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Protocols for Determining the Mean Epilimnetic Total Phosphorus Concentration and Secchi Disc Depth in the Wapato Basin of Lake Chelan

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Introduction

Lake Chelan is one of the most pristine water bodies in North America due to low concentrations of nutrients and other pollutants. The ultra-oligotrophic status of the lake, which is threatened due to population growth pressures, was determined from various water quality studies. Phosphorus was identified as the limiting nutrient in Lake Chelan during the comprehensive Lake Chelan Water Quality Assessment (Ecology, 1989). In order to protect water quality from the impacts of population growth and various land uses, the Lake Chelan Water Quality Plan was developed in 1991 (Lake Chelan Water Quality Committee, 1991). The goal of the Water Quality Plan is to maintain the ultra-oligotrophic condition of Lake Chelan. It is hypothesized that this goal can be attained by keeping epilimnetic total phosphorus (TP) concentrations in the lower basin below 4.5 μg/L. The lower basin is the focus of this water quality monitoring effort because it is considered to be more sensitive to inputs of TP than is the upper basin, and can be monitored more cost-effectively than the upper basin.

The water quality criterion of epilimnion TP concentration not to exceed 4.5 μg/L was developed from a Total Maximum Daily Load (TMDL) study for phosphorus in the lower basin of Lake Chelan (Lake Chelan Water Quality Committee, 1991). The TMDL study defined the lower basin as that part of Lake Chelan from the outlet to a point midway between Twenty-five Mile Creek and Fields Landing. For the purposes of this monitoring project, the Wapato Basin is considered characteristic of the lower basin regarding epilimnetic TP concentrations. The TMDL identified sources and estimated TP loads due to various land uses and set limits on each of those loads so that epilimnetic TP values would not exceed 4.5 μg/L. An estimate of the epilimnetic TP concentration is needed in order to determine if the water quality and TMDL goal is being met. This document describes the methodology needed to accurately estimate the mean TP concentration in the epilimnion of the Wapato Basin.

Appendix A describes a method for measuring Secchi disc depth in Lake Chelan for the purpose of observing and detecting long-term trends in water clarity at low cost. This long-term monitoring effort should be implemented by members of the local community. Each of these protocols meet Ecology's requirements for planning water quality monitoring activities (Ecology, 1991).

Objective

Determine the mean epilimnetic TP concentration in the Wapato Basin for comparison to the water quality criterion of 4.5 μg/L TP.

Design

The epilimnetic TP concentration should be determined in nearly the same manner as was performed in the 1986-87 study (Ecology, 1989). Sample stations 2, 3, and 4 (Figure 1) should be sampled at depths of 0.3 meters (m), 10m, and 20m, while station 1 should be sampled at 0.3m only. The 0.3m sample should be collected below the surface to avoid

Figure 1. Lake Chelan Sample Station Locations.

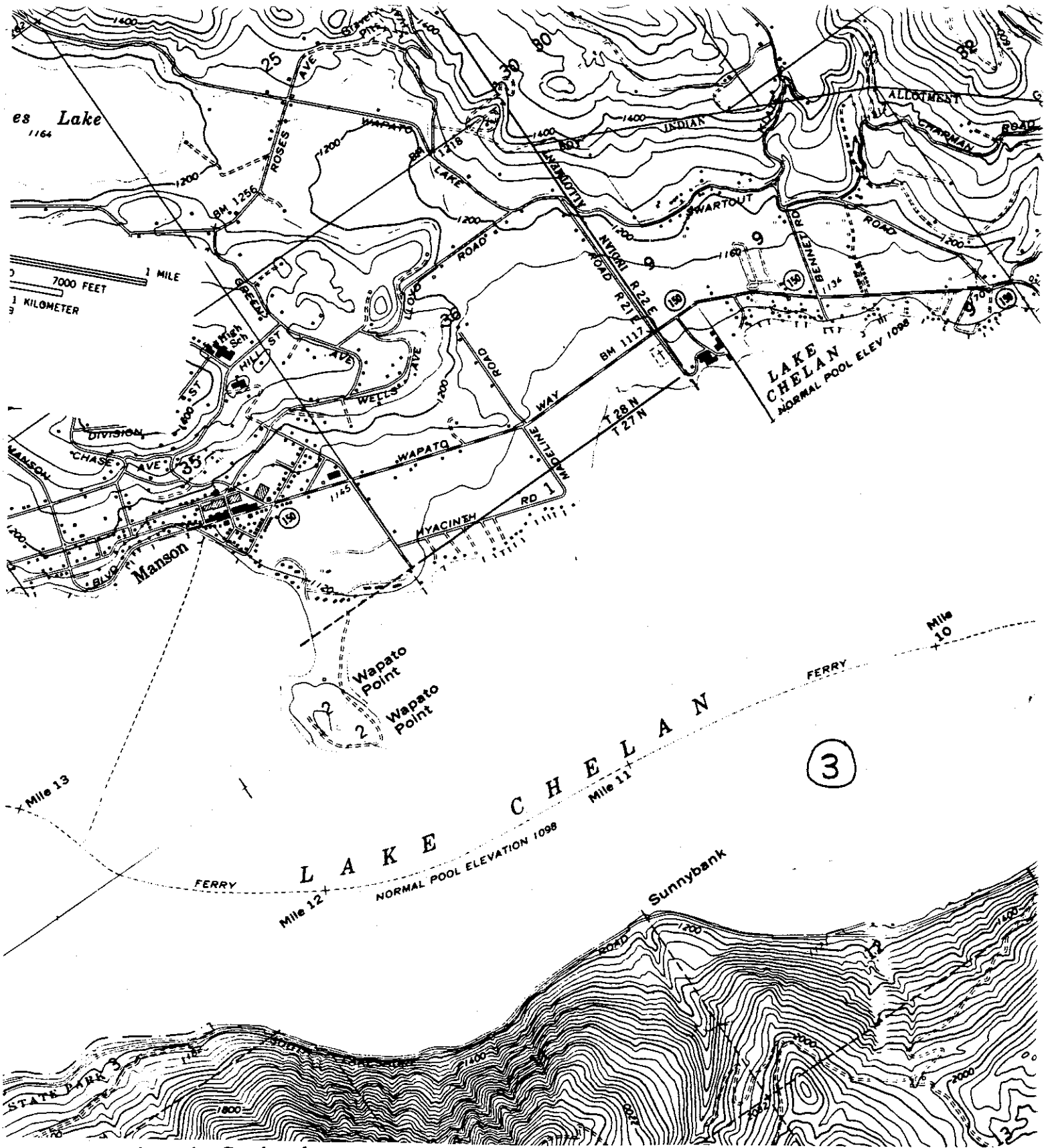

Figure 1. Continued.

