyll *a* measurement precision are determined from annual volunteer replicate sample data based on a cumulative relative percent difference analysis.

Accuracy of the Secchi disk transparency measurements is determined through field observations during side-by-side sampling events. Accuracy of total phosphorus and chlorophyll *a* measurements are determined from annual side-by-side sampling data for these parameters based on a relative percent difference analysis. Accuracy of dissolved oxygen and temperature measurements are from manufacturer specifications for the YSI model 550A and Pro20 meters.

Measurement ranges for Secchi disk transparency, total phosphorus, and chlorophyll *a* are minimum and maximum values that have been measured in the CLMP. Measurement ranges for dissolved oxygen and temperature are from manufacturer specifications for the YSI model 550A and Pro20 meters.

D2. Completeness, Comparability, and Representativeness

The lakes that are sampled in the CLMP are based on volunteer enrollment. A program goal is 90% participation for those lakes enrolled. A follow-up telephone survey is conducted annually with the volunteers on the lakes that are enrolled in the various CLMP parameters but do not complete the sampling or sample turn-in requirements.

For all CLMP parameters, comparability is addressed by the use of standardized VOPs and analytical methods by the volunteers and the MDEQ Lab. Comparability of data within and among parameters is also facilitated by the implementation of QA\QC techniques and performance and acceptance criteria. For all measurements, reporting units and format are specified, incorporated into the field data recording forms, and documented in the MiCorps Data Exchange (MDE). Comparability is also addressed by providing results of QA/QC sample data, such as estimates of precision and bias; conducting methods comparison studies and side-by-side sampling, and conducting interlaboratory performance evaluation studies (see Quality Control Requirements, p. 23, for details.

For the CLMP, the primary sampling station is established at the deep basin of the lake and is intended to represent the open water of the lake as the location to evaluate the trophic status of the lake during the summer growing season and long-term trends in nutrient enrichment in the lake. The individual sampling components designed for each parameter attempt to address representativeness within the constraints of a volunteer monitoring program. Holding time requirements for analyses ensure analytical results are representative of conditions at the time of sampling. Use of replicate and side-by-side sampling provides estimates of precision and bias.

E. Training Requirements

Training for all CLMP projects is held in conjunction with the MLSA annual spring conference in April or early May. MDEQ and MiCorps staff conduct the training sessions. Participants in the Secchi disk transparency and spring and summer phosphorus components are not required to attend a training session. The detailed monitoring instructions and procedures serve as self training materials for these parameters. However, participants in these three components, particularly first time participants, are encouraged to attend the training sessions.

Volunteer training for all other parameters is required to receive monitoring supplies and participate in the advanced components. If volunteers are unable to attend the official annual training, the DEQ Contract Administrator, the Program Manager, or the Project Specialist may train the volunteer personally if circumstances allow this. Otherwise, the volunteers may receive training from a veteran CLMP volunteer with permission from the DEQ Contract Administrator, the Program Manager, and the Project Specialist. This permission is given based on the veteran volunteer’s amount of experience and proven track record of accuracy and is done on a case by case basis.

Starting in 2015, online webinars held by MiCorps staff can substitute for in-person training. The webinars may or may not be held each year, depending on demand.

Resource personnel are available throughout the summer sampling season to answer questions, and provide assistance with sample collection, handling, and species identification. In addition to training, volunteer samplers are provided detailed written monitoring procedures for each project in which they participate.

The effectiveness of volunteer training is assessed through the use of two types of evaluation surveys. The first, administered immediately after each training session at the MLSA annual spring conference, asks volunteer trainees to provide feedback on the clarity of training and suggestions for training improvement. A second evaluation survey is administered by program staff during side-by-side sampling visits, during which volunteer sampling performance is observed and deviations noted, and, following sampling, volunteers are given the opportunity to provide feedback on the sampling procedures, written instructions, training, and other program components. Program staff make use of the results of all evaluation surveys to improve program training, sampling procedures and instructions; and to address concerns specific to individual volunteers.

The exact training requirements for each component are detailed in the VOPs.

F. Documents and Records

The CLMP relies extensively on printed forms and documents to facilitate a number of important tasks. Print materials are provided to volunteers for registration, training, sample collection and sample handling and delivery. Other documents are used for data storage, report writing and to facilitate communication between MDEQ and MiCorps personnel. Each parameter includes detailed instructions, data recording forms and the contact information of MDEQ and MiCorps personnel.

Starting in 2015, the VOP procedures in the CLMP are not included in the QAPP. These procedures have been turned into their own standalone document called the CLMP Manual. All of the CLMPs documentation meant for the public- the application, the CLMP Manual, datasheets, fact sheets, quick references procedures- can be found in their most recent version at https://micorps.net/lake-monitoring/clmp-documents/.

The primary document used internally by CLMP staff is Appendix 1**.**

The retention longevity of forms and documents depends upon the purpose of the document. Administrative forms and letters, such as registration materials and waivers are retained three to five years. Data documents such as volunteer sampler field sheets and laboratory reporting forms are, as of this time, retained at the MDEQ central office indefinitely. These documents are still available from the early years of the former Self Help program.

Electronic data files are retained by the MDEQ Program Manager. The CLMP sample results are retained on the Laboratory Information Management System. The MDE files are retained on the MDE database. The database is housed on a MySQL database platform on a server at the Great Lakes Commission. The GLC backs up all of their server data daily, and retains back-ups for two weeks before overwriting. Records will be retained on the system as long as it remains in operation, and, by contract, would be turned over to the DEQ, should the GLC discontinue database maintenance.

G. Volunteer Operating Procedures (VOP)

(Sampling Design, Sampling Procedures, Sample Handling and Shipping)

The VOPs for each of the CLMP parameters are included in the CLMP Manual, https://micorps.net/lake-monitoring/clmp-documents/.

Each project's VOP includes a description of the utility of the parameter being sampled, sampling design, equipment and supplies used, sampling procedures, sample labeling instructions, sample handling and preservation, shipping requirements, training requirements, safety precautions and technical support contacts. The sampling methods requirements are summarized in Table 7.

Timing and Frequency of Collection:

Secchi Disk:

- Once a week through the summer.
- The first week is the full week that includes May 15th.
- The last week is the week that includes September 15th.
- These dates are listed in the Secchi data sheet every year.

Spring Phosphorus:

- Starting in 2015: Volunteers take water sample within 2 weeks of ice out as judged by themselves.
- Previously: DEQ would predict ice out dates for all counties and assign sampling date ranges.

Late Summer Phosphorus:

- There are five sample ranges and turn in dates based on County tier.
- The five tiers are determined by a north-south gradient and are listed on the late summer phosphorus schedule.
- The southern-most tier of counties turn in their sample the Tuesday of the last full week in September. The sample must be taken in a five day range with the final day of the range falling on the day before the turn in date. i.e. if the turn-in is September 29, the sample must be taken September 24-28.
- The next County tier, heading in a northern direction, turns their samples in on the Tuesday a week before the southern-most tier, and so on heading north through the tiers so the whole process takes 5 weeks.

Chlorophyll:

- One sample in each date range: May 10-20, June 10-20, July 10-20, August 10-20.
- The September sample falls in the same date range as the late summer phosphorus sample.

Dissolved Oxygen/Temperature

- Take every other week from mid-May through mid-September. No exact dates are prescribed.

Plants and Score the Shore

- Volunteers are asked to do the assessments mid to late summer, after full plant growth has been achieved.

Table 7. CLMP Sampling Methods Requirements					
Matrix	Parameter	Sampling Equipment	Sample Holding Container	Method Sample Preservation	Maximum Holding Time
water	transparency	Secchi disk	none	none	immediately
water	total phosphorus	sample holding container	screw top, polypropylene bottle (250 ml)	freeze sample post-delivery acidification	6 months frozen
water	chlorophyll *a*	composite sampler	wide-mouth amber polypropylene bottle (250 ml)	MgCO3, filter and freeze sample	4 months frozen
water	dissolved oxygen and temperature	YSI 550A, Pro20 meter	none, in-lake measurement	None	immediately
water and substrate	aquatic plants ID and mapping, exotic plant watch	plant rake	self-sealing plastic bags	dry in plant press & mount	indefinite
Water and land	Shoreline health (visual inspection only)	None	None	NA	NA

The volunteer sampling, sample handling, sample turn-in, and sample shipping schedules are designed to get the samples to the lab so they can be analyzed within the prescribed holding times for each parameter. If delays occur and holding times are exceeded, the data for these samples are coded and reported.

H. Laboratory and Analytical Methods

CLMP samples requiring laboratory chemical analysis (total phosphorus and chlorophyll *a*) are analyzed at the MDEQ state laboratory in Lansing.

In 2002 the CLMP late-summer total phosphorus samples were analyzed at an approved commercial laboratory due to sample capacity constraints at the MDEQ state laboratory. Results for these samples have been coded accordingly in the CLMP records.

The information collected in the CLMP's Aquatic Plant Identification and Mapping Project is tabulated and analyzed according to the procedures outlined in Chapter Five (Mapping Aquatic Plants in the Lake) of the book *A Citizen's Guide for the Identification, Mapping and Management of the Common Rooted Aquatic Plants of Michigan Lakes* (Wandell and Wolfson 2000). The data collected in the Aquatic Plant Mapping Project are qualitative. These data provide a general description of the lake's plant population, common species present and their relative abundance and location. The data products include a generalized map of the lake’s plant populations and a data sheet of the species found and their relative lake-wide abundance.

The lab uses several error codes commonly for phosphorus and chlorophyll. Below is the code and how it is handled in the CLMP reports, the MDE online database, and trend graphs.

Phosphorus: **W**. Value is less than the method detection limit (3 ug/l). The CLMP treats this results as a 3 for reporting and trends. It is listed as <=3 in reports.

Phosphorus: **T**. Value is less than the reporting limit (5 ug/l). The CLMP treats this results as a 4 for reporting and trends. It is listed as <5 in reports.

Chlorophyll: **ND or <.** Sample values is less than limit of quantification (1 ug/l). The CLMP treats this result as a 0.5 for median calculation in CLMP reports and trend graphs, but it is listed as <1 in reports.

I. Quality Control Requirements

Several types of quality control samples are collected in the field and performed in the laboratory in the CLMP. These quality control samples include:

> Field bottle/preservative blank – Preservative appropriate for the phosphorus/chlorophyll parameter are added to clean sample bottles. The samples are delivered to the laboratory and they are analyzed to check for bottle and preservative purity.
>
> Replicate field sample - Two samples collected at the same site, at the same time, using the same method, and independently analyzed in the same manner. These samples are used to determine the precision of the field sampling methods.
>
> Side-by-side field sample - DEQ staff sample or make observations side-by-side with volunteers at least 10 times per year, dividing the visits between Secchi Disk/Chlorophyll, Spring Phosphorus, Summer Phosphorus, and Dissolved Oxygen/Temperature. DEQ staff and volunteer collect samples or make observations at the same site and the same time. Volunteers use the VOP and the DEQ staff use agency Standard Operating Procedures (SOPs) (Appendix 2). Chemical samples are independently analyzed. Side-by-side sampling provide a check on the VOP and the reliability of the volunteer sampling.
>
> Mail-in field sample: Volunteers mail in voucher samples of plants that they have identified. CLMP biologists double-check the identification.
>
> Second independent reading - Biological samples requiring interpretation are analyzed by two professionals as a check on professional interpretation quality and analytical procedures.

Proficiency audit sample – Annually, samples are obtained from an independent quality control lab. The samples are prepared and analyzed according to the provided instructions. The results are then submitted to the source for evaluation. Participation in these studies is used as a means to independently monitor this method's performance and to compare its performance against that of the other participants.

These quality control samples are incorporated in the CLMP sampling components as outlined in Table 8.

Table 8. CLMP Quality Control Samples

QC Sample Type	**Secchi Disk**	**Spring Total Phosphorus**	**Summer Total Phosphorus**	**Chlorophyll**	**Dissolved Oxygen & Temperature**	**Aquatic Plant Mapping**	**Exotic Plant Watch**	**Score the Shore**
Field bottle/preservative blank	NA	1%	1%	NA	NA	NA	NA	NA
Replicate field sample	NA	10%	10%	10%	NA	NA	NA	NA
Side-by-side field sample	10 total visits divided between these parameters					NA	*	*
Mail-in field sample	NA	NA	NA	NA	NA	NA	10%	NA

* Not a required part of the program, but staff try to conduct several side-by-side visits a year on these parameters to make sure volunteers understanding the training and can produce similar results to staff.

The following actions are taken when a quality control sample reveals a sampling or analytical problem.

Field bottle/preservative blank - Bottles are checked for contamination and the preservative is exchanged at the laboratory for a new allotment.

Replicate field sample - The problem is discussed with the volunteer sampler to identify any possible abnormal environmental conditions or nonconformity with sampling procedures.

Side-by-side field sample - Volunteer sampling procedures and equipment are reviewed for comparability with state agency standard operating procedures.

Mail-in field sample – In case of plant misidentification by the volunteers, CLMP biologists will revise the volunteers final reports to reflect the corrected plant identification. This is done after communicating with the volunteers to ensure that this is the appropriate course of action (e.g. the voucher sample represents that plants they saw at all sites).

J. Equipment Testing, Inspection and Maintenance Requirements

At the beginning of each sampling season, the CLMP volunteers are directed to check their monitoring equipment for damaged or missing parts. An equipment checklist is included in the monitoring procedures for each parameter. Damaged or missing parts are replaced and the equipment is repaired prior to sampling.

For the total phosphorus components, new sample bottles are shipped to the volunteers prior to each sampling event. The sample bottles are capped at the laboratory supply facility prior to shipment. The volunteers are directed to request a replacement bottle should they receive an un-capped bottle.

A full sampling and filtering kit is provided at the annual training session to volunteers who are enrolled in the chlorophyll component for the first time. The full kit includes new equipment and supplies which are assembled and inspected by CLMP staff. A re-supply kit is provided to the volunteers who are continuing in the chlorophyll component. The re-supply kit includes replacement reagents and supplies for filtering and sample storage for each sampling event. Replacement parts for the sampling and filtering equipment are also available if needed.

