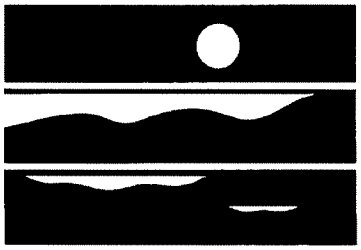


# Protocol for Determining the Mean Epilimnetic Total Phosphorus Concentration in the Wapato Basin of Lake Chelan

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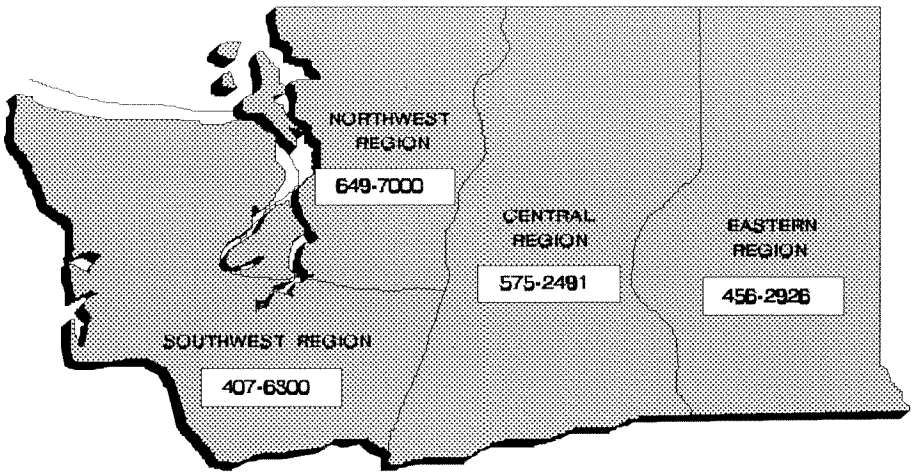


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# Protocol for Determining the Mean Epilimnetic Total Phosphorus Concentration in the Wapato Basin of Lake Chelan

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# Table of Contents

# Abstract

The goal of the Lake Chelan Water Quality Plan is to maintain the ultra-oligotrophic condition of the lake by keeping epilimnetic total phosphorus concentrations in the Wapato Basin of the lake below 4.5 µg/L. Water quality studies in the late 1980's led to a TMDL threshold of 4.5 µg/L total phosphorus. This protocol was developed to sample and analyze for trace levels of total phosphorus found in Lake Chelan for comparison to the TMDL threshold.

# 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. This document meets Ecology's Quality Assurance Project Planning requirements (Ecology, 1991) for planning water quality monitoring activities.

Procedures for measuring Secchi disc depth in Lake Chelan were developed by Ecology in 1995 and refined by Chelan County PUD1 during 1995-96. Chelan County PUD1 should be contacted to obtain the refined Secci disc procedures since they are not included here.

## Objective

Determine the seasonal 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 samples should be collected below the surface to avoid 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 defines roles and responsibilities in carrying out this sampling 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; uses a lab that is accredited by Ecology for the TP method to be used;
- 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
- forwards lab reports to Ecology as appropriate.


Figure 1. Lake Chelan Sample Station Locations.

## Primary Laboratory

Performs sample analyses, provides documentation and reports. Responsibilities include.

- works with project coordinator for all laboratory work;
- follows this protocol unless otherwise approved by Ecology;
- obtains/manufactures low-level TP standards as needed for calibration and check standards.
- fulfills requirements of an Initial Demonstration of Performance (IDP - described below) for the analytical method used prior to each monitoring season;
- splits environmental and performance evaluation samples with Ecology for method comparison as requested;
- gains accreditation for the analytical method used through Ecology's Laboratory Accreditation Program;
- provides Ecology complete documentation of analytical procedures used;
- reports results to the project coordinator for environmental and QA/QC sample analyses within 15 working days (allows time for corrective action); and provides for at least 7 batches of QA/QC samples (e.g., check standards, method blanks) to be analyzed.

## Ecology

Ecology's responsibilities should be carried out by the Environmental Investigations and Laboratory Services Program (EILS) and Water Quality Program (WQP) who will provide assistance to the project coordinator and primary laboratory in:

- drafting, interpreting, and implementing this protocol (Watershed Assessments Section of EILS);
- work with primary lab in meeting requirements of the Initial Demonstration of Performance (Quality Assurance Section and Manchester Environmental Laboratory of EILS);
- accredit the primary lab for the TP analytical method to be used (Quality Assurance Section of EILS)
- evaluate primary lab's capability for analyzing TP at low concentrations prior to season sampling of Lake Chelan (Quality Assurance Section and Manchester Environmental Laboratory of EILS);
- review data from analyses of water quality samples and laboratory quality control (Quality Assurance Section and Manchester Environmental Laboratory of EILS);
- analyze split samples for TP analyses using ICP-MS methods for the 1997 monitoring season (Manchester Environmental Laboratory of EILS);
- assisting with statistical analyses and interpretation of water quality data for final report (EILS); and
- review final report (EILS).