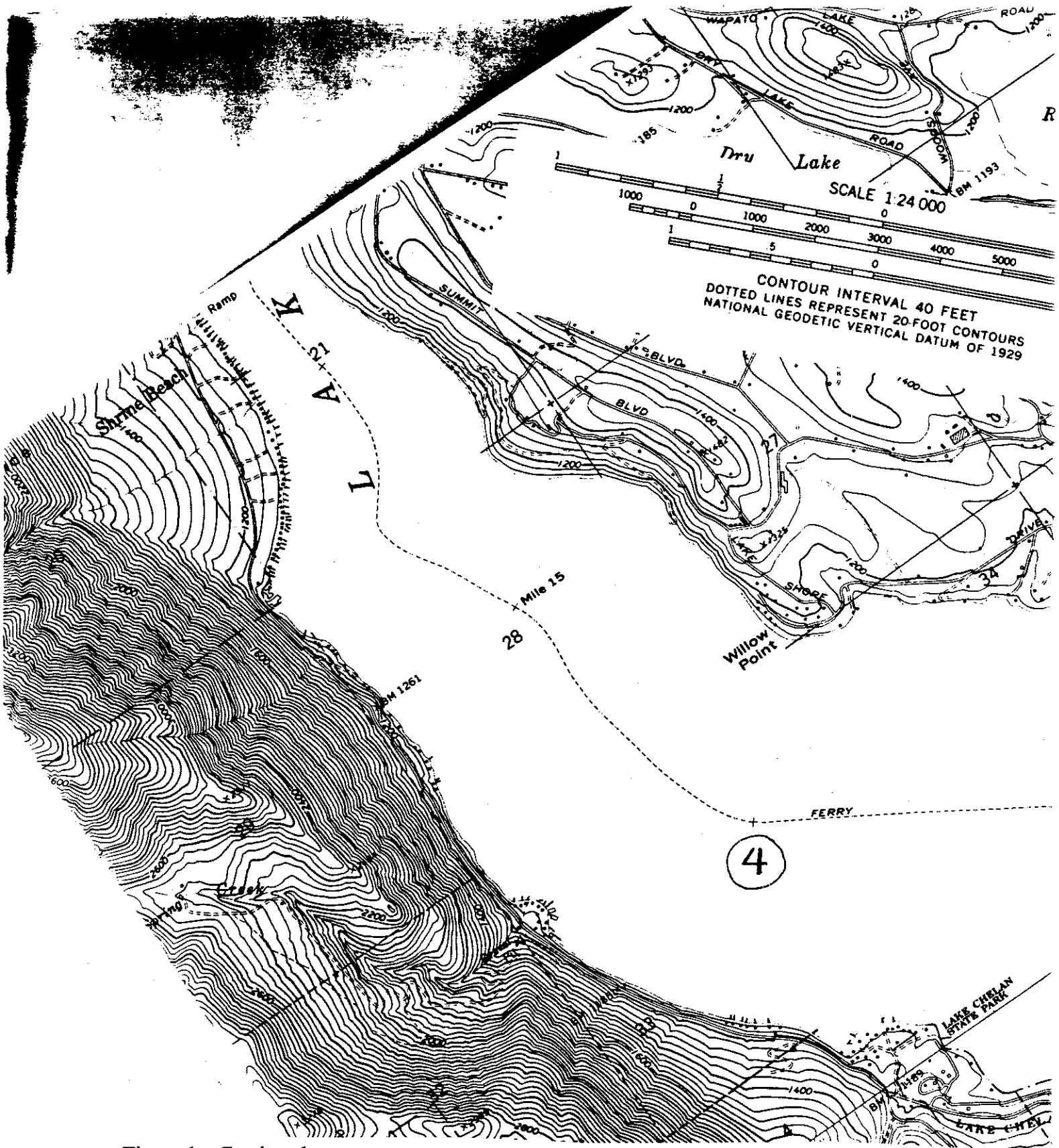

Figure 1. Continued.

particulates associated with the surface microlayer. Seven sampling events should take place at approximately evenly-spaced time intervals (3-5 weeks) between mid- to late April and late September.

For this protocol, the mean value for TP should be determined for the season by calculating a volume-weighted average using acceptable data from all four stations. For this calculation, the lower boundary of the epilimnion should be assumed to be at 30m. Vertical strata used in calculating the volume-weighted mean should be 0-5m, 5-15m, and 15-30m. Epilimnetic volumes associated with each station and sample depth should be the same as those used in the TMDL, and will be supplied by Ecology. Vertical profiles of temperature should be measured at each station in order to verify that the thermocline is located at about 30m depth.

Project Organization and Responsibility

The following describes general duties and responsibilities in carrying out this sampling protocol. These duties and responsibilities should be revised in more detail when organizations commit to following this protocol.

Project Coordinator

Coordinates all activities associated with the monitoring program. Responsibilities include:

- incorporates this protocol for monitoring TP into a Quality Assurance Project Plan;
- manages the fiscal activities of the program;
- coordinates the sample collection and transport activities;
- coordinates laboratory services; select an Ecology accredited lab for the analyses to be performed;
- serves as primary contact for informing and coordinating with public and private organizations and individuals;
- manages water quality data;
- implements quality assurance/quality control procedures;
- facilitates communication among all parties involved in the monitoring effort;
- reports the results of the monitoring effort to concerned interests (e.g., Lake Chelan Water Quality Committee and Ecology);
- coordinates citizen volunteer monitoring activities (e.g., Secchi disc program);
- notifies Ecology when QA/QC results are exceeding specified limits; and
- sends lab reports to Ecology.

Primary Laboratory

Responsibilities include:

- coordinates with project coordinator for all laboratory work;
- coordinates with Ecology on method development/documentation and QA/QC procedures
- receives, logs, tracks, and analyzes water samples;
- reports results for both environmental and QA/QC sample analyses within 10 working

days (allows time for corrective action if necessary);
- tabulates and/or plots results of method blanks and lab splits over time;
- controls chart results of check standard analyses;
- provides documentation of procedures used;
- obtains/manufactures low-level TP standards as needed for calibration and check standards; and
- takes corrective actions as needed to meet data quality objectives.

Ecology

Ecology's responsibilities should be carried out by the Environmental Investigations and Laboratory Services Program (EILS) and Water Quality and Financial Assistance Program (WQ&FAP) who will provide assistance to the project coordinator and primary laboratory in:
- drafting, interpreting, and implementing this guidance (Watershed Assessments Section of EILS);
- assisting primary lab in validating the analytical procedure for low-level TP analyses by May 31, 1995 (Quality Assurance Section of EILS);
- assisting in review of analytical quality control data (Quality Assurance Section of EILS);
- assisting with statistical analyses and interpretation of water quality data for final report (EILS); and
- reviewing of final report (EILS).

Keith Seiders (Watershed Assessments Section) should be the primary contact for Ecology EILS.

Ecology's WQ&FAP, Central Regional Office, should be responsible for coordinating financial assistance needs for this effort and interpreting the result of the TP monitoring effort in the context of the water quality TMDL goal of 4.5 μg/L TP. Max Linden (Ecology's Central Regional Office) should be the contact for these tasks. Theresa Fisher of WQ&FAP is Ecology's overall Section 319 grant coordinator.