For the dissolved oxygen and temperature component, the YSI Model 550A and Pro20 DO/temperature meters are checked and serviced each year prior to the monitoring season. Batteries and oxygen probe membrane caps and electrolyte solution are replaced for each meter. The meters are calibrated according to the manufacturer's specifications in the lab prior to distribution to the volunteers at the annual training session. The volunteers are instructed on meter calibration at the annual training session and the meters are re-calibrated by the volunteers prior to each use in the field. Should a meter fail to calibrate in the field, the volunteer is instructed to contract the CLMP program manager for the appropriate course of action. A replacement meter may be provided if necessary. At the end of the sampling season, the meters are returned and checked by the CLMP program manager prior to post-season storage. If a meter has been damaged or failed to function according to manufacturer's specifications it is returned to the manufacturer for repair. All pre- and post-season calibration and service records are kept by the CLMP program manager. Lake associations or volunteers who have purchased a YSI Model 550A or the Pro20 DO/temperature meters for individual lake use are instructed to follow the same pre- and post-season maintenance schedule as outlined for the CLMP program equipment.

K. Equipment Calibration

As described above, the YSI Model 550A, and Pro20 DO/temperature meters are calibrated, prior to each monitoring event, according to the manufacturer's specifications. Calibration results are recorded on the dissolved oxygen and temperature data forms which are returned to the CLMP program manager at the end of each monitoring season. Calibration procedures are contained in the VOP for the dissolved oxygen and temperature component.

L. Acceptance Requirements for Supplies

A number of supplies are required for the CLMP. A brief overview of the required supplies is listed here. For more detailed information, consult the individual parameter monitoring procedures in the CLMP Manual, http://www.micorps.net/documents/CLMP_Manual.pdf

The MDEQ laboratory provides all of the sample collection bottles and appropriate labels. MLSA staff assembles Secchi disks that may be purchased by the volunteer sampler. If the volunteer sampler chooses to build their own Secchi disk, instructions are provided. MDEQ and MiCorps staff assembles the chlorophyll *a* composite sampling equipment. The chlorophyll filter apparatus are purchased from a scientific supply company and given to volunteers during their training session. Volunteers assemble plant rakes according to detailed instructions in the monitoring procedures.

All supplies and equipment are inspected for problems and defects by MDEQ or MiCorps personnel before being given to the volunteer samplers. If any defects develop during sampling supplies and equipment are to be returned to MDEQ or MiCorps personnel for replacements. MDEQ and MiCorps personnel also inspect supplies and equipment being used by the volunteer samplers during side-by-side sampling.

Preservatives required for sample preparation, such as sulfuric acid (H_2SO_4), are provided by the MDEQ laboratory but are not handled by volunteers.

M. Outside Program Information Requirements

There are two special information requirements for the CLMP, hydrographic and topographic maps. Hydrographic maps are required to determine the deepest basin of the lake, which is the primary sampling location for several CLMP components. The maps are also useful in the aquatic plant mapping project. Individual lake hydrographic maps are available from Michigan Department of Natural Resources web-site (http://www.michigan.gov/dnr/0,1607,7-153-30301_31431_32340---,00.html). Additionally, Sportsman's Connections (http://www.sportsmansconnection.com/#top) offers books of hydrographic maps for Michigan counties. These maps are based upon work done by the MDNR's Institute for Fisheries Research over several decades. Maps are available for about 2000 Michigan lakes. If a map of the lake is not available the volunteer sampler must use a fathometer to locate the deepest spot in the lake.

Topographic maps are helpful to volunteers to obtain the altitude and, optionally, the latitude/longitude location of the lake to be sampled. These data are needed to calibrate the dissolved oxygen meter and identify the lake location. Topographic maps are available to the volunteers on the internet web-site http://www.topozone.com to look up and determine the altitude and location of their lake.

N. Data Management

For CLMP monitoring components that require sample handling and shipping to the MDEQ laboratory (spring and summer total phosphorus and chlorophyll *a*), a tracking log is maintained to maintain the chain of sample custody. The log records when sampling materials are delivered to the volunteer sampler, receipt of the samples into the MSUE processing office and delivery to the MDEQ laboratory and finally receipt of analytical results from the laboratory. The log allows for identification of missing samples as well as the tracking of samples to insure their analysis within required holding times.

Volunteer field sheets are used for all parameters. The field sheets are reviewed by the MDEQ program manager and MiCorps project specialists for completeness and discrepancies. If problems are identified on the field sheets the data may be 1) excluded from the program results if the problem is significant, 2) included in the results but the problem noted or 3) accepted. Table 9 provides a summary of data management actions when incomplete field sheets and improperly collected or handled samples.

Table 9. Data Management Actions for Completeness and Discrepancies

Parameter -condition	**Accept Data**	**Accept Data and Note Problem**	**Reject Data**
SD Transparency			
- sampling time	9 AM – 6 PM	+/- 1 hour outside sampling time	all other times
Total Phosphorus			
- sampling dates	5 day sampling window	+/- 1 week outside sampling window	all other dates
- sample bottle condition	normal condition	bottle over full – unable to stand up	bottle and/or cap cracked
- sample frozen	frozen	delivered un-frozen but collected within 4 hours of delivery	shipped un-frozen

		and frozen prior to shipping	
<u>Chlorophyll</u> - sampling dates - foil wrapped vials - sample frozen - replicate sample	 target sampling date +/- 5 days wrapped in foil frozen	 +/- 6 to 10 days from sampling dates delivered un-frozen but collected within 4 hours of delivery and frozen prior to shipping	 greater than +/- 10 days from sampling dates no foil or poorly wrapped shipped un-frozen not collected at same location as primary sample
<u>All parameters</u> - sampling location - other sampling event data (i.e. instrument calibration)	 deep primary station complete and within tolerances	 deep secondary station incomplete, but data within tolerances	 non-representative location – shoreline, inlet, outlet, or other incomplete, and data beyond tolerances

If samples or measurements are properly collected by the volunteer sampler but incomplete in terms of adequate numbers for the data summary calculations (i.e seasonal averages, medians, TSI values, etc.) the data are reported but the data summary calculations are not included in the annual report.

Laboratory reporting forms are reviewed by the MDEQ program manager and the MiCorps project specialists. Any unusual or highly variable data are questioned. Unusual high or low data values may be compared with other values reported in the sampling run for consistency. They may also be compared to historical or other data sources for the lake in question. If necessary the laboratory may be asked to rerun the samples if holding times have not been exceeded.

Data from the laboratory reporting forms (spring and summer total phosphorus, chlorophyll) and field sheets (all parameters) are entered in the MDE by the volunteers via the internet or MiCorps data management personnel. Each volunteer data collector can gain password-protected access to the data entry system via an internet interface at https://micorps.net. Data can be entered via electronic forms that mirror the field forms. Critical fields are fixed with minimum and maximum value limitations that will not allow unreasonable data to be entered and help eliminate data entry errors. MiCorps and MLSA staff enter the remaining data into the system using the same web interface. Data sheets with missing or problem data are flagged for verification by the database manager. Once data are entered into the system, MiCorps staff briefly review all records (as they come in) to verify that data entries are reasonable before considering the data “accepted.” Problematic data sheets are further reviewed and either rejected or flagged as “accepted, with comment”, and a comment describing the problem is entered. All data that are accepted (with or without comment) are then available for public review through the data view web interface.

Lab results for total phosphorus and chlorophyll *a* are submitted electronically from the DEQ Environmental Lab once or twice per year, as results are generated. The lab data are imported into the MDE after the metadata is completely entered. Lab records are manually matched with field records by comparing STORET codes (also known as Field ID number) and lake and county names.

From the MDE, results are tabulated for reporting in the annual report. Means, medians, ranges, and trophic state index values calculations and dissolved oxygen/temperature profile graphs are compiled using Excel spreadsheet data management format. Formulas are checked for accuracy and computations are spot checked to assure the formulas have been correctly applied and to minimize calculation or data handling errors. Once all data have been entered and reviewed for inclusion in the annual report, MiCorps staff randomly check the data entry for approximately 5-10% of the tabulated data for each parameter by comparing original field forms and lab analytical reports to the tabulated data.

O. Reports

2013 and earlier: An annual report is prepared each year for the CLMP that gives program summary information. The report is included on the MiCorps web-site. The report includes a general description of lake classification, eutrophication, measures of eutrophication and each water quality parameter monitored in the CLMP. Complete sampling results for Secchi disk, spring and summer total phosphorus and chlorophyll *a* are presented in tables. Representative sample results for dissolved oxygen/temperature and aquatic plant identification and mapping are included in the report. Summary results for each parameter are included in the report. In addition to the annual report, each lake that has been enrolled in the CLMP Secchi disk transparency, summer total phosphorus, and chlorophyll components for eight years or greater receives an apparent trend-line graph for that parameter. Reporting errors in the prior annual report are identified in the current report.

2014 and later: A data report is generated for each individual lake, giving trend graphs, results, and trophic status. A more general summary report is also produced, which gives program averages and a list of volunteers. All individual lake reports and the smaller annual report are available on the Micorps website.

P. Data Review, Validation and Verification Requirements

All CLMP field and laboratory data are reviewed by the MiCorps project specialists and the MDEQ program manager to determine if the data meet QAPP objectives. Decisions to reject or qualify data are made by the program manager and program specialists collaboratively after review and evaluation of the data.

Q. Data Validation and Verification Methods

The data are reviewed for outliers, unusual values, discrepancies between samples and replicates and discrepancies between volunteer collected data and MDEQ collected side-by-side data.

As noted previously, field collected data sheets are verified for acceptability during at least two points in the data review process. First, when the field sheets are entered into the data entry interface, the database is programmed to reject sheets with critical missing data or values exceeding criteria. Illegible or other problematic data sheets may be identified at this point. The data are further verified by the database manager after the sheets are entered into the system, but before they are made publicly available. Minor problems are noted in a comment field. All field forms remaining in the system are validated once the data entry error check is completed, and the error rate is below 5%. If any problems are identified the appropriate section of the table or the entire table is assessed and redone if necessary.

When problems are identified these data are compared with previously collected data to determine if they are within the target range of variability. If outside the target range of variability field sheets are reviewed to identify possible explanations. The volunteer sampler may be contacted to go over collection procedures, equipment performance, supplies used and unusual environmental conditions on the day of sampling. If necessary the sample may be rerun if still within holding times or the site may be re-sampled.

Replicate Sampling:

Each year a comparison is made of the volunteer collected samples and the replicates collected. Data from previous years to the current sampling event are plotted, graphed and assessed for agreement. Historically there has been a very high degree of agreement between the volunteer collected samples and replicates. Figure 3 illustrates the cumulative results for the replicate spring overturn total phosphorus samples since the quality assurance program was implemented in 1993. Figure 4 illustrates the cumulative results for the replicate late summer total phosphorus samples since this parameter was added to the CLMP in 1998. Figure 5 illustrates the cumulative results for the replicate summer chlorophyll *a* samples since this parameter was added to the CLMP in 1998.

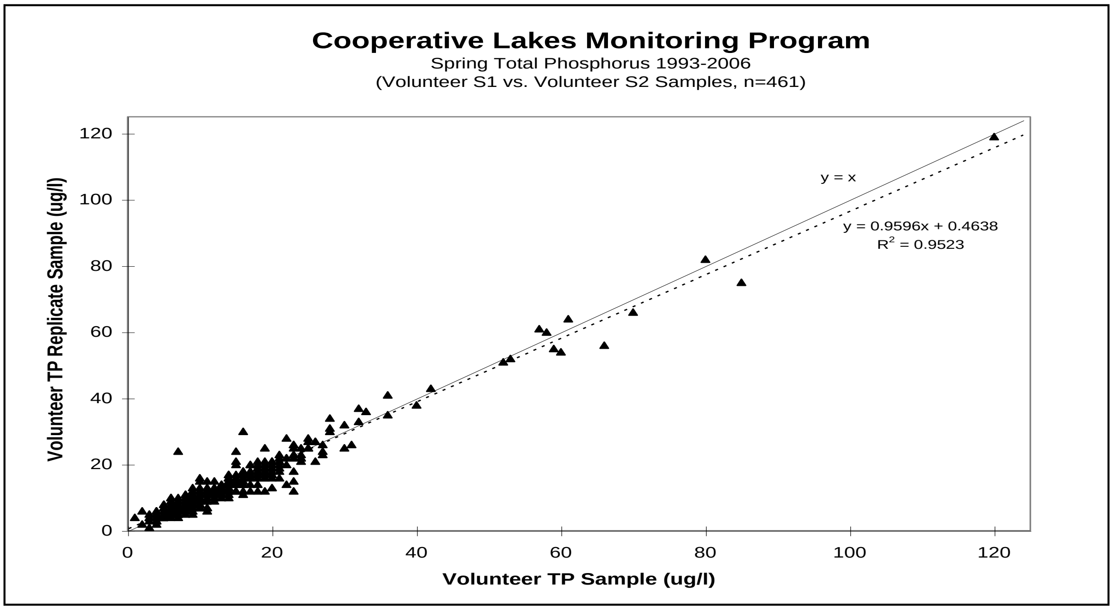

Figure 3. CLMP Spring Total Phosphorus Replicate Quality Assurance Samples.