Keith Seiders (Watershed Assessments Section) is the primary contact for Ecology EILS. Max Linden (Ecology's Central Regional Office, WQP) is the person responsible for coordinating financial assistance needs for this effort.

# Estimated Laboratory Costs

Laboratory costs for analyzing low-level TP can be a limiting factor in determining Lake Chelan water quality. The cost for analyzing a single sample for TP varies depending on the procedure used. Automated methods (perhaps $15 to $30 per sample) are usually less expensive than manual methods (about $50 per sample). The cost of an emerging method that uses Inductively Coupled Plasma Mass Spectrometry (ICP-MS) is estimated to cost more than $100 per sample. Costs can also increase due to such things as method modification for low-level TP and additional documentation of method performance. 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 (analytical duplicate) | 1 | (may or may not be charged - lab dependent) |
| equipment blank | 1 | |
| total samples per outing: | 13 | (10 water quality samples, 3 QA/QC) |
| total samples per season: | 91 | (70 water quality samples, 21 QA/QC) |

| 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 |
| @ $50 per sample: | $650 | @ $50 per sample: | $4550 |

Additional lab costs should be anticipated for the Initial Demonstration of Performance and other documentation: these requests are beyond services customarily provided and need to be funded.

# 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

Analytical precision and total precision (which includes sampling and analytical precision) of the water quality sample results will be estimated from analytical and field split sample results, respectively. 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%. No precision targets for field duplicates or lab splits less than 3 µg/L are stated. Precision usually decreases as results approach the detection limit. Precision should be determined, reported, and discussed for duplicates and splits whose results less than 3 µg/L.

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 and reported 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. This process should be defined in the primary laboratory's Standard Operating Procedures (SOPs) or otherwise documented as part of the laboratory accreditation process. The target %RSD for check standards is 10%.

## Bias

Bias is a measure of systematic error in a measurement system. Every analytical system is subject to various sources of bias. Bias may be inherent in the analytical system or the sampling methodology. 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. The use of field blanks will help determine the presence of bias due to field operations. The use of laboratory blanks will help determine the presence of bias in the analytical method. The presence and characteristics of any bias should be described as well as how the bias might affect the sample results and their interpretation. Ecology currently has no guidance on how to determine the need for correction for bias, or a procedure to correct for bias. Instead, prompt attention must be given to QA results and corrective actions taken in lab or sampling protocols if blank sample results suggest the presence of bias. A required limit for bias is not specified here because of limitations of current TP analytical procedures.

## Representativeness

The spatial and temporal coverage of sample collection should produce data that are representative of epilimnetic phosphorus concentrations in the Wapato Basin during the growing season (May to October). 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.
- 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 30% of the data (lake water and QA/QC samples) might prohibit a meaningful and useful determination of the mean epilimnetic TP concentration. A statistical evaluation that quantifies an acceptable amount of lost data may need to be performed and is not presented here. Such an evaluation may be needed if many data are lost.

## Comparability

Comparability of this project's data to the water quality goal 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. The data generated through these protocols may or may not be useful for analyzing for low-level TP trends over time because of decreasing confidence in the analytical results as the detection limit is approached. So, the comparability of data to other year's data (e.g. 1987, 1995, 1996) will need to be evaluated on a case-by-case basis and should be addressed in annual or project reports. Ehinger (1996) discusses data quality objectives for long-term monitoring and trend analysis and should be consulted if trend detection becomes the primary objective.

# 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 in time and space.

## 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.

** The use of sulfuric acid as a preservative should be reviewed due to the potential of the sulfuric acid being contaminated with phosphorus.

## Field Notes

All pertinent information on field activities should be recorded in a log book. 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 will 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 method detection limit for the commonly used persulfate digestion/ascorbic acid colorimetric method (EPA 365.1), which is 1-3 µg/L. (Reporting limit values may typically be 1 to 10 times the actual method detection limit, depending on methods and laboratories.) An analytical procedure that uses Inductively Coupled Plasma Mass Spectrophotometry (ICP-MS) technology has achieved a method detection limit of 0.5 µg/L. While more expensive than the colorimetric methods, this method should be considered for use when it receives formal approval by the scientific and regulatory community (perhaps by 1998).