Estimated Laboratory Costs

The cost for analyzing a single sample for TP using the procedures described in this protocol is estimated to be higher than the cost for the more commonly used automated methods (about $15 to $20 per sample). The number of samples and total costs at various unit costs are estimated below.

Regular Samples	Number of samples
Station 4, 3 sample depths	3
Station 3, 3 sample depths	3
Station 2, 3 sample depths	3
Station 1, 1 sample depth	1
field split	1
lab split	1
equipment blank	1

total samples per outing: 13
total samples per season: 91

Potential lab cost per outing:		Potential lab cost per season:	
@ $20 per sample:	$260	@ $20 per sample:	$1820
@ $30 per sample:	$390	@ $30 per sample:	$2730
@ $40 per sample:	$520	@ $40 per sample:	$3640

For comparison, the estimated lab costs for TP samples in the preliminary draft Lake Chelan PUD1 Monitoring Plan (Lake Chelan PUD1, 1995) were:

17 samples per outing @ $20 per sample:	$340
119 samples per season @ $20 per sample:	$2380

Thus, per sample lab charges in excess of $26 exceed the preliminary lab budget identified by Lake Chelan PUD1 (Lake Chelan PUD1, 1995).

Data Quality Objectives and Data Assessment Procedures

The data quality objectives (DQOs) described below address the level of quality needed for this project. Assessment procedures to determine if these objectives are met are also described. Analytical and Quality Assurance/Quality Control (QA/QC) procedures are discussed in separate sections. The project manager should review all QA/QC data as they become available in order to determine if DQOs are being met, and if necessary, implement corrective actions as soon as possible.

Precision

Precision of lab and field sample analyses should be estimated through the use of lab and field split samples. Sample splits are described in the Quality Control Procedures section. These results will be used to estimate sources of variability in the data and can help determine if sampling and analytical protocols are adequate. Precision should be determined and reported using the standard deviation and the percent relative standard deviation (%RSD). The %RSD is defined as the standard deviation of the two results divided by the mean of the two results, multiplied by 100 to express as a percent. For two results from a split sample, an estimate of standard deviation is given by D divided by the square root of 2, where D is the absolute value of the difference between the two results. The target %RSD for lab splits is 10% for results greater than 5 μg/L, and 15% for results between 3 and 5 μg/L. The target %RSD for field splits is 15%.

For lab splits, the lab should specify the first and second result of the split. For field splits, the project coordinator should similarly identify and report the first and second result of the split. The project coordinator should calculate, and track over time, the standard deviation and %RSD for both the lab and field splits. At the end of the season, the pooled standard deviation for the lab and field splits should be calculated in order to help characterize the variability of the data.

The precision of the lab analytical procedure should also be evaluated on a short-term basis by plotting the results of check standard analyses on a control chart. The control chart should be developed at the beginning of the study by analyzing 10-20 separately prepared check standards to develop the limits on the control chart. Subsequent results of check standard analyses should then be plotted on the control chart to help determine the stability of the analytical method. The target %RSD for check standards is 10%.

Bias

Every analytical system is subject to various sources of bias. Careful adherence to established procedures for the collection, preservation, transportation, storage, and analysis of samples should reduce or eliminate most sources of bias for this study. Blank correction should be incorporated into the analytical procedure so results should be unbiased. The use of field blanks will determine the presence of, and need for correction of, bias due to field operations. The analytical procedure should be developed by the primary lab with assistance from Ecology. Standard Operating Procedures (SOPs) should be developed and include: instrument calibration, method blanks, blank-correction, preparation and analysis of standards and samples, and quality control procedures.

Representativeness

The spatial and temporal coverage of sample collection should produce data that are representative of epilimnetic phosphorus concentrations in the Wapato Basin. This sampling scheme is nearly identical to the design used in the 1986-87 study from which the water quality criterion of 4.5 μg/L TP was developed. The difference between this plan and the 1986-87 study is that this sampling plan does not include station 5. Station 5 is not included for two reasons:

- Elimination of station 5 reduces costs of this monitoring effort and helps to offset costs associated with QA/QC procedures.

- Use of the stations 1 through 4 in the Wapato Basin is considered to be more sensitive to increases in TP levels and should provide adequate data to achieve the objective of this monitoring effort.

Completeness

It is anticipated that some data will not meet project DQOs and be excluded from calculating the mean epilimnetic TP concentration. Completeness should be calculated by dividing the number of useable data by the number of data originally planned to be collected (e.g., 70

individual lake water TP determinations are planned for calculating the mean volume-weighted epilimnetic TP concentration). Loss of more than 15% of the data (lake water and QA/QC samples) planned to be collected might compromise attaining the project objectives. Loss of more than 25% of the data (lake water and QA/QC samples) might prohibit a meaningful and useful determination of the mean epilimnetic TP concentration and the season's sampling effort may need to be repeated the following year.

Comparability

Comparability of this project's data to the water quality goal, as well as to data from the 1986-87 study, should be ensured by using procedures outlined in this project plan. Any deviations from these procedures should be evaluated and documented (as to their impact on the comparability of project data) prior to their implementation.

Sampling Procedures

Collection of uncontaminated water samples is extremely important to this study. Prescribed sample collection, handling, and preservation methods should reduce the risk of contamination. Water samples for low-level phosphorus determination should be collected with sampling equipment dedicated specifically for this monitoring effort. The preferred equipment for obtaining water samples is a Van Dorn® sampler.

Sample Containers

Sample containers for TP should be cleaned following steps a-d below. Sample containers for TP should be polyethylene (e.g., Nalgene) and hold a minimum of 250 mL. Sample containers should be purchased new and used only for epilimnetic TP samples. A sample identification system should be used that will explicitly describe the sample location.

Equipment Cleaning

The cleanliness of items that can potentially contaminate the water sample should be considered. These include the working deck area, sampler cable or line, interior and exterior of the sampler, and the weighted messenger. Equipment that comes into direct contact with the sample (e.g., interior of the Van Dorn sampler) should be cleaned prior to each sampling outing using the following protocol:

a. wash with phosphorus-free soap and water
b. rinse minimum of 3 times with tap water
c. acid rinse with a 10% hydrochloric acid solution
d. rinse with deionized water
e. cover exposed parts with a clean plastic bag to reduce risk of contamination
f. rinse with lake water immediately prior to sampling
g. cover exposed parts with a plastic bag between sites to reduce risk of contamination

(NOTE: If chlorophyll *a* samples are to be collected, ensure that there is no acid residue in the sampler. A thorough rinsing of the sampler with lake water should be sufficient to remove any trace of acid).