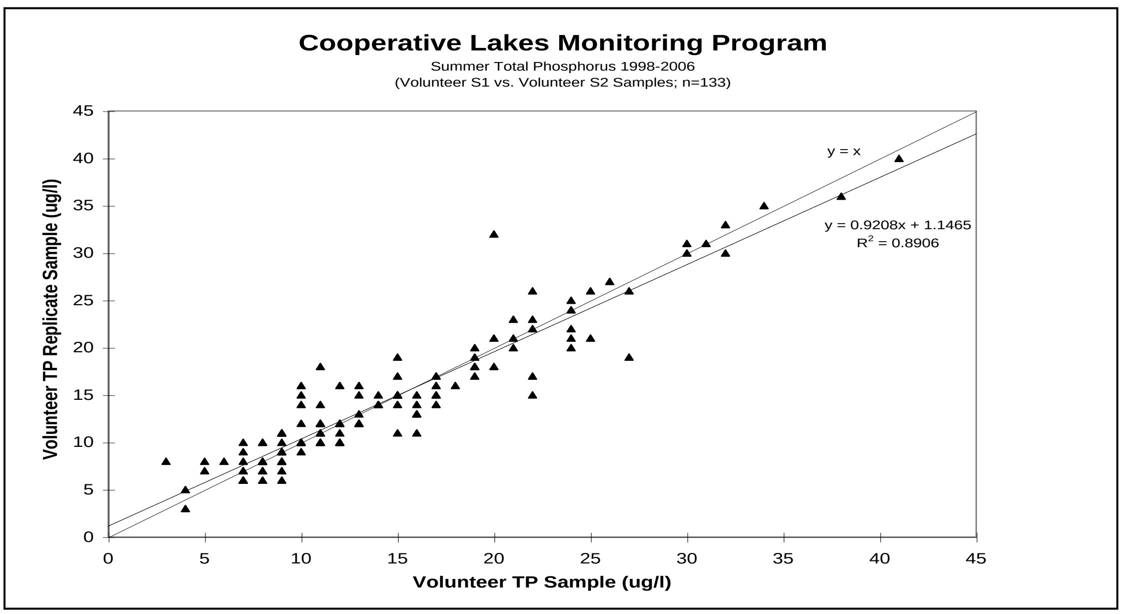

Figure 4. CLMP Late Summer Total Phosphorus Replicate Quality Assurance Samples.

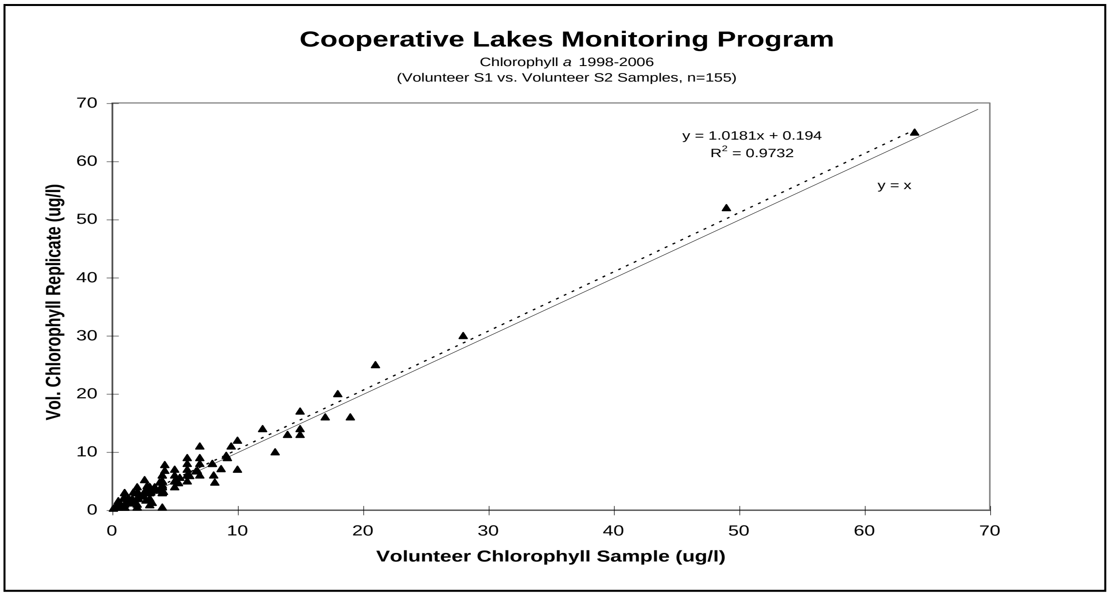

Figure 5. CLMP Summer Chlorophyll *a* Replicate Quality Assurance Samples.

The high correlation of agreement indicates that volunteer chlorophyll and phosphorus sampling are consistent.

Side-by-Side Sampling

In addition to the volunteer replicate agreement assessment, results of volunteer and professional sampling conducted side-by-side are compared annually. Data are plotted, graphed and assessed for agreement. Historically, there has been a high degree of agreement between results of the volunteer and professional side-by-side sampling efforts.

Phosphorus: DEQ samples yield slightly more phosphorus than volunteer samples, but there is no significant change in difference as phosphorus increases.

For Spring phosphorus (Figure 6), both the intercept and slope are close to an ideal distribution (intercept of 0, slope of 1.0). The intercept (1.3184 ug/L) is significantly different from 0, indicating that DEQ sampling methods result in slightly more phosphorus per sample. The slope (1.0293) is above 1.0, but not significantly different from the ideal 1.0, indicating little change in the DEQ-Volunteer relationship as phosphorus increases.

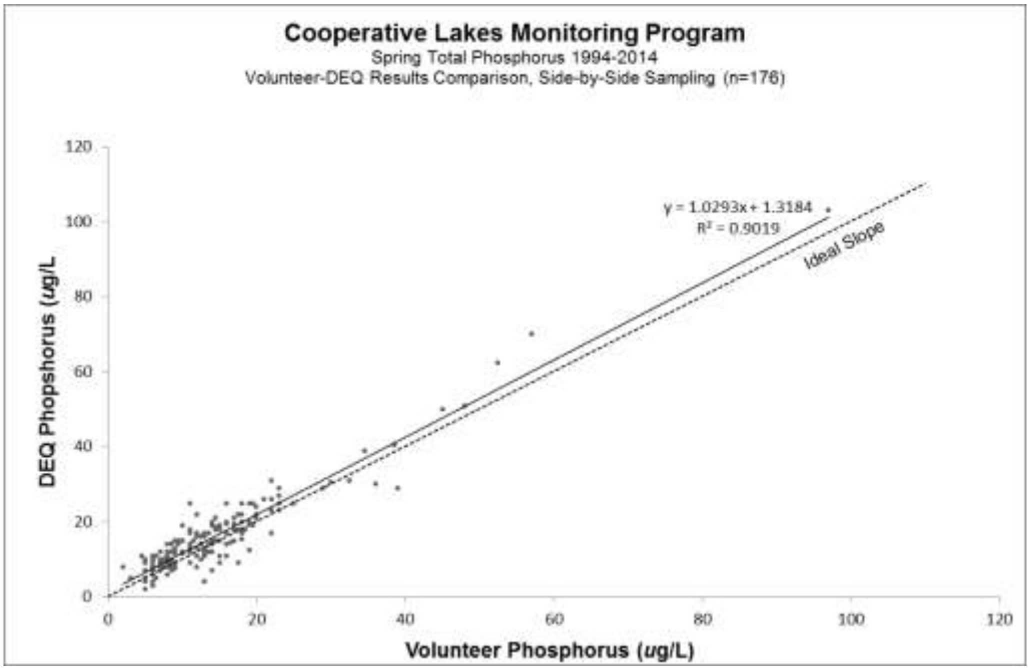

Figure 6. CLMP Spring Total Phosphorus Side-by-Side Quality Assurance Samples.

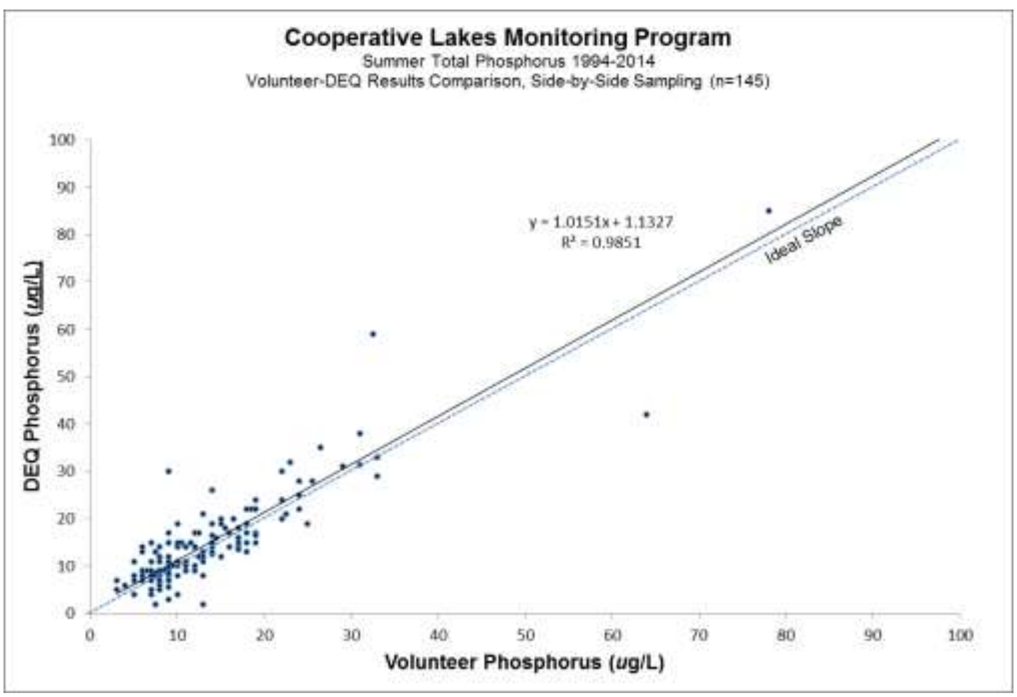

Figure 7. CLMP Late Summer Total Phosphorus Side-by-Side Quality Assurance Samples. Please note that a single very high summer phosphorus value (460-470 ug/l) was not depicted on the chart for illustration purposes, but was included in the analysis.

For Summer phosphorus (Figure 7), like Spring phosphorus, both the intercept and slope are close to, but slightly exceed, an ideal distribution (intercept of 0, slope of 1.0). The slope (1.0151) is slightly greater than the ideal 1.0, although the difference is not statistically significant. The intercept (1.1327 ug/L) is significantly different from 0,

The Spring and Summer phosphorus DEQ-Volunteer relationships are consistent. Slight but statistically significant higher DEQ intercepts, and slight but not significant slopes.

In lay terms, this means DEQ phosphorus values are consistently ~ 1 *u*g higher than volunteer values, and the relationship changes little as phosphorus increases.

The fractional but consistent exceedance of volunteer values by DEQ values likely results from the different preservation methods used by volunteers and DEQ. DEQ staff immediately preserve samples with sulfuric acid. However, sulfuric acid is not available to volunteers because of safety concerns.

Instead, volunteers preserve phosphorus samples by freezing, accomplished in home freezers upon return to shore after sampling. There may be a fractional loss of phosphorus from volunteer samples to sample container walls during the interval between sample collection and freezing.

Because of the lack of acidification, a small fraction of volunteer phosphorus may be lost to the sides of sample containers at each sample collection. This loss would not increase much with increasing phosphorus concentration if the available phosphorus binding sites were complexed by the initial fraction of phosphorus.

The side-by-side phosphorus comparisons indicate an acceptable degree of agreement between CLMP volunteer data and DEQ data.

Chlorophyll: Volunteer and DEQ results agree

For Chlorophyll (Figure 8), both the intercept and slope are close to an ideal distribution (intercept of 0, slope of 1.0). The intercept (0.4762 ug/L) is slightly above 0, but not significantly different from 0. The slope (1.0261) is slightly above 1.0, but not significantly different from the ideal 1.0.

The side-by-side chlorophyl comparisons indicate an acceptable degree of agreement between CLMP volunteer data and DEQ data.

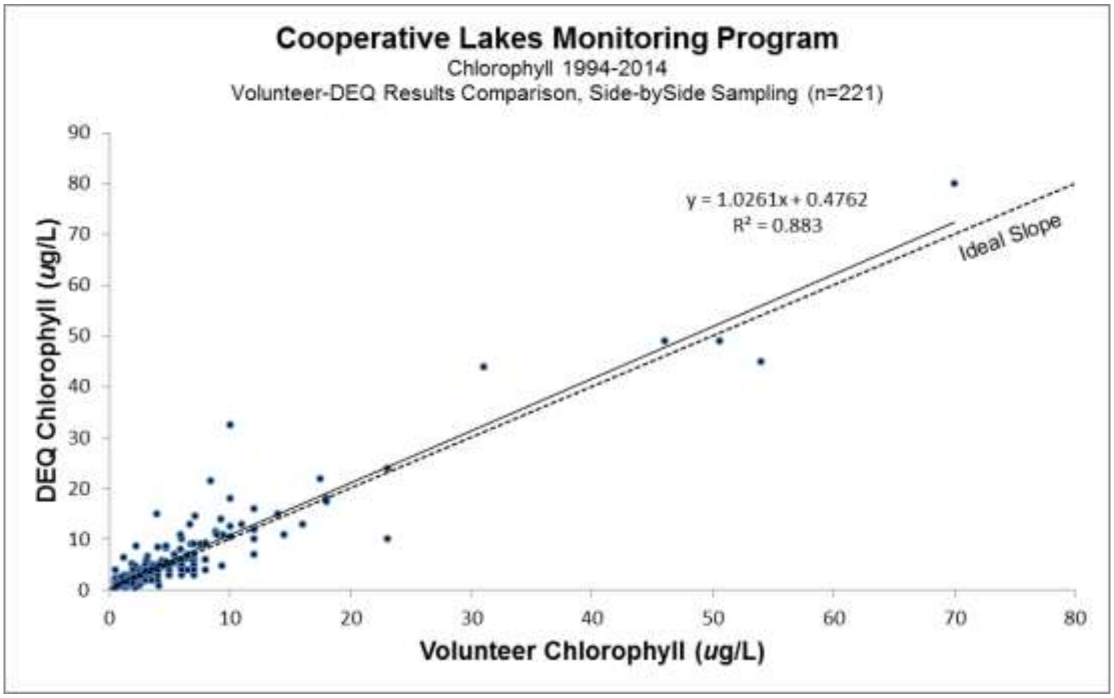

Figure 8. CLMP Chlorophyll *a* Side-by-Side Quality Assurance Samples.