Considerable debate remains in the scientific community surrounding analyses and interpretation of trace-level constituents in water. Much of the debate is concerned with the uncertainty of analytical results that are close to or possibly beyond our technical abilities to measure. Different

definitions of "detection limit" add to the controversy and become significant factors at the lower end of our measurement systems. The multitude of "detection limit" definitions and casual use of the term can also confuse scientists, resource managers, and the public. For this project, the "method detection limit" as defined in 40 CFR 136, Appendix B, Revision 1.11, pp. 525-527, 89th Edition, will apply. While the method detection limit is one indicator of analytical method performance, other characteristics of the measurement system are needed. The following analytical procedures are designed to provide information about the performance of the measurement system which should help with the interpretations of water quality sample data.

# Method

The strengths and weaknesses of various methods to quantify total phosphorus incorporate many factors such as method limitations, laboratory facility, cost, instrumentation, and expertise of chemists. While various methods (with or without modifications) have been proposed for determining trace levels of TP, none have yet been specifically selected for this project. Instead, performance characteristics of the analytical method used for this monitoring effort need to be determined and the capability to determine low-level TP demonstrated before the collection and analyses of water quality samples. The following requirements must be met:

- the method (including any modifications) be reviewed by Ecology's Lab Accreditation Program and that the laboratory be accredited for the method used;
- complete documentation of the method used be provided to Ecology;
- an Initial Demonstration of Performance (IDP) be done at the beginning of each monitoring season and approved by Ecology;
- complete documentation of all analytical work performed be provided to Ecology

documentation of meeting these requirements.

# Initial Demonstration of Performance

An Initial Demonstration of Performance (IDP) is required for the analytical method used to determine total phosphorus (TP) in lake Chelan water samples. The IDP will give information on the method detection limit, recovery, and bias for the low-level standard and method blanks. The IDP must be completed and approved by Ecology each year before lake water quality samples are collected and analyzed.

The following IDP procedure was derived from EPA Method 200.9. Many other EPA methods contain essentially the same language and requirements. A low-level TP standard (e.g. 3.0 µg/L) is analyzed seven times to determine the method detection limit (as defined in 40 CFR 136, Appendix B). In addition, at least 8 (preferably 11) method blanks are analyzed alternately with the check standards (*i.e.*, blank, standard, blank, standard, etc.). The standards and method blanks used in the IDP must be processed and analyzed in the same manner as actual samples are prepared.

Deliverables for the evaluation of the IDP shall include all data necessary to allow Ecology to perform an independent assessment of the analytical method and results. Copies of original documents should be provided to Ecology rather than original documents. Original documents shall be maintained on file at the laboratory responsible for producing the data. All copies provided to Ecology must be legible. The deliverables shall include:

1. Chain of Custody Record: Include all relevant chain of custody documentation related to the project.
2. Case Narrative: Discussion of any abnormalities or difficulties encountered during analyses, such as matrix interferences, spike recoveries, precision data, method blank contamination, holding time violations, or other considerations affecting the data reviewer should know about. Data qualifiers used are to be defined.
3. Data Summary Information: A summary of the IDP results and associated method quality control sample results shall be provided. Dates that samples were prepared and analyzed shall be included. All analytical responses and results shall be reported without any rounding, censoring, or adjustment of significant figures.
4. Quality Control and Quality Assurance Summary Data: Data and summaries of the following shall be included: target analyte recoveries, precision data, duplicate results, spike results, laboratory control sample results, check standard results, spiking levels, quality control (QC) limits, and method blank summaries.
5. Instrument Response Printouts (Raw Data): All charts, graphs., spectrograms, chromatograms, or other instrument A/D printouts including recorder traces will be provided. All raw data must be dated and initialed by the analyst responsible for data generation.
6. Calibration or Standardization Information: The following shall be provided: all data pertaining to standards used for identification and quantitation including raw data from both the initial and continuing calibration standards. Indicate which standards were used in the calculations for the analyte concentrations.
7. Preparation/Digestion/Extraction Information: Provide all dates of preparations, initial sample amount used for analysis, any aliquots or dilutions taken, final volumes or weights, and names of the analysts performing the work.

# Calibration

A five-point, calibration using standards of 0, 2.5, 5, 7.5, and 10 µg/L is suggested. The calibration standards should be prepared by careful dilution of a low concentration standard solution prepared from pure reagent. The analytical method must clearly define how the calibration standards are processed before using to calibrate the instrument. Calibration should be performed before each batch of samples is run.

## Check Standards

Check standards of low concentrations must be used. A concentration of 2 µg/L TP is suggested (as per the method detection limit determination in 40 CFR 136). Check standards should be prepared similarly to, but independently from, calibration standards. 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.

## Method Blanks

Method blanks are samples of deionized water which are analyzed along with and exactly like the field samples. Preparation and analysis of the method blanks should be described in the analytical procedure. At least two method blanks must 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.