Sample Collection and Preservation

Sample collection should begin at station 4, then 3, 2, and finally 1. Sampling order at each station should be from the deepest site to the shallowest site; this allows adequate rinsing of the sampler. Water samples for TP analysis should be collected before other water samples are obtained from the same site. The sample for TP should not be used for any field measurements due to the potential for contamination. Sample collection and preservation should adhere to the following procedures:

a. prepare the sampler for operation, taking care not to contaminate the interior
b. rinse the sampler thoroughly in the lake and lower it to the desired depth
c. activate the sampler
d. retrieve the sampler
e. examine sampler to ensure security of the sample collected at depth
f. flush stopcock or sampler hose with sample
g. rinse sample container and cap 3 times with sample **
h. fill sample container
i. preserve sample with sulfuric acid to pH of less than 2.0 Standard Units **
j. cap container and cool to 4°C in the dark
k. analyze sample within 7 days.

** An alternative to acidifying the sample after its collection is to use pre-acidified sample bottles. These would contain the proper amount of sulfuric acid so that when filled with sample, the preserved sample would have a pH of less than 2.0 S.U. In this case, the sample bottles would not be rinsed prior to filling.

Field Notes

All pertinent information on field activities should be recorded in a logbook. All entries should be made in indelible ink. Any corrections should be done by drawing a single line through the entry and initialing the change. The notes should be of sufficient detail to allow someone else to repeat the field activity in the absence of the original sampling crew. At a minimum, the following entries should be made about the sampling effort that day: the date; names of sampling crew; times and locations of sample collection; pertinent details of the sampling effort, particularly deviations from standard operating procedures; any relevant field observations, including weather; results of field measurements (e.g., temperature); sample identification; and sample storage and transport information.

Sample Custody

Chain of custody procedures should be followed to ensure the integrity of the sample from the time of sample collection to the time of sample analysis. A chain of custody record should be developed and used. This record should contain, at a minimum, the following

information: project name; date; sample type and identification data; a record of the dates and times when the custody of the samples was transferred; signatures of those involved in relinquishing or receiving sample custody; notes on the method of sample transport (e.g. courier, bus, UPS) . Each person who has custody of the samples should sign the form and ensure that the samples are stored and transported correctly, and secured in a tamper-proof fashion. Custody seals or custody tape should be used to detect unauthorized tampering with the samples.

Analytical Procedures

The volume weighted, mean seasonal TP value derived from this monitoring effort should be compared to the water quality criterion of 4.5 µg/L TP. A major challenge is the fact that the criterion for TP (4.5 µg/L) is below the reporting limit for most labs (10 µg/L) and is just above the actual detection limit for the commonly used persulfate digestion/ascorbic acid colorimetric method (EPA 365.1), which is 1-3 µg/L. (Reporting limit values are typically 3 to 10 times the actual detection limit, depending on methods and laboratories). It is possible to obtain reliable results below 5 µg/L by applying various techniques and adhering to quality control and assurance procedures.

Method

Ecology's Lakes Water Quality Assessment Program (LWQAP [Hallock, 1995]) evaluated several laboratories and methods for low-level TP analytical capabilities. The evaluation included review of the analytical method, limit of detection, calibration factor, precision, and bias. The method selected to meet the needs of the LWQAP was determined to be Standard Methods 4500-P D (APHA, 1992), using a spectrophotometer with a 10 centimeter (cm) light path. This method, performed manually, uses a stannous chloride reduction as opposed to the more commonly used ascorbic acid reduction (SM 4500-P E and EPA Method 365.1).

For this monitoring effort, either the stannous chloride or ascorbic acid reduction method is satisfactory. If a manual method is used, then a 10 cm light path should be used. A shorter path length may be considered for automated methods if the following performance criteria can be met:

- limit of detection that is less than or equal to 1.0 µg/L TP;
- precision of lab splits (%RSD) less than or equal to 10% for results greater than 5 µg/L, and less than or equal to 15% for results from 3 to 5 µg/L;
- documentation of meeting these requirements; and
- documentation of procedures used.

The use of a consistent time window for color development for all samples will help achieve more precise results. Color or absorbance should be measured at a defined and consistent time interval after adding the final reagents. While manual procedures have been performed by various labs, specific documentation is not yet available. The primary lab should develop

this procedure with assistance from Ecology by May 31, 1995. The documented procedure should then be incorporated into this protocol.

Detection Limit

A detection limit study should be performed at the beginning of each monitoring season. Method blanks should be used to determine the limit of detection as defined and described in Manchester Laboratory's Standard Operating Procedure #6 (Ecology/EPA, 1986 [Appendix B]). A minimum of 11 individual method blanks should be processed for use in determining the limit of detection. The detection limit will then be closely tracked throughout the season by monitoring the responses of method blanks. If the results of subsequent method blanks fall outside the range of the original method blanks (as determined during the limit of detection study) then corrective actions should be taken. Detection limits that are greater than 1.0 μg/L should be reviewed for their impact on this monitoring effort. If a different procedure for the detection limit study is proposed, it must be acceptable to Ecology.

Calibration

A five-point, blank-corrected calibration using standards of 0, 3, 5, 10, and 20 μg/L is suggested. The calibration standards should be prepared by careful dilution of a low concentration standard solution prepared from pure reagent. For analytical work so close to the limit of detection, the calibration standards should be processed as a regular sample (digested and reduced) before using to calibrate the instrument (Dewey and Wilson, undated). Calibration should be performed before each batch of samples is run. More detailed calibration SOPs should be developed by the primary lab with Ecology's assistance.

Check Standards

Check standards should also emphasize low concentrations. Check standards should be prepared independent of the calibration standards. A check standard concentration of 4.5 μg/L is suggested. Check standards should be prepared similarly to, but independently from, calibration standards. All responses from samples and check standards should be blank-corrected and all raw data reported (sample response, blank response, and blank-corrected result). Check standards should be analyzed at least twice for each batch of samples, one at the start of the run and the other near the end of the run. Results from analyzing the check standards should be within control chart limits. The control chart for check standards should be developed by analyzing 10-20 check standard "samples" during validation of the analytical method. If results are outside these limits, corrective actions should be pursued which include checking the spectrophotometer for noise, preparing new calibration standards, and recalibrating. If corrective action does not resolve the problem, sample results should be flagged as estimates.

Method Blanks

Method blanks should be prepared by obtaining an adequate aliquot of high-purity water and processing that aliquot as a regular sample. At least two method blanks should be run with each batch of samples. The calibration standard having a value of 0 μg/L TP should not be counted as method blank. All sample and check standard results should be reported as blank

corrected by subtracting a method blank response from the sample response. For blank-correcting individual sample responses, the method blank value to use should be randomly selected from the two method blank values obtained for that batch of samples.

Data Reduction, Review, and Reporting

Data reduction is the process of converting raw data to final results. Data review involves checking the data for errors or omissions. Reporting addresses the format in which lab data are delivered to the project manager, and the formats in which project data are compiled and reported to various audiences.

Lab data should be reported to the project coordinator and include those items described in Quality Assurance Reports below. All sample responses should be reported, even if they are below detection limits. Sample responses should not be censored or truncated in lab reports.