R. Reconciliation with Data Quality Objectives

As soon as the data are reported from the laboratory for each CLMP parameter each year, the results are reviewed and evaluated both individually and collectively. The relative percent difference (RPD) is determined for the replicate and side-by-side data for the total phosphorus and chlorophyll parameters. An annual average RPD is calculated for each set of data and compared to the cumulative average RPD for each parameter. These data quality indicators are used to determine the precision and accuracy of the date as compared with the program specifications. If the data quality indicators do not meet the program specifications the data set will be evaluated and may be coded or discarded from the database. Individual data may also be coded if a problem was found in the sample collection, handling and shipping, processing, and laboratory analysis steps. The cause of failure will be evaluated and corrected. Any limitations on data use will be noted in the annual report and other documentation as needed. If failure to meet project specifications is found to be unrelated to equipment, methods, or sample error, specifications may be revised for the next sampling season and the QAPP will be updated.

S. References

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Appendix 1. CLMP Internal Planning Documents

Appendix 1a
Positions among CLMP Staff

COOPERATIVE LAKES MONITORING PROGRAM

Program Positions as of 2018

Position	Position Title	Position Affiliation	Currently held by
DEQ	DEQ Representative	MDEQ	Ms.Marcy Knoll Wilmes
MCA	MiCorps Contract Administrator	GLC	Ms. Laura Kaminski
MPM	MiCorps Program Manager	HRWC	Dr. Paul Steen
CA	CLMP Administrator	MLSA	Ms. Jean Roth/Mr. Scott Brown
CC	CLMP Consultant	MSU	Dr. Jo Latimore
DES	Data Exchange Specialist	GLC	Ms. Michelle Leduc Lapierre
LUS	Laboratory Unit Supervisor	MDEQ	Mr. Mark Knotterus
LSC	Laboratory Sample Coordinator	MDEQ	Ms. Melissa Smith

Appendix 1b.
Monthly Activities Plan

AUGUST

SAMPLING PERIOD - MONTH ONE

Position	Name	Responsibility
All	Paul leads	Review/comment on registration materials for this month's meeting
MCA	Laura	Update MiCorps/CLMP on-line enrollment site for upcoming year
MPM	Paul	Get updated registration postcard to Jean

SAMPLING PERIOD - MONTH 13

Position		Responsibility
CPA	Jean	Mail out bottles, labels and materials for summer total phosphorus.
CC	Jo	Begin to receive first summer total phosphorus samples and second round of chlorophyll samples (UP samples).
CC	Jo	Select late summer total phosphorus replicates and provide to Jo
DEQ	Marcy	Schedule late summer TP, chlorophyll, Secchi disk and oxygen side-by-side sampling events with volunteers
DEQ	Marcy	Schedule late summer total phosphorus and chlorophyll samples with DEQ lab
DEQ	Marcy	Email reminder to collection sites that samples will be coming in
DEQ	Marcy	Send insulated shipping containers and labels to UP District and Bay City offices for late summer samples
DEQ	Marcy	Notify District Offices that DO meters will be returned by volunteers at the end of season.
MPM	Paul	Electronically store spring total phosphorus data, create Excel spread sheet, post on MiCorps website

Appendix 1b.
Monthly Activities Plan

SEPTEMBER

SAMPLING PERIOD - MONTH TWO

Position	Name	Responsibility
MCA	Laura	Registration must be up by 9/30
CA	Jean	End of the month: Send out postcards about registration opening on October 1.

SAMPLING PERIOD - MONTH 14

Position	Name	Responsibility
CA	Jean	Telephone volunteers that signed up for but did not turn in samples
CC	Jo	Receive (5 weeks), preserve, process and turn in summer total phosphorus samples
CC	Jo	Receive (5 weeks), process and turn in chlorophyll samples
CC	Jo	Select late summer total phosphorus replicates
DEQ	Marcy	Side-by-side sampling for Secchi disk, total phosphorus, chlorophyll a, dissolved oxygen

Appendix 1b.
Monthly Activities Plan

OCTOBER

SAMPLING PERIOD - MONTH THREE

Position		Responsibility
CA	Scott/Jean	Produce quarter ending finanical and activity report
MPM	Paul	Promote CLMP on social media (annoucing registration open)

SAMPLING PERIOD - MONTH FIFTEEN

Position		Responsibility
DEQ	Marcy	Collect DO/temp. meters turned in to District offices
DEQ	Marcy	Collect DO meters from samplers
DEQ		Perform post-use maintenance on and store DO/Temp meters
CC	Jo	Forward any aquatic plant reports to DEQ
CC	Jo	Provide chlorophyll and phosphorus data forms to Jean by end of October, so Jean can enter information into MDE.
MPM	Paul	Quality check the DO/Temp data forms
MPM	Paul	Provide DO/Temp data forms to Jean by end of October, so Jean can enter information into MDE.

Appendix 1b.
Monthly Activities Plan

NOVEMBER

SAMPLING PERIOD - MONTH FOUR

Position	Name	Responsibility
	Jean/Every one	Save juice cans if you see them

SAMPLING PERIOD - MONTH 16

Position		Responsibility
CA	Jean	Enter all data, give data forms to Marcy, phone calls to DO/Temp participants who did not send in data forms
DEQ	Marcy	Obtain lab data and sent to Paul
CC	Jo	Drawing for free registrations
MPM	Paul	QAPP updates
MCA	Laura	Create certificate of participation, give to Jean.

Appendix 1b.
Monthly Activities Plan

DECEMBER

SAMPLING PERIOD - MONTH FIVE

Position	Name	Responsibility
CA	Jean	Prepare and make mailing of registration materials (paper application to lakes from the previous year who have not registered online
CA	Jean	Inventory supplies/parts for equipment building day & order what is necessary

SAMPLING PERIOD - MONTH 17

Position		Responsibility
MPM	Paul	Starts to create the individualized data reports for each lake
MPM	Paul	Update thank you letter that Jean sends to volunteers
CC	Jo	Prepare an aquatic plants mapping/exotic plant page for each lake; send to Paul
DEQ	Marcy	Contact side by side volunteers and share results with them

Appendix 1b.
Monthly Activities Plan

JANUARY

SAMPLING PERIOD - MONTH SIX

Position		Responsibility
All	All	Schedule date in February to build chlorophyll sampling equipment
All	All	Develop initial plan for the Annual Conference training session.
CA	Scott/Jean	Revise and produce announcement of program for MLSA website and riparian magazine
CA	Jean	Purchase materials for making Secchi disk and deliver to volunteer for production.
CA	Scott/Jean	Produce quarter ending finanical reports
CA	Jean	Print "MgCO3" and "WARNING" labels for chlorophyll sampling equipment building event
DEQ	Marcy	Order sampling supplies for dissolved oxygen, as needed (membranes, probe solution)(any new meters are ordered in March when enrollment is near complete)
DEQ	Marcy	Order MgCO3, bottles, H2SO4 for Jo and for DEQ side-by-sides, and CLMP-specific labels from Lab
MCA	Laura	Promote CLMP on social media

SAMPLING PERIOD - MONTH 18

Position		Responsibility
MPM	Paul	Finalize individualized data reports
CA	Jean	Print and mail thank you letters and certificates of participation
CA	Jean	Send individualized reports out through email and mail (mail version goes out with the thank you and certificate of participation)

Appendix 1b.
Monthly Activities Plan

FEBRUARY

SAMPLING PERIOD - MONTH SEVEN

Position		Responsibility
All	All	Equipment building day
All	All	Finalize plan for Annual Conference training session
MPM	Paul	Prepare and deliver to partners sampling schedule and sample turn in schedule for all parameters
MPM	Paul	Update all materials on clearinghouse for new sampling year
MPM	Paul	Put together training aids and demonstration equipment for the training. Need to inventory kits and get replacement parts during the equipment building day.
CA	Jean	Check status of account with UPS for shipping samples; Check UPS pick up schedule

SAMPLING PERIOD - MONTH 19

Position		Responsibility
MPM	Paul	Continues work on reports (goal should be end of February)

MARCH

SAMPLING PERIOD - MONTH EIGHT

Position	Name	Responsibility
DEQ & CC	Jo & Marcy	Jo gets acid preservative from Marcy
DEQ	Marcy	Organize and provide shipping containers and shipping labels to collection centers
DEQ	Marcy	Coordinate with laboratory (LUS) regarding incoming samples
DEQ	Marcy	Do pre-use maintenance on DO meters
DEQ	Marcy	Deliver updated water analysis lab sheets to Jo
DEQ	Marcy	Coordinate with collection centers Note to DEQ District Offices: DEQ MiCorps assistance staff changes? Courtesy note to DEQ Field Coordinator: program is continuing Subsequent note to DEQ MiCorps assistance staff: Sample collection-shipment dates; what to do, and updated UPS information
CA	Jean	Mail spring total phosphorus packets (3 weeks before sampling dates)
CA	Jean	Notify DEQ by March 10 of the number of spring total phosphorus lakes being sampled by district
CA	Jean	Create DO groups and leaders; put into a list to hand out at conference (with Marcy and Paul assisting as needed)
CA	Jean	Prepare packets/equip for Secchi disk, DO, chlorophyll (new) and resupply, aquatic plants and bring to conference
CA	Jean	Remind aquatic plant mapping participants that they must attend training session
CA	Jean	Provide DEQ with shipping labels for shipping containers for all District offices
MCA	Laura	Sends out last minute registration to listserv
MCA	Laura	CLMP documents updated on website

SAMPLING PERIOD - MONTH 19

Position		Responsibility
MPM	Paul	Finishes work on reports; works with everyone getting them distributed; Jean to print and mail, Laura to help on website uploads.
MPM	Paul	Update QA/QC replicate and side-by-side data charts.
MPM	Paul	Produce annual summary report.
MPM	Paul	All files go into clearinghouse and website as appropriate

Appendix 1b.
Monthly Activities Plan

APRIL

SAMPLING PERIOD - MONTH NINE

Position	Name	Responsibility
CA	Scott/Jean	Produce year ending financial and project reports.
All		Those giving presentations to update and get files to Paul
All		Conduct Annual Conference training session (April or May)
MPM	Paul	Upload training powerpoints to clearinghouse and website and announce it to conference registrants; also provide pdfs for printing and note taking

MAY

SAMPLING PERIOD - MONTH TEN

Position		Responsibility
CA	Jean	Calculate number of shipping labels needed for each group drop off location and obtain shipping labels.
CA	Jean	Send shipping labels for all sample collection sites to DEQ (Marcy) for late summer samples
CA	Jean	After conference, mail packets to those who did not attend conference.
DEQ	Marcy	Inventory Shipping Coolers
DEQ	Marcy	Supply insulated shipping containers and shipping labels for drop-off at collection centers
DEQ	Marcy	Confirm side-by-side selected lakes (date, where to meet, need for boat)

Appendix 1b.
Monthly Activities Plan

JUNE

SAMPLING PERIOD - MONTH 11

Position	Name	Responsibility
MPM	Paul	Reminder to volunteers to turn in Spring Samples through email or listserve
CA	Jean	Email out information and materials about the Great American Dip-in if available
CA	Jean	Parameter Lists showing who is registered (done for each parameter- Secchi, Summer T.P, DO, Chlorophyll, Exotic Plant, Full Plant)
CA	Jean	Put together list of & distribute to everyone
CA	Jean	Provide list of all volunteer names and email addresses to whole team (checks against MDE for quality assurance purposes, used for end of year annual report needed for various communications)
DEQ	Marcy	Supply Jean with bottles and labels for late summer TP packets
CC	Jo	Receive, preserve, process and turn in spring total phosphorus samples
CC	Jo	Process and turn in 1st batch of chlorophyll samples (see handling chl sample tab in this file).
MPM	Jo	Decide which samples will be duplicated (i.e. random 10% , lakes of concern)

Appendix 1b.
Monthly Activities Plan

JULY

SAMPLING PERIOD - MONTH 12

Position	Name	Responsibility
CA	Jean	Prepare summer phosphorus packets
CA	Scott/Jean	Produce quarter ending finanical and activity report
CC	Jo	Plan for side-by-sides for aquatic plant mapping projects.
DEQ	Marcy	Request spring TP results batch file from lab and give to Paul when it arrives

Handling Total Phosphorus Samples

Supplies Needed

- Space to set out bottles to thaw.
- Sulfuric acid preservative (from DEQ)
- Fine-tipped waterproof markers (Sharpies work pretty well, if label is dry.)
- Sharp/mechanical pencils (for completing lab forms)
- Extra labels
- Total Phosphorus enrollment log
- Towels for drying off bottle labels and hands
- Field ID# list
- Box opener/scissors
- Fan to speed thawing
- Blank Lab Forms

Receiving

1) Samples arrive via UPS 10:00-11:00 a.m. Wednesdays.
   - See spring and summer turn-in schedules.
2) Remove samples from mailing coolers to thaw.
3) Check samples against enrollment log
   a. Note any missing or extra samples.

Quality Control

1) Check for cracked bottles/caps.
2) Note any samples that were not frozen/cold upon arrival.
3) Check for missing replicates.
   a. If a replicate selected for analysis is missing, chose a different lake's replicate to analyze.
4) Check/correct field forms.
   a. Were they submitted?
   b. Is Field ID# included and correct?
   c. Is sample date included?
5) Check/correct bottle labels.
   a. Is label present?
   b. Is label legible?
   c. Is sample date included? Does it match the field form?
   d. Is Field ID# included? Correct? Match field form?
   e. Is location field complete (lake name)?
   f. Is Parameter Code (GA) included?
   g. Are replicates labeled as such ("REP")?

Sample Preservation

1) Discard replicate samples, except:
   a. Replicates identified for analysis (see log)
   b. Those where the original sample is bad (leaky, etc.)
2) Preserve remaining samples with 5 drops of sulfuric acid.
3) Add to label: Chemical Added (H_2SO_4) and PF#.
4) **If it is the first or last week of sampling,** create a bottle blank for processing:
   a. Add 5 drops of sulfuric acid to an empty bottle.
   b. Label as "Bottle Blank".
   c. Keep bottle upright.
   d. Add "Bottle Blank" to lab form (see below).