## Blank Correction

Various opinions exist regarding the need for and appropriateness of blank-correcting sample responses and/or results. This protocol defers to the analytical method used in this project. The analytical method must address whether or not blank correction is to be performed and, if so, how and when it is to be performed. Ecology has no policy regarding the blank-correction of data. These protocols consider the application of blank-correction techniques to be a part of data interpretation rather than part of the analytical method. Should a blank-correction procedure be pursued in the future, the method blank data needed to do so will have been generated.

# 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 and summaries beyond that customarily reported are required for this project. This will allow Ecology to perform an independent assessment of the analytical results. The required deliverables are the same as those described above for the Initial Demonstration of Performance. Sample responses must not be censored or truncated in lab reports. However, results that are less than or equal to the method detection limit must be qualified with something like: "below detection limit - estimated value" or "value below detection limit - use with caution." If copies of instrument outputs are included in reports, handwritten notes should be used on such reports as needed to help identify and interpret the output.

Project water quality and related data should be organized in spreadsheet formats 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 (formula given below). The project coordinator should design the main spreadsheet and Ecology will provide the 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 QA/QC sample results should be reported in tables 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 suggest that transformations are necessary, Ecology should be consulted on appropriate techniques to use. The circumstances and rationale for decisions concerning data validity should be documented in the final report.

Should there be sample results that are qualified (such as estimated values), these 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 can assist the project coordinator with these decisions.

Discussion of volume-weighted statistics can be found in Reckhow (1983) and Gilbert (1987). Ecology spreadsheets mentioned above use these formulas for volume-weighted calculations:

- The volume-weighted mean is: the summation across all strata of (Wh* Xh), where:

  Wh= volume of stratum h / total volume of all strata
  Xh= mean value of stratum h across all sample events

- The square of the volume-weighted standard error is: the summation across all strata of [(Wh^2 * Sh^2)/nh], where:

  Wh^2 = Wh squared
  Sh^2= variance in stratum h
  nh= number of observations in stratum h

To compare the mean volume-weighted epilimnetic TP concentration to the TMDL threshold of 4.5 µg/L, the upper 95% confidence limit of the mean volume-weighted epilimnetic TP concentration should be determined. The volume-weighted standard error should be used in this determination. Then, a one-sided t-test should be performed to determine if the upper 95% confidence limit equals or exceeds 4.5 µg/L (Ho: upper 95% CL is greater than or equal to 4.5 µg/L). For the t-test, n represents the total number of sample results and not the total number of strata sampled as previously interpreted.

# 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 equipment blank, 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 and fill 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 should initiate additional QA/QC procedures (as described in the Corrective Actions section) in order to determine the nature and source of contamination.

Results from, and the precision of, field splits and lab splits must be reported for individual pairs of splits and as a pooled estimate for the entire season's sampling effort. Precision for individual pairs of splits is determined as described in the previous section on "Precision." The pooled standard deviation is: the square root of the sum of the squared differences between paired results divided by twice the number of pairs of duplicates).

# 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. While the analysis of Standard Reference Material (SRM) can help evaluate the performance of a laboratory's measurement system, this evaluation cannot be performed because there are no low-level TP SRMs.

The performance of the analytical system should be constantly evaluated by the procedures described in the analytical method and laboratory protocols. These procedures should 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 project coordinator is responsible for ensuring that all systems involved in sample collection and analysis are maintained in good working order. The primary laboratory is 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.

# 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 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 project coordinator should carefully review the entire sampling process, including container storage, sampler cleaning, sample collection techniques, sample storage, and sample transport. The primary laboratory 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 primary laboratory should report all analytical results to the project coordinator and Ecology on an ongoing basis. This will help determine whether or not changes in the sampling or analytical approaches are needed before the next sampling event. (Reporting of results within 15 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 forward a copy of all laboratory reports to Ecology.

# References


Ecology, 1989. Lake Chelan Water Quality Assessment. Prepared for Washington State Department of Ecology, January 1989, by Harper-Owes Consulting Engineers, Seattle, WA.

Ecology, 1991. Guidelines and Specifications for Preparing Quality Assurance Project Plans. Ecology publication 91-16. Washington State Department of Ecology, Olympia, WA.

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Gilbert, R., 1987. Statistical Methods for Environmental Pollution Monitoring. Van Nostrand Reinhold Company, New York. (see Chapter 5 on Stratified Random Sampling).

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Reckhow, K. and S. Chapra. 1983. Engineering Approaches for Lake Management: Volume 1- Data Analysis and Empirical Modeling. Butterworth Publishers, Boston. (see Chapter 5 on Sampling Design).