Project water quality and related data should be organized in spreadsheet formats (e.g., Lotus 1-2-3 or Excel) for calculating and reporting purposes. Two spreadsheets are recommended: one for all project water quality and related data; and another for calculating the mean volume-weighted epilimnetic TP concentration. The project coordinator should design the main spreadsheet and Ecology will provide a spreadsheet for calculating the mean volume-weighted epilimnetic TP concentration. All data should be reviewed for transcription errors and errors corrected. Where results from split samples are obtained, only one value should be entered in the spreadsheet and used in calculating the mean TP value. The value used should be the one from the sample that is drawn first from the sampling device (the second sample drawn should consistently be labeled the field QA sample and be submitted blind to the laboratory).

The QA/QC sample results should be reported in a table separate from environmental sample results, and should be used to estimate lab and field precision. QA/QC data reduction, review, and reporting are discussed in the Data Assessment section.

The distribution of TP data collected during the season from all four stations should be examined, and unusual values identified and examined. The nature and possible causes of unusual values should be described, and a decision made to determine whether or not to include them in calculating the mean epilimnetic TP. Data transformations should not be performed. However, if the distribution of the data indicate that transformations are necessary, Ecology should be consulted on actions to follow. The circumstances and rationale for decisions concerning data validity should be documented in the final report.

Sample results that are qualified (such as estimated values) should be reviewed and a decision made whether or not to include them in calculating the mean epilimnetic TP concentration. The nature of the qualified values and the rationale for decisions made should be documented in the final report. Missing values (results that are lost or unusable) should be similarly

evaluated and decisions made about how these will be used. Ecology EILS can assist the Project Coordinator with these evaluations and decisions.

Quality Control Procedures

This section addresses how sampling and analytical precision should be determined, and how field contamination may be determined. QA/QC procedures for TP for each sample outing should include a field split, and a lab split of the field split.

A field split from the sampling device should be taken during each sample outing in order to measure the combined variability due to sampling and analysis. The location of the field split should be randomly chosen. Two samples should be drawn from the sample device, one immediately after the other. The first sample should be designated as the regular field sample while the second sample should be designated as the field split. The field split is sent to the lab as a blind sample (the lab should not know the precise source of the sample). This blind field split should then be used for the lab split. The lab should split the sample and process the resulting two samples separately.

An equipment blank should be developed and submitted to the laboratory as a blind sample for each sample outing. This blank should be collected part-way through the day's sampling activities. Blank water (deionized water known to be phosphorus free) supplied by the laboratory should be used to rinse the sampling device. A sample for TP should then be drawn from the sampler (just like an actual sample) and submitted to the laboratory as a blind sample. Equipment blanks that produce any response (after method blank correction) should initiate additional QA/QC procedures (as described in the Corrective Actions section) in order to determine the nature and source of contamination.

Performance and Systems Audits

Performance and systems audits should be conducted to detect problems so that corrective actions can be taken. The lab chosen to analyze TP samples from this project should be reviewed for their routine participation in such programs. The analysis of Standard Reference Material (SRM) can help evaluate the performance of a laboratory's measurement system. However, there are no low-level TP SRMs, so this evaluation cannot be performed.

The performance of the analytical system should be constantly evaluated by the procedures described in this document. These procedures include the use of check standards, method blanks, and equipment blanks. The results from these samples should be tracked and reported so that the characteristics of the measurement system are known.

Preventive Maintenance

The survey coordinator should be responsible for ensuring that all systems involved in sample collection and analysis are maintained in good working order. The laboratory project officer should be responsible to the project coordinator for ensuring that all lab equipment and systems needed for meeting the needs of this survey are maintained in good working order. Required use of an Ecology-accredited laboratory will help to ensure that preventive maintenance procedures are documented.

Corrective Actions

Corrective actions will be taken as determined by results of QA/QC procedures. The need for, and results of, corrective actions should be documented in the final report's QA section.

If precision targets are exceeded, the magnitude and frequency of exceedences should be examined and corrective actions taken. A determination should also be made whether or not to reject all data from that sample outing. Ecology's Quality Assurance Section should be consulted to assist with this examination and determination should it be necessary.

Corrective actions should include taking steps to determine the source of poor precision. For field activities, the monitoring coordinator should carefully review the entire sampling process, including container storage, sampler cleaning, sample collection techniques, sample storage, and sample transport. The lab coordinator should review all laboratory procedures including holding times, quality of reagents, instrumentation, cleanup procedures, analysts' techniques, etc. After the source of poor precision is found and corrected, re-analysis of all samples is recommended in order to obtain data meeting the DQOs.

Quality Assurance Reports

The laboratory coordinator should report all analytical results to the project coordinator on an ongoing basis so that lab results can be used to determine if changes in the sampling or analytical approaches are needed before the next sampling event. (Reporting of results within 10 working days from receipt of sample is suggested). The final report prepared by the project coordinator should include a Quality Assurance section that describes and summarizes all QA/QC procedures and results of this survey. The project coordinator should initially forward a copy of all laboratory reports to Ecology's Quality Assurance Section so that Ecology can assist in the QA/QC interpretation of these data.

The lab's report to the project coordinator should include the following:

date of analysis
raw data for calibration
calibration curve
check standard results
sample identification
sample volume
sample raw result
method blank results

sample result (blank-corrected)
control chart of results from check standard analyses

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Appendix A
Protocol for Determining Secchi Disc Depth in the Wapato Basin of Lake Chelan

Project Description

Lake Chelan is one of the most pristine water bodies in North America and has exceptional water clarity. Presently, there is no long-term (10+ years) water quality monitoring strategy or resources committed to monitoring Lake Chelan. A long-term monitoring program that measures water clarity with the Secchi disc can provide useful information at low cost. Costs would be minimized by engaging volunteers to establish and maintain the monitoring program. Citizen involvement is also beneficial to local ownership, education, and management aspects of the Lake Chelan watershed. This document describes a method for measuring Secchi disc depth in Lake Chelan for the purpose of observing and detecting long-term trends in water clarity. This long-term monitoring effort should be implemented by members of the local community. This protocol is adapted from Ecology's Lake Water Quality Assessment (LWQAP) Quality Assurance Program Plan (Rector, 1995; Hallock, 1995). This protocol also meets Ecology's requirements for planning water quality monitoring activities (Ecology, 1991).

Objectives

1. Gather long-term data on the water clarity of Lake Chelan's Wapato Basin.
2. Minimize monitoring costs by having volunteers implement the program.
3. Evaluate trends in water clarity when a large enough data set has been compiled (5-10 years).

Project Organization

The following describes general duties and responsibilities in carrying out this monitoring protocol. More specific duties and responsibilities should be developed and written in detail when an organization commits to implementing this protocol.