Appendix 1c.
Handling Total Phosphorus Samples

Lab Forms

1) Batch samples by DEQ District, to keep lab work orders reasonably sized.
   - Avoid batches with >5 pages (50 samples); break up as necessary.
2) Complete lab forms for each batch.
   a. Refer to past examples.
   b. Field ID: Include STORET#, lake name, and county (& "-REP" if a replicate).
      - Group samples with replicates to be analyzed at the beginning of the list.
   c. Fill in Sample Collected Date and Time (from field form).
   d. Comments: Form should already say "frozen date sampled, thawed & preserved."
      - add date thawed and preserved below that. Use " to repeat info for each sample.
   e. In bottom half of form, circle "GA", "Tot P", and the # of samples listed on the form.
   f. Print name/affiliation and sign.
   g. On back, include Preservative Tracking Number for GA/GG (H_2SO_4).
      - See preservative bottle.

Delivery to State Lab: 3350 N Martin L King Jr Blvd, Lansing, MI 48906

Deliver samples to lab by 3:00 pm; if necessary, hold preserved samples cool and dark until next day.
Carry Photo ID at all times.

Getting In

1) Tell gate attendant your affiliation and that you are delivering environmental samples.
2) Follow drive to Visitor Parking/Sample Receiving Parking.
   - Carts are available inside, if necessary.
3) Sign in with building security inside entrance, who will call for an escort once you are ready.
4) Escort will take you to the third floor.
5) Sign in with third floor receptionist.

Deliver samples to Sample Receiving Room.

1) Set out samples on tables in order listed on lab sheets.
2) Lab staff will check samples against lab forms.
3) Staff will provide receipt (lab form copies) to you.

Departure

1) Sign out with third floor receptionist.
2) Be escorted to ground floor.
3) Sign out with security by turning in nametag.

Follow-up

1) Deliver original field forms to DEQ Administrator (M. Wilmes)
2) Keep lab receipt forms for your records.
3) Contact volunteers to correct minor mistakes (call or email), including:
   a. Use of non-permanent ink on bottle labels.
   b. Field ID# errors.
4) Notify volunteers in writing of serious errors resulting in unprocessed samples, including:
   a. Sampling outside of approved sampling date interval.
   b. Sampled wrong site.
   c. Cracked bottle or cap.

Appendix 1d.
Procedures for Mailing Total P Packets

Procedures for mailing total phosphorus packets

1. Receive mailing envelopes from ML&SA
a. 11x15 envelopes for 2 bottles and 4 bottles
b. 15x20 envelopes for 6 bottles
2. Receive mailing labels from ML&SA
a. If possible labels should be grouped by DEQ district
3. Have excel log to keep track of mailing and receiving of samples. Get log from ML&SA.
4. Get bottles and bottle labels from DEQ
5. What goes into envelopes
a. Introduction letter from DEQ
b. A copy of the sampling procedures
c. Sampling schedule
d. Data form (one if two bottles, two if four bottles, three if six bottles).
e. Bottles - two for each lake to be sampled.
f. Bottle labels - one for each bottle plus one extra for a backup.
6. Create three sample packets (2 bottles, 4 bottles and 6 bottles) just as to be mailed.
7. Take sample packets to post office and determine the cost for mailing each packet.
a. Packets can vary in weigth slightly. If weight is close to next cost bracket use higher mailing cost.
8. Get stamps or money for stamps from ML&SA.
9. Mail packets two to three weeks in advance of the sampling date.
10. Make three mailing (UP and N. Lower, Central and Southern districts).
11. Before putting materials in envelopes put on necessary stamps, return address and mailing label.
12. Place materials in envelopes and seal.
13. Take packets to post office
14. At post office take sample packets to postal clerk and verify sufficiency of stamps.
15. Ask clerk what to do with the rest of the packets.
16. Fill in excel log for dates packets were mailed.

Handling Chlorophyll *a* Samples

Supplies Needed

- Space to lay out samples for sorting.
- Fine-tipped and regular waterproof markers (Sharpies work pretty well, if label is dry.)
- Sharp/mechanical pencils (for completing lab forms)
- Extra labels
- Chlorophyll enrollment log
- Towels for drying off foil, labels and hands
- Field ID# list
- Box opener/scissors
- Plenty of copies of DEQ Lab Form for turning in to lab (two-sided)
- Blank Lab Forms

Receiving

1) May, June samples are turned in mid-June with spring Total Phosphorus samples
   - See turn-in schedules for dates.
   - remote samples arrive by UPS on Wed a.m.
2) July, Aug. & Sept. samples are shipped with late summer Total Phosphorus samples.
   - See turn-in schedules for dates.
3) Check samples against enrollment log
   a. Note any missing or extra samples.

Quality Control

1) Note any samples that were not frozen/cold upon arrival.
2) Check/correct field forms
   a. Were they submitted?
   b. Mark as received on log
   c. Is Field ID# included and correct?
   d. Is sample date included & within sampling window (10th-20th of May-Aug, required Sept dates)?
      - Can give some leniency, especially if collected during SxS.
   e. Did they filter <50 cc? If so, note volume filtered on Lab Form (see below).
3) Are lake name and sample month on the foil the vials are wrapped in?
4) Are lake name, county, and Field ID# on the ziploc bags the samples are in?
5) Check for missing replicates.
   a. If a rep chosen for processing is missing, choose a new rep to run.
6) Check/correct vial labels if you have to unwrap foil.
   a. Is label present?
   b. Is label legible?
   c. Is sample date included? Does it match the field form?
   d. Is Field ID# included? Correct? Match field form?
   e. Is location field complete (lake name)?
   f. Is Parameter Code (CA) included?
   g. Is the Chemicals Added field complete ($MgCO_3$)?

Sample Turn-In

1) Turn in all replicates (may be wrapped in same piece of foil (preferred)).
   a. Only list on lab form those replicates you want analyzed (see below).
2) Keep samples frozen until turn-in.

Appendix 1e.
Handling Chlorophyll a Samples

Lab Forms

1) Batch samples by DEQ District, to keep lab work orders reasonably sized.
   - Avoid batches with >5 pages (50 samples); break up as necessary.
2) Complete lab forms for each batch.
   a. Refer to past examples.
   b. Field ID: Include STORET#, lake name, and county (& "-REP" if a replicate).
      - Group samples with replicates to be analyzed at the beginning of the list.
   c. Fill in Sample Collected Date and Time (from field form).
   d. Comments: Form should already say "field filtered and frozen date sampled"
      - Use " to repeat info for each sample, as appropriate
      - If <50 cc filtered, indicate volume filtered in Comments field.
   e. In bottom half of form, circle "CA Chlorophyll", and the # of samples listed on the form.
   f. Print name/affiliation and sign.
3) Back of lab form should already be pre-filled with "No" for every question.

Delivery to State Lab: 3350 N Martin L King Jr Blvd, Lansing, MI 48906

Deliver samples to lab by 3:00 pm; keep samples frozen until turn-in.
Carry Photo ID at all times.

Getting In

1) Tell gate attendant your affiliation and that you are delivering environmental samples.
2) Follow drive to Visitor Parking/Sample Receiving Parking.
   - Carts are available inside, if necessary.
3) Sign in with building security inside entrance, who will call for an escort once you are ready.
4) Escort will take you to the third floor.
5) Sign in with third floor receptionist.

Deliver samples to Sample Receiving Room.

1) Set out samples on tables in order listed on lab sheets.
2) Lab staff will check samples against lab forms.
3) Staff will provide receipt (lab form copies) to you.

Departure

1) Sign out with third floor receptionist.
2) Be escorted to ground floor.
3) Sign out with security by turning in nametag.

Follow-up

1) Deliver original field forms to DEQ Administrator (M. Wilmes)
2) Keep lab receipt forms for your records.
3) Contact volunteers to correct minor mistakes (call or email), including:
   a. Use of non-permanent ink labels.
   b. Field ID# errors.
   c. Replicates not provided.
4) Notify volunteers in writing of serious errors resulting in unprocessed samples, including:
   a. Sampling outside of approved sampling date interval.
   b. Sampled wrong site.
   c. Vials not wrapped in foil or otherwise kept dark.

Dissolved Oxygen Equipment Post-Season Calibration and Winter Storage

1. Collect DO meters from volunteers at end of monitoring season Options:
a. MiCorps manager may retrieve meter during late-season site visit with volunteer
b. volunteers may drop off meters at DEQ Headquarters in Lansing, DEQ District Offices (District staff bring to Lansing), or at MiCorps Conference
2. Conduct Post-Season Checks
a. Check for parts and visible damage.
b. Calibrate
c. If there are calibration problems, troubleshoot; arrange repairs as approvable if troubleshooting is unsuccessful
3. Process for winter storage.
a. Discard membrane cap.
b. Remove probe corrosion as needed according to manufacturer's manual
c. Rinse probe tip with tap water. Dry probe tip with tissue.
d. Screw probe guard on over probe tip.
e. Store probe dry without membrane cap
f. Repack DO/Temp. equipment in box.
g. Store on shelves in equipment cage at Filley Street Facility.

Appendix 2. MDEQ Field SOPs

STATE OF MICHIGAN
DEPARTMENT OF NATURAL RESOURCES

DNR

QUALITY ASSURANCE MANUAL FOR WATER SEDIMENT AND BIOLOGICAL SAMPLING 1994

Prepared By:
Surface Water Quality Division

PRINTED BY AUTHORITY OF THE FEDERAL CLEAN WATER ACT, P.L. 92-500, AS AMENDED
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MICHIGAN DEPARTMENT OF NATURAL RESOURCES DNR

storage and care instructions. Batteries should be replaced prior to spring turnover sampling each year and, if needed, prior to summer stratification sampling.

4.D.3.f. Alkalinity, Major Cations and Anions

Water column samples for alkalinity and major cations (Ca, Mg, Na, K) and anions (Cl, SO_4) are taken from the Kemmerer grab samples at surface, mid-water column, and three feet off the bottom depths during spring turnover sampling. These samples are kept in plastic 250 ml bottles and they should be preserved and handled in accordance with the procedures in Chapter 3 of this manual. Generally, alkalinity and the major cations and anions are only measured once per lake for background levels.

4.D.3.g. Nutrients

Water column samples for ortho and total phosphorus, nitrate/nitrite, ammonia, and Kjeldahl nitrogen are also taken from the Kemmerer grab samples at discrete depths for each lake. For spring turnover sampling, these samples are collected at the surface, mid-water column, and three feet off the bottom of the lake. For summer stratification sampling, these samples are taken at the surface and at three feet off the bottom of the lake as well as at the mid-thermocline depth. Nutrient samples are kept in plastic 250 ml bottles and they should be preserved and handled in accordance with the procedures in Chapter 3 of this manual.

4.D.3.h. Sediment Samples

Sediment samples should be collected by slowly lowering an Eckman dredge to the bottom being careful not to dissipate the sediment upon impact or flush it through the top of the dredge. Sediment should be skimmed off the top with a teflon spoon or scoop to obtain the most recently deposited material. For paleolimnological analyses, sediment cores should be taken, however for general sediment analyses, the surficial sediment layer is most representative of current lake conditions. When both inorganic and organic parameters are to be analyzed, a single sediment sample should be prepared, thoroughly mixed and then subsampled. This will insure that each sample is approximately the same percent of total solids. Both percent total solids and percent organics should be run on each sample to allow for inter sample comparisons.

4.D.3.i. Macrophytes Survey

A qualitative macrophyte survey is conducted for each lake during the summer sampling period to determine general aquatic plant distribution and density around the lake. For most lakes, 300 to 500 foot sections of the littoral zone along each orientation of the lake (usually four or more areas) are surveyed for macrophyte types and density. The back of the field data sheet is used to tally the species present and location as well as their density in general terms (i.e. found, sparse, moderate, dense, impaired use). A garden rake is used in shallow water and a weighted multi-tined grabbling hook sampler is used for deeper water to bring the aquatic plants to the surface for identification.

Use the following steps when measuring transparency.

-- Anchor the boat before measuring the transparency to ensure that the Secchi disc is observed straight down, instead of on an angle.

-- Attach a graduated line (one foot increments) to the disc.

-- Disc measurements should be obtained by lowering the disc into the water on the shaded side of the boat. The observer should lean over the side of the boat, directly over the disc as it is lowered. The depth at which the disc just disappears is noted. It is then raised slowly until it again becomes visible and that depth is noted. The point half-way between the two readings is the Secchi disc measurement. The disc should then be raised several feet and the procedure repeated and an average for the two values calculated. Round results to the nearest one-half foot (e.g., 6, 6½, 7, 7½ feet) and record on the field data sheet. If Secchi disc is visible at the bottom, note this on the field data sheet.

4.D.3.b. Chlorophyll a Samples

After the Secchi disc depth has been determined, measure out twice this length of rope and mark it with a clip or knot. This is the depth of the euphotic zone through which the depth integrated composite water sample for chlorophyll a will be collected.

Use the weighted sampling container with two tubes through the cap. The tubes provide escape of air and uniform entry of water while the container sinks and then is retrieved through the water column. See Figure 4.D.-3 for an example of a chlorophyll a sampler.

The sampling container should be rinsed with lake water at each site prior to collecting the sample. Lower the sampler to a depth of twice the transparency and then raise it to the surface. The sampler should be lowered and raised at a uniform speed such that the sampling container is slightly less than full as it reaches the surface. If the sampler is full, do not use it for the sample. Empty it and re-sample. The size of the opening in the sampler and/or speed of lowering and raising should be adjusted as necessary. The object of this procedure is to ensure that water is collected from the entire euphotic zone. Figure 4.D.-2 diagrams this procedure.

Extreme care must be taken not to contaminate the sample by resuspending the bottom sediments. Therefore for shallow lakes with depths less than twice the Secchi disc transparency, the sampling container should not be lowered to a depth closer than three feet from the bottom. Invery shallow lakes (ie. <10 feet) the sampling container may be carefully lowered closer to the bottom.

A subsample should be poured into a 250 ml brown bottle, preserved with one drop $MgCO_3$, and handled according to the procedures in Chapter 3, Sample Preservation and Handling.

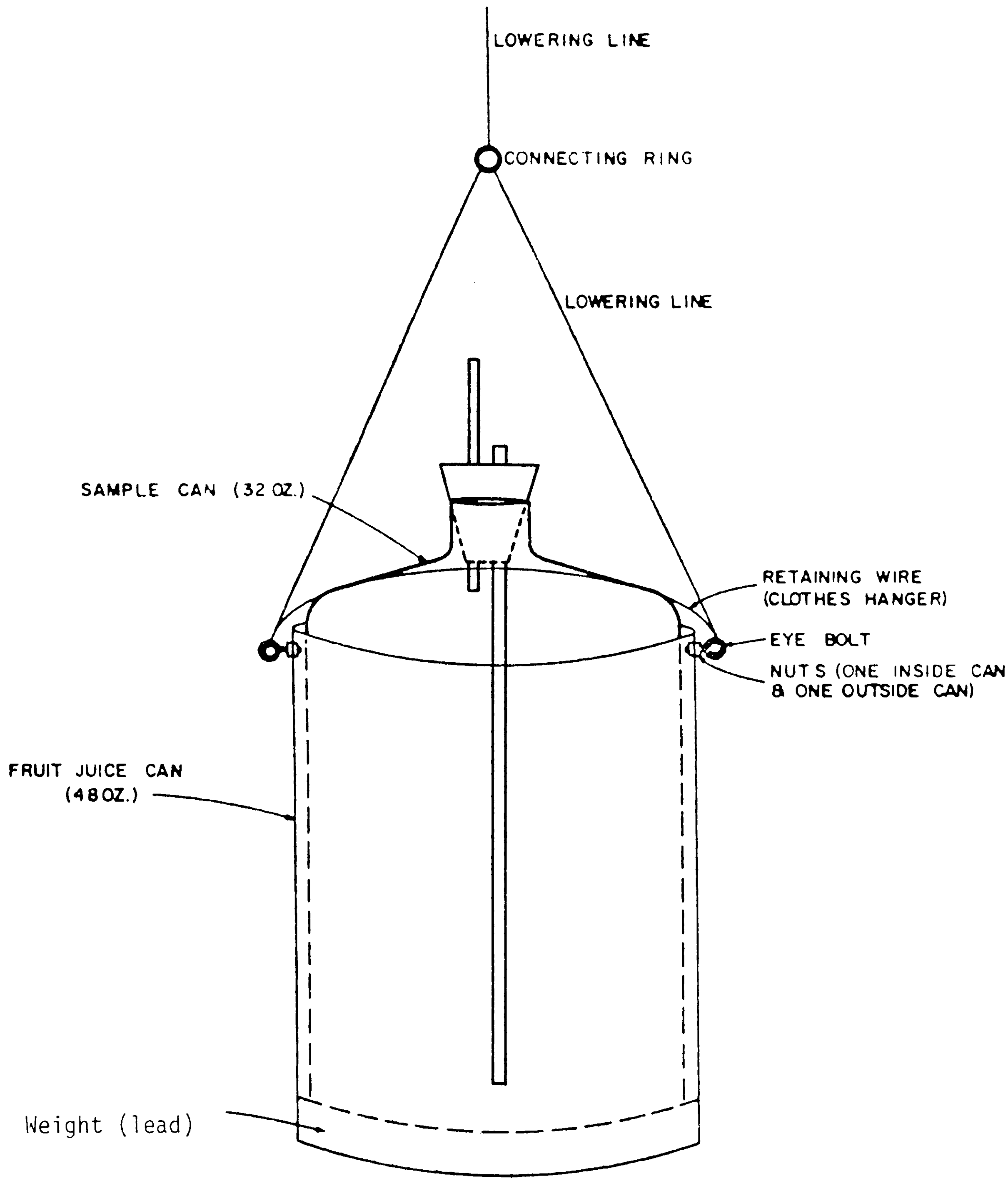


Figure 4.D.-3

Phytoplankton (Chlorophyll) Sampler Construction Plans

Chlorophyll a samples only have a 48 hour holding time prior to filtering. If these samples can not be delivered to the lab within this time period, they must be field filtered and stored in 90% acetone as per the following procedures:

-- The chlorophyll a field filtering apparatus consists of a Millipore vacuum pump, filter funnel, and flask.

-- Connect the vacuum end of the pump to the filter funnel with a high-pressure rubber hose and secure filter funnel to flask.

-- Place a 0.45 u membrane filter on suction pad and secure funnel cup.

-- Wet pad with chilled distilled water, turn on vacuum pump, and set vacuum to 12 to 15 in. Hg. Turn off vacuum pump.

-- Shake $MgCO_3$ preserved sample vigorously and pour a 50 ml aliquot into a graduated cylinder.

-- Pour the 50 ml aliquot into the funnel, wash sides of graduated cylinder with chilled distilled water into funnel, and turn on vacuum pump.

-- When all of the sample has filtered through, wash sides of filter cup with chilled distilled water and allow all water to filter through. Turn off vacuum pump.

-- Remove the filter cup, then carefully remove the membrane filter from filter pad using forceps.

-- Fold membrane filter into quarters and place in fluted test tube.

-- Dispense 10 ml of 90% acetone into test tube and cap with cork stopper. The membrane filter should dissolve in the acetone.

-- Label test tube and cork stopper with lake name and date, mark a line on outside of test tube at level of acetone, and seal cork stopper with parafilm wrap.

-- Store test tubes in dark container on ice in ice chest.

4.D.3.c. Temperature and Conductivity

Lake water column profiles of temperature and conductivity are measured using a YSI model 3000 T-L-C meter. Generally, these parameters are measured at ten equally spaced depth intervals between the surface and within three feet of the bottom. If the lake basin is less than 50 feet deep, sample every 5 feet. For lakes designated as coldwater fishery lakes by the DNR, additional measurements should be taken at 2 1/2 foot intervals through the thermocline. Record all measurements on the field data sheet.

The T-L-C meter should be calibrated before and after each

CHAPTER 3

SAMPLE PRESERVATION AND HANDLING

Prepared by
State of Michigan
Department of Natural Resources
September, 1994

CHAPTER 3. SAMPLE PRESERVATION AND HANDLING

3.A INTRODUCTION

Analysis of all samples immediately after collection at the sampling site would be ideal from the standpoint of holding time. However, this is generally impractical and only occurs when immediate analysis is an absolute necessity. As an alternative, special sample preservation and handling techniques are used in an attempt to stabilize the constituents of interest until analyses can be practically performed.

Complete stabilization of every sample constituent is impossible to achieve. Preservation techniques are generally used to retard chemical, biological, or physical changes in a sample. Sample containers, preservation, handling, and holding times must be strictly controlled to maintain sample integrity.

3.B METHODS OF PRESERVATION

Preservation methods are generally limited to temperature control, pH control and chemical addition. These techniques are used to retard biological actions, slow hydrolysis of chemical complexes, and reduce the volatility of constituents.

3.B.1. TEMPERATURE CONTROL

Refrigeration or icing of samples is a common preservation technique used for many constituents. Refrigeration generally does not cause changes which will result in interference's with most analytical methods. Sample refrigeration is often the preferred preservation technique if it does stabilize the constituents of interest. Icing of samples is practical for most field work.

Freezing of water samples may be an effective long term preservation technique for some applications, but it is generally not recommended. Freezing and thawing of samples may cause changes in some sample components, particularly various residues. Freezing of fish tissue and other biological samples is often recommended, and becomes a necessity if analysis is delayed substantially.

3.B.2. pH CONTROL AND CHEMICAL ADDITION

pH control is often used to affect the solubility of a constituent or retard biological action. For example, nitric acid is added to samples to maintain metal ions in a dissolved state.

Other chemicals may be required for proper preservation of other constituents. For example, sulfide is readily oxidizable under aerobic conditions. Zinc acetate is added to cause precipitation of sulfide as zinc sulfide, which is relatively inactive.

Some precautions must be considered when chemicals are added to samples.

-- Chemical preservatives are generally intended for <u>water</u> samples. Violent reactions can occur if certain chemicals are added to some wastes. For example, acid preservation of a highly caustic (basic) sample could result in violent spattering and considerable heat generation. KNOW AS MUCH ABOUT YOUR SAMPLE SOURCE AS POSSIBLE AND USE COMMON SENSE. Proper safety precautions should be used as the situation dictates (i.e., safety glasses, goggles, face shield, apron, gloves, etc.). The laboratory should also be warned of potential problems.

-- Chemical preservatives should be used in the recommended dosage. If a little preservative is good, a lot is not necessarily better. An ideal chemical preservative should have no detrimental effects on any subsequent chemical analysis. However, this is not always the case. Many chemical reactions are particularly pH dependent. Samples with excess amounts of chemicals added may produce erroneous results.

-- Some recommended preservatives may also be required for the subsequent analysis to proceed properly. For example, the sulfuric acid preservation for total organic carbon is used to inhibit degradation. But it is also necessary to convert inorganic carbon present (carbonates and bicarbonates) to carbon dioxide, which is removed later. Lack of adequate acid preservation results in erroneously high results.

-- Chemical preservatives must be free from contaminants which will affect the validity of results. Only preservatives supplied and verified by the Environmental Laboratory should be used. It is the responsibility of field personnel to maintain the integrity of the chemicals in an assigned field preservative kit. If it is suspected that preservatives may have become contaminated, they should be returned to the laboratory and replaced. The laboratory can verify contamination if requested. All kits should be replenished periodically, with six months being the maximum time between replacements. Use of field blanks is discussed in Chapter 5, Field Quality Control Procedures.

3.B.2.a. Dechlorination of Samples

Chlorinated samples must be immediately dechlorinated upon collection to prevent possible oxidation of some compounds or other chemical reactions which may invalidate subsequent analyses. The best procedure is to measure the residual chlorine content of a sample and then add a slight excess of the appropriate dechlorinating agent. Large excesses of dechlorinating agents may result in additional analytical problems. If there is some doubt as to whether a sample is fully dechlorinated, the sample can be rechecked for residual chlorine after addition and mixing of the dechlorinating agent.

3.B.2.a.1. Cyanide and Thiocyanate Samples

Chlorine and other oxidizing agents decompose most of the cyanides and convert Thiocyanate to toxic cyanogen chloride. The "free" cyanide test (cyanides amenable to chlorination) is actually a quantification of the cyanides which are destroyed by chlorination. After the amount of residual chlorine has been measured, dechlorinate with 0.6 g/l ascorbic acid before preservation with sodium hydroxide to pH greater than 12.

3.B.2.a.2. Phenolics Samples

Phenolic compounds will be partially oxidized if chlorine and other oxidizing agents are not removed immediately after sample collection. After the amount of residual chlorine has been determined, dechlorination with ferrous ammonium sulfate (FAS) should occur before preservation with sulfuric acid to pH less than 2. On unchlorinated samples, the total recoverable phenolics analysis will be taken from the same sample container (GA bottle) as chemical oxygen demand (COD) and total organic carbon (TOC). A separate container for phenols is required for a dechlorinated sample (GP code) because the dechlorinating agent could invalidate COD and TOC results. One drop (0.05 ml) of 0.141 N $Fe(NH_4)_2(SO_4)_2$ for each 250 ml sample will destroy 1 mg/l residual chlorine.

3.B.2.a.3. Organic samples

Because chlorine may oxidize some organic compounds, samples for acid extractables, base-neutral extractables, and purgeable organics should be dechlorinated with sodium thiosulfate upon collection. While $Na_2S_2O_3$ does not interfere with most organic analyses, a large excess should be avoided. One drop (0.05 ml) of 0.141 N $Na_2S_2O_3$ will destroy 1 mg/l residual chlorine in a 250 ml sample and 6 mg/l residual chlorine in a 40 ml sample.

3.B.3. PRESERVATION GUIDELINES

The preservation techniques recommended by the Environmental Laboratory are listed in Table 3.B.-1, "Collection and Preservation of Water, Sediment, Tissue, and Waste Samples". Most of these are in accordance with EPA recommended procedures specified for NPDES samples (Table II, Guidelines Establishing Test Procedures for Analysis of Pollutants Under the Clean Water Act, 40 CFR Part 136). A present discrepancy with the existing guidelines includes:

-- Dissolved metals, orthophosphate, and other dissolved constituents should be membrane filtered immediately after collection in the field. Because this is not always practical and can cause sample contamination if all necessary precautions are not taken, the lab will filter samples for dissolved constituents, however the sample to be filtered in the lab should be delivered to the lab within 24 hours and the filtration should take place at the lab immediately.

3.C. CONTAINERS

Sample containers and caps are supplied by the Environmental Laboratory. Only these containers are to be used for sample containment and transfer. Sample containers are recommended based upon the following factors:

- lack of interference with constituents to be analyzed,
- cost,
- ability to be cleaned or sterilized,
- durability,
- availability,
- size, and
- weight.

As a general rule, glass containers are used for pesticides, oil and grease, other organics, and dissolved oxygen samples. Disposable plastic containers are used for most inorganic constituents, because of the time and cost involved in properly cleaning containers for reuse. The laboratory periodically checks containers for contamination. Proper use of field blanks also serves as a routine check on sample container contamination.

The construction of the cap and cap liner must be carefully considered also. Polyethylene caps are generally used unless the container requires a tight seal or organics are to be used. Then a bakelite cap with an appropriate liner is used. Liner material is generally either wax coated paper (do not use with organics), aluminum foil (may contaminate sample with some metals), or Teflon (inert but expensive). Because bakelite caps are made from a phenolic resin, special precautions must be followed if phenolics are to be analyzed.

Container construction must be considered for special samples. Wide mouth containers are necessary for solid or semi-solid samples. Volatile hydrocarbon samples must be collected in a tightly sealed bottle to prevent loss of the constituents.

The sample containers that the Environmental Laboratory presently recommends and supplies are listed in Table 3.B.-1.