Project Coordinator

Coordinates volunteer activities associated with monitoring Secchi disc depth.
Responsibilities include:
- recruit and train volunteers;
- coordinate volunteer activities in obtaining Secchi disc readings;
- obtain, distribute, and maintain Secchi disc equipment;
- manage Secchi disc depth data (Ecology's LWQAP may also provide this service);
- implement quality assurance/quality control procedures;
- facilitate communication between all parties involved in the monitoring effort;
- coordinate the reporting of results of the monitoring effort to concerned interests.

The Lake Chelan Water Quality Committee may wish to assume the role of Project Coordinator.

Ecology

The project coordinator may seek to have the Lake Chelan Secchi disc monitoring effort included in Washington's Citizen Lake Monitoring Program. Julie Rector, of Ecology's EILS Program, may be contacted for information about the Citizen Lake Monitoring Program.

Data Quality Objectives and Quality Control

The data quality objectives (DQOs) described below address the level of quality needed for this monitoring effort. Assessment procedures to determine if these objectives are met are also described.

Precision

Precision for Secchi depth data should be determined using duplicate readings taken with and without a viewing tube. A duplicate reading is taken each outing as discussed in the Sampling Procedures section discussed below. This duplicate reading is taken in order to evaluate short-term variability in Secchi disc depth due to clouds or glare. The precision of each pair of duplicate results should be evaluated using the percent relative standard deviation (%RSD) which is the standard deviation of the readings divided by their mean, multiplied by 100 to express as a percent. Pairs of Secchi disc readings whose %RSD exceed 10% should be qualified as estimates. These duplicate Secchi readings are not truly independent of each other since the sampler knows the result of the first reading before taking the second reading. For %RSDs greater than 10%, results should be flagged as estimates and the source of imprecision investigated. A pooled estimate of precision should be made after each monitoring season. The root mean square (RMS) of the %RSDs for the entire set of duplicate readings from the lake for any one season at any one site should be less than 5%. If the RMS of the season's %RSDs is greater than 5%, that season's data will need closer evaluation before being used in trend analyses.

Accuracy

The accuracy of Secchi disc data can be affected by several factors:

1. Eyesight of the individual taking the reading (evaluate with side-by-side checks with professional staff).
2. Wave action and glare (minimize by use of a viewing tube).
3. Angle of incident light which is affected by time of day (minimize by taking readings between 10 am and 2 pm).
4. Elasticity of the sounding line (minimize by using a brass sounding chain designed for limnological studies).
5. Curve or angle of the sounding line due to boat drift (minimize by maintaining position and increasing weight on the Secchi disc; note presence or absence of angle/curve in sounding chain in field notes).

Since there are no reference standards for Secchi depth, accuracy or bias cannot be determined. However, other volunteer programs that measure Secchi depth often use side-by-side measurements with professional staff to evaluate volunteer-collected data. The following method for evaluating accuracy should be performed. For Ecology's Citizen's Lake Monitoring Program (CLMP), Ecology staff observe volunteers' techniques and do side-by-side comparisons twice per year. Volunteer measurements that are within 10% (%RSD) of professional staff readings are acceptable. Where volunteer measurements are greater than 10% %RSD, the entire data set should be flagged as estimates and the source of inaccuracy sought and documented.

The sounding chains used should be carefully calibrated using a steel tape measure and marked in meters or feet with a resolution of 0.1 meter or 0.25 foot. This calibration should be checked and recorded at the beginning and end of each field season for each Secchi disc assembly. Pre-marked chain, if purchased from a vendor, should be checked for correct marking. Rope or line made of synthetic or natural materials should not be used due to shrinkage or stretch over time. Past experience has shown that such materials are susceptible to shrinkage.

Representativeness and Comparability

Secchi depth data should be representative of the station sampled. Sample stations should include, at a minimum, one of the stations sampled in the 1986-87 study (preferably station 4 - deepest part of the Wapato Basin). Additional stations in the Wapato or Lucerne Basins could be added if there are volunteers available for monitoring.

Comparability of these data to historical and future data collection efforts will be ensured by using two methods to read the Secchi depth. Secchi depth readings should be obtained both with and without use of a viewing tube as described in the Sampling Procedures section. Readings taken with a viewing tube will be comparable to each other and should be used for long-term trend analyses. Readings taken without a viewing tube will be comparable to historical data. Construction details for a viewing tube are shown in Figure A1.

Data collected using this protocol should be comparable with data collected for Ecology's LWQAP. As such, these data may be reported to Ecology and entered into Ecology's long-term database. This database is used for inter-lake comparisons, trend analyses, and lake assessments (the latter are required by Section 314 of the Federal Clean Water Act).

Completeness

Volunteers should measure Secchi depth at two-week intervals between mid-May and mid-October. A complete data set for each station for the monitoring season would consist of 11 sets of readings. It is not presently known how much incomplete data will affect the application of trend analyses on Secchi data, but having at least 7 samples for the season seems like a realistic target for completion. This represents a target completeness of 64 percent.

Sampling Procedures

Ecology's CLMP coordinator could provide assistance and training to the volunteer group that will be monitoring Lake Chelan. The following sampling procedures are modified from Ecology's CLMP Procedures (Rector, 1995):

Safety

- Personal safety on the water is the greatest concern. Volunteers should be experienced boaters and demonstrate knowledge of boating safety, particularly on Lake Chelan. Use of a personal floatation device (PFD) is recommended while boating and particularly for obtaining Secchi disc readings. Prior to obtaining readings, consideration should be given to safety factors such as: developing a float plan, weather, condition of boat and crew, wind and wave action, temperature, boating traffic, Lady of the Lake ferry schedule, etc.

Equipment

- 20-centimeter diameter limnological Secchi disc, weighted with approximately two pounds, and attached to a calibrated brass sounding chain
- Underwater viewing tube

Timing

- Start mid-May and stop in mid-October, each season
- Take measurements every 12-16 days

Best Conditions for Taking Secchi Readings

- Between 10:00 AM and 2:00 PM, calm winds and minimum wave action
- Avoid taking readings when it is raining or when water is choppy due to wind or boating activity

Locate Sampling Station

- Describe station location in terms of landmarks and map
- Locate station using description and map
- Maintain station position by judicious use of oars or motor

Measure Secchi Disc Depth Without Using View Tube

- Remove sunglasses
- Take reading from shady side of boat
- Lower disc to where it is no longer visible: then raise it to where it is just barely visible. This is the first Secchi depth.

- Record the Secchi depth to the nearest 0.1 meter or 0.25 foot. Record results and other parameters as described in the CLMP data card (Figure A2)
- Remove Secchi disc from the water and then repeat Secchi disc depth measurement and record results as the second reading.
- Add a comment about the straightness or curvature of the sounding chain or difficulty in maintaining station position due to wind effects
- Indicate that the readings were obtained without use of the view tube

Measure Secchi Disc Depth Using the View Tube

- Repeat the procedure above using the view tube
- Two people may be needed; one to view and the other to help with the sounding chain
- Indicate use of the view tube in recording the results

If the monitoring effort is part of the CLMP, complete and mail a data card (Figure 2) for each method of reading the Secchi depth (with and without a view tube).

Data Reduction, Review, and Reporting

All data associated with Secchi disc readings should be recorded/tabulated in a field notebook or field sheets and then entered on to a computer spreadsheet designed specifically for these data. Ecology can assist in designing or providing the field sheets and spreadsheet to the local project coordinator. Once data are entered into the computer spreadsheet, they should be checked for errors and omissions, and corrections made. The results of QA/QC checks should be recorded and reported as well, and taken into consideration during data analyses. All field sheets should be retained for possible future use. Data reduction and analyses involve presenting the QA/QC information as well as the raw data. Results from within each season at each site may be described. Ecology can assist in designing the processes for analyzing and reporting these data.

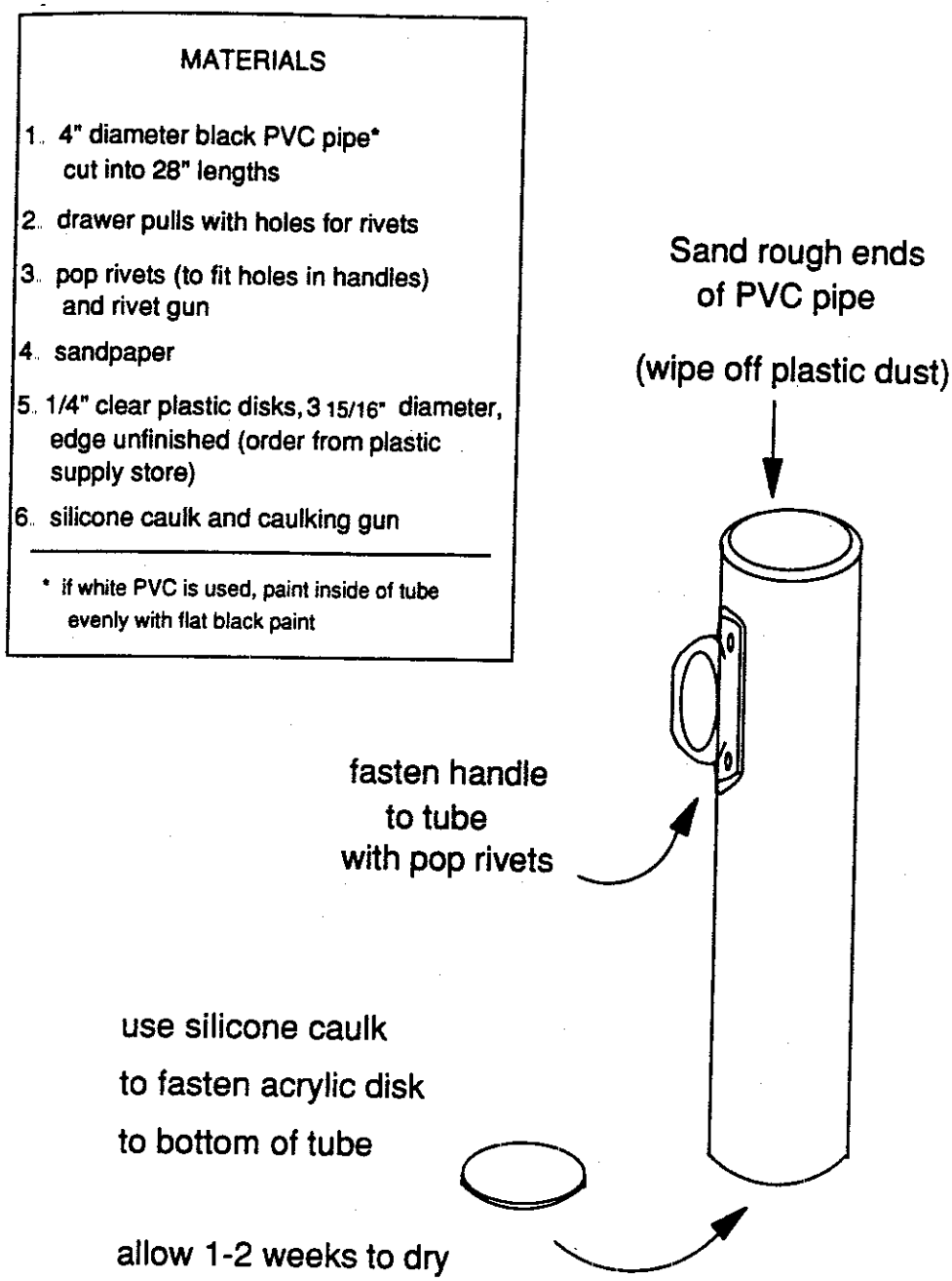

Figure A1. View Tube Construction.

WASHINGTON'S CITIZEN LAKE MONITORING PROJECT

Your Name _____ Sample Date_____

Lake/County _____ Sample Time _____

1st Secchi Reading _____feet 2nd Secchi Reading _____ feet
Did the Secchi disk: ☐ hit bottom ☐ enter weeds ☐ N/A

Surface Water Temperature _____ degrees

Percent Cloud Cover: 0% 10% 25% 50% 75% 90% 100%
Rain Within Last 2 Days: None Trace Light Moderate Heavy
Wind: Calm Light Breezy Strong Gusty Lake Height _____ ft/in

Water Color:
Light Green Moderately Green Pea-Soup Green Other:_____
Light Brown Dark Brown Greenish-Brown
Black Milky Green Clear

Field Observations/Questions/Comments

NO POSTAGE
NECESSARY
IF MAILED
IN THE
UNITED STATES

BUSINESS REPLY MAIL
FIRST CLASS MAIL PERMIT NO. 433, OLYMPIA, WA

POSTAGE WILL BE PAID BY ADDRESSEE
ATT: JULIE RECTOR
DEPARTMENT OF ECOLOGY
PO BOX 47600
OLYMPIA WA 98599-7600

Figure A2. Washington's Citizen Lake Monitoring Project Data Card.

Appendix B

MANCHESTER LABORATORY

STANDARD OPERATING PROCEDURE #6
(SOP #6)

ESTIMATION OF THE CRITERION OF DETECTION AND
THE LIMIT OF DETECTION BASED ON THE
VARIABILITY OF BLANK RESPONSES

The basis for establishing the criterion of detection and the limit of detection is the variability of the blank measurement. The criteria of detection is that concentration which a sample result must exceed in order to conclude (with a 5 percent chance of being wrong) that the analyte is present. The limit of detection is the concentration which must be present in the sample in order to be 95 percent certain of detecting its presence (i.e. 95 percent certain that the result will be greater than the criteria of detection). In practice, this means that results greater than the criterion of detection would be reported as positives, while results less than the criterion of detection would be reported as less than the limit of detection. For example, if the criterion of detection were 5, and the limit of detection were 10, a result of 7 would be reported as such while a result of 3 would be reported as less than 10.