3.C.1. SAMPLE BOTTLE LABELING AND CODES

A Department of Natural Resources label and Law Enforcement Division Criminal Enforcement Label have been developed for labeling sample containers. The DNR label is white (Figure 3.C.-1) and is used for all routine sampling. The Law Enforcement Division uses a green label for all criminal investigations (Figure 3.C.-2). When the green labels are used, they must bear an investigation number assigned by the Law Enforcement Division. The use of sample bottle codes is recommended. All bottle codes are to be clearly marked in the designated area of the sample bottle label. The codes are used by field and laboratory personnel for identification and sorting of sample containers. They indirectly indicate if chemical preservation should have been added to a sample. The sample bottle codes are listed in Table 3.B.-1.

Each batch of samples gets a unique log number and the samples in the batch are assigned sample numbers sequentially by the lab computer.

3.D. HOLDING TIMES

The holding time for a sample is the time delay between when the sample is collected and when it reaches a critical stage in the analytical procedure. For example, many organic compounds have two holding times. One is from collection to the extraction step and the other is from the extraction step to quantification. For time composite samples, the holding time clock is started after sample compositing is completed. However, proper preservation must be followed during compositing if possible.

Each analytical constituent has a recommended maximum holding time. Depending upon its stability, the holding times range from immediate analysis (temperature) to 6 months (most trace metals). The holding times that the Environmental Laboratory presently follows are included in Table 3.B.-1. These generally follow the guidelines established by the EPA for NPDES compliance monitoring. Variance from these holding times require special studies and approval. Although it is impossible to state exactly how much time may elapse on a particular sample before it changes significantly, studies have shown the recommended holding time to be suitable for many environmental water samples.

It is a good practice to deliver the samples to the lab as early as possible. Field staff should as a goal plan their work so that samples will be recieved by the lab within 48 hours of collection. Except samples with 2 day holding times and samples needing lab filtration must be brought in within 24 hours and samples needing filtration should be filtered immediately.

Table 3.B-1 COLLECTION AND PRESERVATION OF WATER, TISSUE AND SEDIMENT SAMPLES

BOTTLE CODE	PARAMETER GROUP	NOTES	BOTTLE TYPE	SIZE/COMMENTS	COOL TO 4 C° X = YES	PRESERVATIVE	AMOUNT	MAXIMUM HOLDING TIME
GENERAL CHEMISTRY								
O	DISSOLVED OXYGEN	1	GLASS	250 ML GLASS STOPPER	X	FIX ON SITE (WINKLER)		8 HR
GN	GEN CHM/NEUTRAL	2,3	PLASTIC	500 ML	X			2 DA, 7 DA, 28 DA
GA	GEN CHM/ACIDIC	3,4	PLASTIC	500 ML	X	H_2SO_4 TO pH < 2	10 DROPS/ 500 ML	28 DA
GG	GEN CHM/PHENOLICS	5	GLASS	250 ML SCREW CAP	X	H_2SO_4 TO pH<2	5 DROPS/ 250 ML	28 DA
GB	GEN CHM/BASIC	3,6,7,8	PLASTIC	250 ML OR 500 ML	X	10N NaOH TO pH=12	10 DROPS/ 250 ML	14 DA (24 HR)6
S	SULFIDE	1	PLASTIC	250 ML	X	1N ZnAC, 10N NaOH TO pH>9	10 DROPS 1 DROP/ 250 ML	7 DA
CA	CHLOROPHYLL A	9	PLASTIC	250 ML	X OR FREEZE	1% $MgCO_3$	5 DROPS/ 250 ML	2 DA
HW	FLASH POINT		GLASS	250 ML	X			
GS	GEN CHM/SEDIMENT	16	GLASS	250 ML W.M.	X			
INORGANIC								
MA	METALS/TOTAL ACIDIC	10	PLASTIC	500 ML		1:1 HNO_3 TO pH<2	5 ML/ 500 ML	28 DA, 6 MO
MAD	METALS/ACIDIC FIELD DISSOLVED	10,11	PLASTIC	500 ML		FILTER ON SITE THEN ADD 1:1 HNO_3 TO pH<2	5 ML/ 500ML	28 DA, 6 MO
MD	METALS/LAB DISSOLVED	11	PLASTIC	500 ML	X	LAB FILT. & PRES.		W/IN 24 HRS.
MN	MINERAL/NEUTRAL	12	PLASTIC	500 ML	X			W/IN 24 HRS, 2 DA, 14 DA, 28 DA
MB	METALS/MINERALS BRINE	12	PLASTIC	500 ML	X			14 DA,28 DA
MS	METALS/SOIL, SEDIMENT		GLASS	250 ML W.M.	X			
M	METALS/TISSUE		GLASS	250 ML W.M.	X OR FREEZE			
MO	METALS/OIL, WASTES (LIQUID/SOLID)		GLASS	250 ML W.M.	X			
MX	METALS/ TCLP/SPLP OR ASTM LEACHATE		GLASS	250 ML W.M.	X			
OG	OIL & GREASE		GLASS	2 x 250 ML W.M.	X	H_2SO_4 TO pH < 2	20 DROPS/ 500 ML	28 DA
ORGANIC								
POV	PURGEABLE VOLATILES SCAN 1 & 2 , BTEX/MTBE 601/8010, 602/8020, 8260	13,14	GLASS	2-40 ML SEPTUM VIALS	X	1:1 HCl TO pH<2	5 DROPS/ VIAL	14 DA
OV	PURGEABLE VOLATILES/SOIL 8260 / BTEX/MTBE		GLASS	2-125 ml SEPTUM JARS	X			14 DA
ON	ORG./NEUTRAL EXT. 608/612 (SCAN 3)	14	GLASS	1000 ML AMBER FOIL-LINED CAP	X	CK AND ADJUST pH TO 5-9, NaOH or H_2SO_4		7 DA
OB	ORG/BASIC EXT. 625/8270 (B/N)	14	GLASS	1000 ML AMBER FOIL-LINED CAP	X			7 DA
OA	ORG./ACID EXTRACTABLES, 625 (SCAN 8)	14	GLASS	1000 ML AMBER FOIL-LINED CAP	X			7 DA
OS	ORG./SOIL, SEDIMENT 8081/8121 & 8270		GLASS	250 ML W.M.	X			14 DA
OL	ORG/WASTES OIL, (LIQ./SOLID)	15	GLASS	250 ML W.M.	X			
OX	TCLP VOLATILES		GLASS	250 ML SEPTUM JARS	X			14 DA
AR	ORG/AIR TOXICS (VOLATILE)		STAINLESS STEEL	CANNISTER				

NOTES

1 EXTRA CARE SHOULD BE TAKEN DURING COLLECTION SO THAT THE SAMPLE IS NOT AERATED BEFORE PRESERVATION.

2 GN, GEN CHM/NEUTRAL, INCLUDES THE FOLLOWING PARAMETERS WITH THEIR HOLDING TIMES: SETTLEABLE RESIDUE, NITRITE, ORTHOPHOSPHATE, BOD, AND TURBIDITY (2 DAYS); TOTAL, FILTERABLE, NONFILTERABLE AND VOLATILE RESIDUES (7 DAYS); SILICATES (28 DAYS).

3 ADD SUFFIX "D" TO BOTTLE CODE WHEN SAMPLE IS FIELD FILTERED.

4 EXCESS ACID PRESERVATIVE WILL CAUSE INTERFERENCE...COUNT DROPS CAREFULLY, CHECK pH, ADD MORE ACID IF NECESSARY (pH=2). GA INCLUDES CHEMICAL OXYGEN DEMAND (COD), TOTAL ORGANIC CARBON (TOC), NITRATE PLUS NITRITE, AMMONIA, KJELDAHL NITROGEN, AND PHOSPHORUS.

5 CHLORINATED SAMPLES FOR PHENOLS SHOULD BE COLLECTED IN A SEPARATE BOTTLE AND DECHLORINATED WITH .141N FAS (FERROUS AMMONIUM SULFATE, USUALLY ONE DROP) BEFORE PRESERVATION (USE BOTTLE CODE GP).

6 GB INCLUDES TOTAL CYANIDE, AND CYANIDE AMMENABLE TO CHLORINATION (FREE). HOLDING TIME IS 24 HOURS IF SULFIDES ARE PRESENT.

7 CHLORINATED SAMPLES FOR CYANIDES MUST BE DECHLORINATED WITH ASCORBIC ACID (0.6 G/L) IMMEDIATELY AFTER COLLECTION AND THEN PRESERVED WITH NaOH.

8 THE PROPER CONTAINER DEPENDS ON PARAMETERS REQUESTED. 250 ML FOR TOTAL ONLY, 500 ML FOR AMENABLE

9 IF SAMPLE IS FILTERED ON SITE AND THE MEMBRANE FILTER ADDED TO 90% ACETONE (SUPPLIED BY THE LAB) AND REFRIGERATED, OR IF UNFILTERED SAMPLE IS FIELD FROZEN, HOLDING TIME IS ONE MONTH.

10 RECOMMENDED MAXIMUM HOLDING TIME FOR MERCURY, SODIUM, POTASSIUM, MAGNESIUM, CALCIUM (28 DAYS); OTHER METALS (6 MONTHS).

11 IF FIELD FILTRATION IS NOT AVAILABLE, SEND UNFILTERED SAMPLE TO THE LAB AS SOON AS POSSIBLE (WITHIN 24 HOURS). DO NOT ADD ACID TO DISSOLVED METAL IF UNFILTERED.

12 MN, MINERALS/NEUTRAL INCLUDED THE FOLLOWING PARAMETERS WITH THEIR HOLDING TIMES: pH (ANALYSES SHOULD BE PERFORMED IMMEDIATELY ON SITE); HEXAVALENT CHROMIUM (24 HOURS); ALKALINITIES (CO_3, HCO_3, TOTAL ALK) (14 DAYS); SPECIFIC CONDUCTANCE, CHLORIDE, SULFATE (28 DAYS).

13 FILL BOTTLE COMPLETELY (NO AIR BUBBLES) AND MAKE SURE TEFLON SIDE OF SEPTUM FACES SAMPLES. DUPLICATE VIALS REQUIRED.

14 CHLORINATED WATER SAMPLES FOR ORGANIC COMPOUNDS SHOULD BE DECHLORINATED BY ADDING .141N $Na_2S_2O_3$ (SODIUM THIOSULFATE) TO THE BOTTLE BEFORE FILLING WITH SAMPLE.

15 INCLUDES PETROLEUM HYDROCARBONS, SPILL IDENTIFICATIONS, METHANOL (RCRA) EXTRACTION FOR SCANS 1 AND 2.

16 GEN CHM/SEDIMENTS INCLUDES: TOTAL PHOSPHORUS, KJELDAHL-N, CYANIDE, PHENOLICS AND COD.

Collector's Initials	DEPT. OF NATURAL RESOURCES	Date
Field ID	Location	
Analysis or parameter code	Chemicals added	

Figure 3.C.-1 DNR Sample Bottle Label

ENVIRONMENTAL ENFORCEMENT DIVISION
INVESTIGATIVE SECTION

Date	Time	File No	File Class	Priority
Location (Corp — Stream — Landfill)				
Description of Evidence				
Lab ID Sticker				
Station	Officer			

R2801

Figure 3.C.-2 EED Sample Bottle Label
(Criminal Enforcement in green and Non-criminal Enforcement in white.)

Recommended holding times which are not met for many samples include analyses for pH and sulfite (analyze immediately), Winkler set dissolved oxygen (DO) (eight hours), hexavalent chromium (twenty-four hours), cyanides (24 hours when sulfides are present). Analysis for pH should be performed by an approved procedure in the field if compliance or litigation is involved. Winkler set DO samples should be titrated in the field if practical. Storing set DO samples in the dark at 4°C does appear to effectively prolong the holding time for non-effluent samples. A practical method of routinely setting bacti samples within the six hour holding time is not available from the Environmental Laboratory. Extended holding times for hexavalent chromium may result in oxidation of trivalent chromium or reduction of hexavalent chromium.

3.E. SAMPLE PACKAGING AND SHIPPING

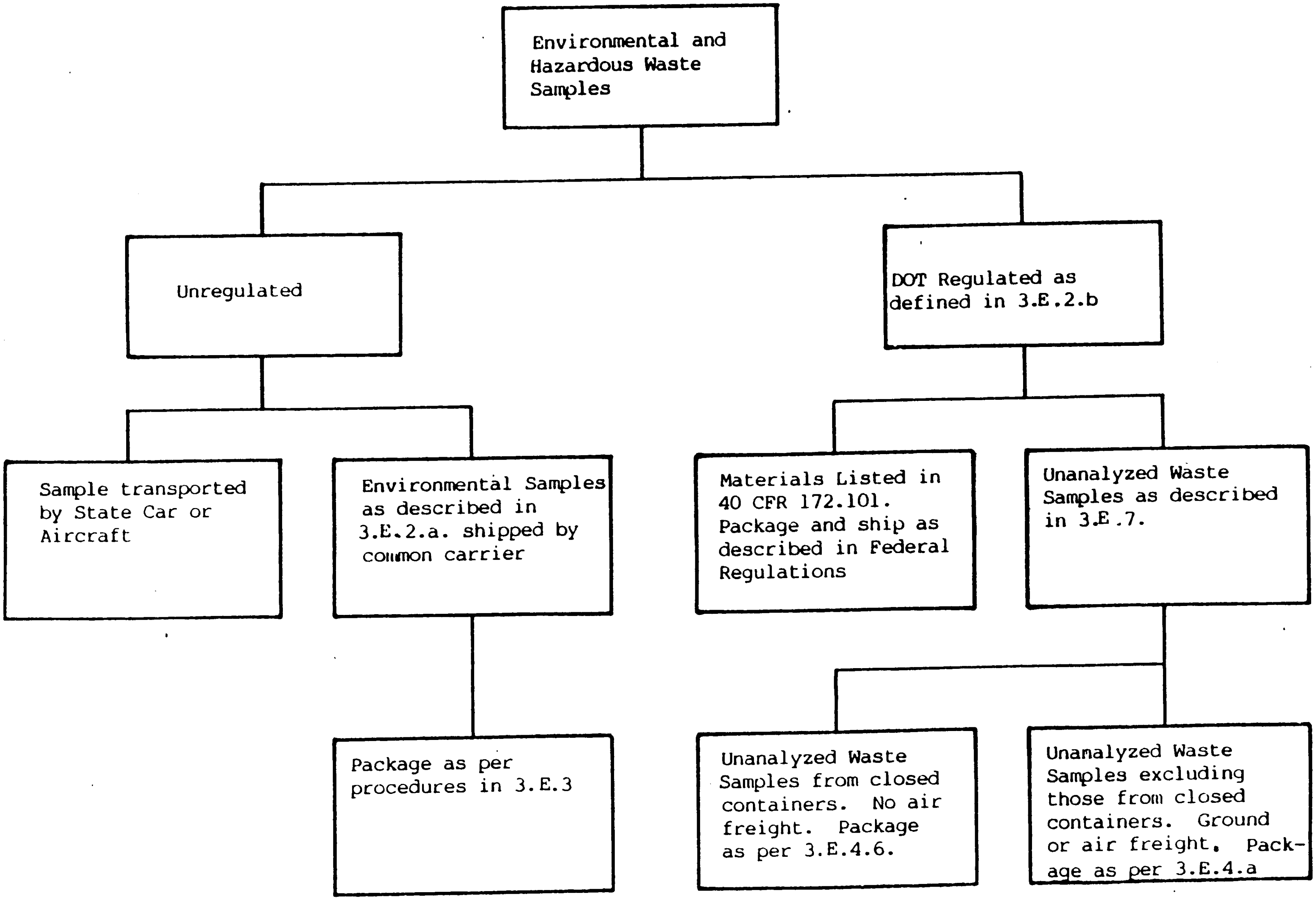
3.E.1. INTRODUCTION

The purpose of this Section is to review alternatives and provide guidance for transporting environmental and waste samples from field locations to the Laboratory or a commercial laboratory and to convey general information concerning transport services, packaging requirements and other considerations.

A schematic description of sample shipment requirements based on sample type is provided in Figure 3.E.-1. This guidance is necessary to help staff comply with Department of Transportation (DOT) regulations (49 CFR, Parts 171-179) covering transport of hazardous materials. DOT regulations place the burden on the shipper to determine if the sample meets the definition of a hazardous material. It is assumed that the shipper has some knowledge concerning the sample and based on that information is able to make a reasonable judgment whether or not the sample is likely to be classified as a hazardous material. When a reasonable doubt exists as to whether a sample is subject to DOT regulations, the shipper should either not ship the samples by common carrier or treat the samples as a DOT regulated material. The shipper is liable for compliance with these regulations. Civil penalties up to $10,000 and criminal penalties up to $25,000 and 5 years are prescribed.

49 CFR, Parts 171 to 179 consist of approximately 1300 pages of regulations concerning shipment of hazardous wastes. This chapter is not intended to cover all aspects of hazardous sample shipment but rather as an introduction to the regulations and to provide general guidance. Copies of the Code of Federal Regulations are available at Document Depository Libraries (In the Lansing area: State of Michigan Law Library and Michigan State University Library). Alternatively, the Code of Federal Regulations can be purchased from the Superintendent of Documents, U.S. Government Printing Office, Washington D.C. 20402. Parts 100-177 and Parts 178-199 are bound in two separate volumes and cost about $13 each. The Code of Federal Regulations is revised annually. Since Parts 178 and 179 refer to Shipping Container Specifications and Specifications for Tank Cars you may wish to purchase only Parts 100-177.

Figure 3.E -1 Packaging and Shipping Requirements for Laboratory Samples



3.E.2. SAMPLE TYPES

For the sake of interpreting applicable federal regulations, samples can be categorized as unregulated and DOT regulated. The DOT regulated category is further divided into Unanalyzed Waste Samples from closed containers, Unanalyzed Waste Samples from open containers and Listed Wastes. These categories are described as follows:

3.E.2.a. UNREGULATED SAMPLES

Unregulated samples include environmental samples such as preserved and unpreserved drinking water, groundwater, ambient water, lake and stream samples, treated municipal and industrial effluent, lake and stream sediments, fish samples, coal samples, and other fuels and uncontaminated or weakly contaminated soils. DOT Hazardous Materials Transportation Regulations do not apply to weak aqueous solutions of HCl, HNO_3, H_2SO_4 and NaOH (environmental samples preserved with the required quantities and concentrations of preservatives).

3.E.2.b. REGULATED SAMPLES

DOT regulated samples include untreated sewage, industrial process samples, spill investigation samples, sludge from industrial processes, and samples from hazardous waste sites which may pose an unreasonable risk to health, safety or property when transported by common carrier. DOT regulated samples are further divided into the following three categories:

- Unanalyzed Waste Samples from closed containers -
- Unanalyzed Waste Samples from open containers or from contaminated waste site soils or liquids.
- Listed Wastes - Samples containing wastes listed on the DOT Hazardous Materials Table, 40 CFR Section 172.101. (Sample content must be known prior to analysis.)

3.E.3. SAMPLE PACKAGING - UNREGULATED

The following procedure is recommended for shipment of unregulated samples:

1. All samples are to be placed inside a strong shipping container. This container should be able to withstand a 4 foot drop on solid concrete in the position most likely to cause damage. A metal picnic cooler lined with hard plastic meets this test. The cooler drainage hole should be secured to prevent the contents from escaping. The cooler should be marked, "This End Up" with arrows indicating the proper upward position. The cooler lid should also be taped shut to prevent leakage in the event that the cooler is overturned.

2. Screw type caps should be tightened before placement in the shipping container. Ground glass stoppers should be secured with nylon reinforced tape. Glass bottles should be separated in the shipping container by cushioning with styrofoam or an absorbent material to prevent breakage. Styrofoam sheets made to fit tightly in the cooler, with circular openings to accept sample bottles snugly are suitable for this purpose. Volatile organic samples (40 ml vials) can be placed inside a larger container and packed with absorbent or cushioning

material to prevent breakage or leakage. Glass sample containers should be packaged so as to survive the 4 foot drop test.

3. Ice should be placed in separate plastic bags and sealed or water should be frozen in plastic sample bottles to prevent melting ice from saturating the packing material or floating the sample bottles. Do not rely on loosely packed ice to cushion glass sample bottles. Sample bottles and packaged ice can also be placed together in a large sturdy plastic bag within the cooler to provide an additional waterproof lining.

3.E.4. SAMPLE PACKAGING REGULATED

The following procedures are required for samples such as untreated sewage, industrial process samples, spill investigation samples, sludge from industrial processes, drum samples, samples from unregulated hazardous waste sites and similar samples which in the judgment of the project leader cannot be considered unregulated samples. For purposes of sample transport and packaging under DOT Regulations, unanalyzed waste samples are divided into two primary categories: Unanalyzed Waste Samples (excluding those from closed containers) and Waste Samples from Closed Containers.

3.E.4.a. UNANALYZED WASTE SAMPLES, EXCLUDING THOSE FROM CLOSED CONTAINERS

This category includes samples which may contain concentrations of contaminants in excess of those normally encountered in preserved drinking water, ambient water, effluent, biological sediment and sludge samples. Waste samples include such samples as leachates, untreated process materials, samples from spill investigations, industrial sludges, and contaminated soils, groundwater and surface water from uncontrolled waste disposal sites.

Procedures for packaging, marking and labeling unanalyzed hazardous waste site samples, excluding those from closed containers are as follows:

1. Collect the sample in a suitable container for the parameters being analyzed. Leave approximately 10% of the container empty to allow for expansion of the sample.

2. Attach a properly completed DNR label (or equivalent) to the sample container.

3. Seal the sample container and place it in a 2 ml or thicker polyethylene bag.

4. Place the sealed bag inside a metal can with incombustible, absorbent cushioning material (e.g. vermiculite or earth) to prevent breakage; one bag per can. Pressure - close the can and use clips, tape or other fasteners to hold the lid securely.

5. Mark and label the metal can with the following information: laboratory name and address and "Flammable Liquid n.o.s." (or if not a liquid) "Flammable Solid n.o.s.".

6. Place one or more metal cans surrounded with incombustible packaging material in a strong outside container, such as a picnic cooler or fiberboard box.

7. Mark and label this outside container as in 5 above and mark the outside container with the words "Laboratory Samples" and "This Side Up" or "This End Up" on the top with upward pointing arrows on all four sides of the exterior container.

8. Complete the carrier provided bill of lading and sign the certification statement. If the carrier does not provide these documents, provide the following information in the order listed: "Flammable Liquid, n.o.s." (or "Flammable Solid, n.o.s.," as appropriate); "Cargo Aircraft Only"; "Limited Quantity" or "Ltd. Qty."; "Laboratory Samples"; "Net Weight _____" or "Net Volume _____" (of hazardous contents), by item, if more than one can is inside an exterior container. The net weight or net volume must be placed just before or just after the "Flammable Liquid, n.o.s." or "Flammable Solid, n.o.s." description.

3.E.4.b. WASTE SAMPLES FROM CLOSED CONTAINERS

Waste samples from closed containers include samples from drums, tanks and other similar containers. Such wastes have not been exposed to the environment, diluted or degraded by mechanisms such as volatilization, hydrolysis, absorption and photochemical and biochemical degradation and are, therefore, potentially more hazardous than exposed wastes.

The following packaging, marking, labeling, and shipping methods represent a worst-case procedure for wastes samples from closed containers by treating them as Poison A materials (49 CFR 173.328). In the absence of reliable data which excludes the possibility of the presence of Poison A chemicals or compounds, these procedures must be followed:

1. Collect the sample in a polyethylene or glass container which is of an outer diameter narrower than the valve hole on a DOT spec. 3A1800 or 3AA1800 metal cylinder. Fill sample container allowing sufficient ullage (approximately 10 percent by volume) so it will not be liquid-full at 130° F. Seal sample container.

2. Attach a properly completed sample label to the container.

3. Lower the container into a metal cylinder partially filled with incombustible, absorbent, loose packaging material (vermiculite or earth). Allow sufficient cushioning material between the bottom and sides of the container and the metal cylinder to prevent breakage. After the cylinder is filled with cushioning material, drop the ends of the string or wire into the cylinder valve hole. Only one sample container may be placed in each metal cylinder.

4. Replace valve, torque to 250 ft-lb (for 1-in opening) and replace valve protection on metal cylinder using Teflon tape.

5. Mark and label cylinder as described below.

6. One or more cylinders may be placed in a strong outside container.

7. Place the following information (either handprinted or on preprinted labels) on the side of the cylinder, or on a tag wired to the cylinder valve protector as well as on any outside packaging: "Poisonous Liquid or Gas, n.o.s." and the laboratory name and address. Place the label "Poisonous Gas" on the cylinder ("Poisonous Liquid" label not acceptable here, even if liquid).

8. Complete the shipper-provided bill of lading and sign the certifi-

cation statement. If the carrier does not provide these documents, provide the following information in the order listed and use abbreviations only as specified: "Poisonous Liquid, n.o.s."; "Limited Quantity" or "Ltd. Qty."; "Laboratory Samples"; "Net Weight _____" or "Net Volume _____" (of hazardous contents), by cylinder if more than one cylinder is packaged in an exterior container. The net weight or net volume must be placed just before or just after the "Poisonous Liquid, n.o.s. marking.

9. A chain-of-custody record form must also be properly executed and included in the container or with the cylinder.

10. A staff member should accompany the shipping containers to the transport carrier and open the outside containers for freight inspection if required.

3.E.5. CHAIN OF CUSTODY REQUIREMENTS

If there is a chance that sample results might be used as legal evidence, chain of custody should be maintained from sample collection until analysis. The use of locked metal picnic coolers during transport by a common carrier will enable the receiver to verify that the cooler has not been opened.

Some carriers offer special custody services which formally transfer custody from the shipper to the carrier and then to the laboratory. Such special custody services are not necessary provided that the shipper and the laboratory can document that the sample package was not opened during transit.

3.E.6. SAMPLE PRESERVATION AND HOLDING TIME

Parameter holding time and the amount of time required to ship samples to a laboratory can be an important consideration of sample shipment. Parameters with 2 to 8 hour holding times, such a pH, dissolved metals sulfite and dissolved oxygen cannot usually be transported to a laboratory within their holding times (via common carrier or state vehicle) and should be analyzed or filtered on site as appropriate. Parameters with 24-48 hour holding times include certain nutrients, chlorophyll a, hexavalent chromium, BOD and turbidity.Samples to be analyzed for these parameters and samples requiring refrigeration as a part of their preservation scheme must be collected and transported to the laboratory within this 24 to 48 hour time period. It is up to the field staff to select a delivery method that will meet the holding times in table 3.B-1. All parameters except metals (excluding hexavalent chromium and mercury should be packaged so as to maintain refrigeration during transport.

Unanalyzed hazardous waste samples should not be "fixed" with preservative or refrigerated with ice or dry ice. Moreover, there are no EPA promulgated holding times for samples such as soils, sludges, oils and wastes. It is generally assumed that decay of waste sample constituents is not significant compared to the levels present. Samples should always be collected, transported and analyzed as soon as conveniently possible.

3.E.7. SAMPLE SHIPMENT

Samples could be shipped from any location in the state to any laboratory in the nation. The shipment could range from a single sample shipped via U.S. Mail to large sample lots packed in several ice chests for overnight delivery. Specific guidance for such diverse shipments is not practical. Consequently, each program manager should investigate the services, pick-up and delivery schedules, and rates of the major carriers from the point of departure to the laboratory. Commercial laboratories will also be able to recommend appropriate carriers.

Carriers such as Federal Express and other types of air freight provide rapid service. Other carriers such as United Parcel Service, U.S. Mail or Bus are slower and should not be used if sample holding time and sample refrigeration needs (if any) cannot be met.

Interdepartmental (I.D.) Mail makes daily pick-up at Grand Rapids, Saginaw, Plainwell, and Jackson. Check with your office manager for pick up times. Environmental samples can be transported to the MDNR laboratory by I.D. Mail provided that their packaged weight does not exceed 50 lbs. The advantages of I.D. Mail are cost and daily pick up from Region III district offices. I.D. Mail should be considered when holding times allow and when refrigeration (if required) can be maintained.