The first step in the calculation of the criterion of detection and the limit of detection is to calculate the within-batch standard deviation of the blank response.

When estimating the standard deviation from the variability of the blank within a single batch, at least 11 separate measurements (i.e. ten degrees of freedom) are suggested. The calculation of the within-batch standard deviation is straight forward:

$$s_{WB} = \sqrt{\frac{\Sigma x_i^2 - (\Sigma x_i)^2/n}{n - 1}}$$

where: x_i = values for individual blank responses

n = number of results

$n-1$ = number of degrees of freedom associated with the estimate s_{wb}.

If several estimates of standard deviation from batches containing unequal numbers of blank determinations are available, these individual estimates can be pooled or combined to give an estimate with a greater number of degrees of freedom by using the following equation.

$$s = \sqrt{(\Sigma \nu_i s_i^2 / \Sigma \nu_i)}$$

where: ν_i = the number of degrees of freedom of the ith estimate, s_i. The estimate, s, has $\Sigma \nu_i$ degrees of freedom.

Finally, if the within-batch standard deviation of the blank is estimated from duplicate blank determinations, the following equation should be used to pool the results.

$$s_{wb} = \sqrt{(\Sigma d_i^2 / 2m)}$$

where: d_i = difference between within-batch determinations of the blank

m = number of duplicate blank determinations.

The number of degrees of freedom associated with the estimate is also equal to m.

Using the estimate of the within-batch standard deviation of the blank obtained from one of the three equations above, the criterion of detection and limit of detection are calculated using the following equations:

$$C_D = 1.41\ t_{0.1}\ s_{WB}$$

$$L_D = 2.83\ t_{0.1}\ s_{WB}$$

where C_D = criterion of detection
L_D = limit of detection
$t_{0.1}$ = the 10 percent point of the t statistic for double sided tests
s_{WB} = the estimated within-batch standard deviation of the blank

The attached t-table can be used to determine the value of $t_{0.1}$ to be used, according to the number of degrees of freedom associated with the estimate s_{WB}.

The following examples may help to clarify how the calculations should be done.

Example 1

Given the following blank measurements in two batches

Batch 1: 0.29, 0.04, 0.13, 0.22 µg/l

Batch 2: 0.35, 0.14, 0.03, 0.26, 0.08, 0.02, 0.17, 0.31, 0.07 µg/l

one can estimate the standard deviations for batch 1 and batch 2 as: $s_1 = 0.1086$ and $s_2 = 0.1225$

The pooled within-batch standard deviation of the blank is then calculated as:

$$s_{WB} = \sqrt{\frac{\Sigma \nu_i s_i^2}{\Sigma \nu_i}} = \sqrt{\frac{3(0.1086)^2 + 8(0.1225)^2}{11}} = 0.1189$$

Once the within-batch standard deviation of the blank is calculated, the criterion of detection and the limit of detection are calculated by the following equations:

$$C_D = 1.41\ (1.795)\ (0.1189) \cong 0.3$$
$$L_D = 2.83\ (1.795)\ (0.1189) \cong 0.6$$

Note that the value of $t_{0.1}$ was obtained from the table with 11 degrees of freedom, and that only one significant figure is necessary for these estimates of C_D and L_D.

Example 2

Given the following blank measurements in ten batches:

Batch	1	2	3	4	5	6	7	8	9	10
Blank 1	0.16	0.18	0.15	0.18	0.19	0.13	0.15	0.12	0.17	0.16
Blank 2	0.16	0.19	0.17	0.14	0.11	0.17	0.13	0.18	0.17	0.14

One can estimate the within-batch standard deviation by pooling the duplicate blanks with the following equation.

$$s_{WB} = \sqrt{\frac{\Sigma d_i^2}{2m}}$$
$$= \sqrt{\frac{0.0145}{20}} = 0.0269$$

The criterion of detection and the limit of detection can then be calculated as:

$$C_D = 1.41\ (1.81)\ (0.0269) \cong 0.07$$
$$L_D = 2.83\ (1.81)\ (0.0269) \cong 0.14$$

Note that the value of $t_{0.1}$ was obtained from the table with 10 degrees of freedom. One significant figure was used for the estimate of C_D, while two significant figures were used for the estimate of L_D in order to indicate clearly that L_D is twice that of C_D.

TABLE 3. PERCENTAGE POINTS OF THE t-DISTRIBUTION

P	25	10	5	2	1	0·2	0·1	$\frac{120}{\nu}$
$\nu=1$	2·41	6·31	12·71	31·82	63·66	318·3	636·6	
2	1·60	2·92	4·30	6·96	9·92	22·33	31·60	
3	1·42	2·35	3·18	4·54	5·84	10·21	12·92	
4	1·34	2·13	2·78	3·75	4·60	7·17	8·61	
5	1·30	2·02	2·57	3·36	4·03	5·89	6·87	
6	1·27	1·94	2·45	3·14	3·71	5·21	5·96	
7	1·25	1·89	2·36	3·00	3·50	4·79	5·41	
8	1·24	1·86	2·31	2·90	3·36	4·50	5·04	
9	1·23	1·83	2·26	2·82	3·25	4·30	4·78	
10	1·22	1·81	2·23	2·76	3·17	4·14	4·59	12
12	1·21	1·78	2·18	2·68	3·05	3·93	4·32	10
15	1·20	1·75	2·13	2·60	2·95	3·73	4·07	8
20	1·18	1·72	2·09	2·53	2·85	3·55	3·85	6
24	1·18	1·71	2·06	2·49	2·80	3·47	3·75	5
30	1·17	1·70	2·04	2·46	2·75	3·39	3·65	4
40	1·17	1·68	2·02	2·42	2·70	3·31	3·55	3
60	1·16	1·67	2·00	2·39	2·66	3·23	3·46	2
120	1·16	1·66	1·98	2·36	2·62	3·16	3·37	1
∞	1·15	1·64	1·96	2·33	2·58	3·09	3·29	0

The function tabulated is t_P defined by the equation

$$\frac{P}{100} = \frac{1}{\sqrt{\nu\pi}} \frac{\Gamma(\frac{1}{2}\nu+\frac{1}{2})}{\Gamma(\frac{1}{2}\nu)} \int_{|t|\geqslant t_P} \frac{dt}{(1+t^2/\nu)^{\frac{1}{2}(\nu+1)}}.$$

If t is the ratio of a random variable, normally distributed with zero mean, to an independent estimate of its standard deviation based on ν degrees of freedom, $P/100$ is the probability that $|t| \geqslant t_P$.

Interpolation ν-wise should be linear in $120/\nu$.

Other percentage points may be found approximately, except when ν and P are both small, by using the fact that the variable

$$y = \pm \sinh^{-1}(\sqrt{3t^2/2\nu}),$$

where y has the same sign as t, is approximately normally distributed with zero mean and variance $3/(2\nu-1)$.