Quality Assurance Project Plan

Lake Chelan Wapato Basin
Total Phosphorus
TMDL Effectiveness Monitoring, 2007

by
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Approvals

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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 concentration in the Wapato Basin of the lake below 4.5 µg/L. Water quality studies in the late 1980s identified phosphorus as the limiting nutrient in Lake Chelan. The purpose of this study is to determine if changes in nutrient levels, including total phosphorus, have occurred as compared to previous studies.

Background

Lake Chelan is located in the Northern Cascades of central Washington (Figure 1). It is the longest and deepest natural lake in the state (Patmont et al., 1989) and one of the most pristine waterbodies in North America due to low concentrations of nutrients and other pollutants.

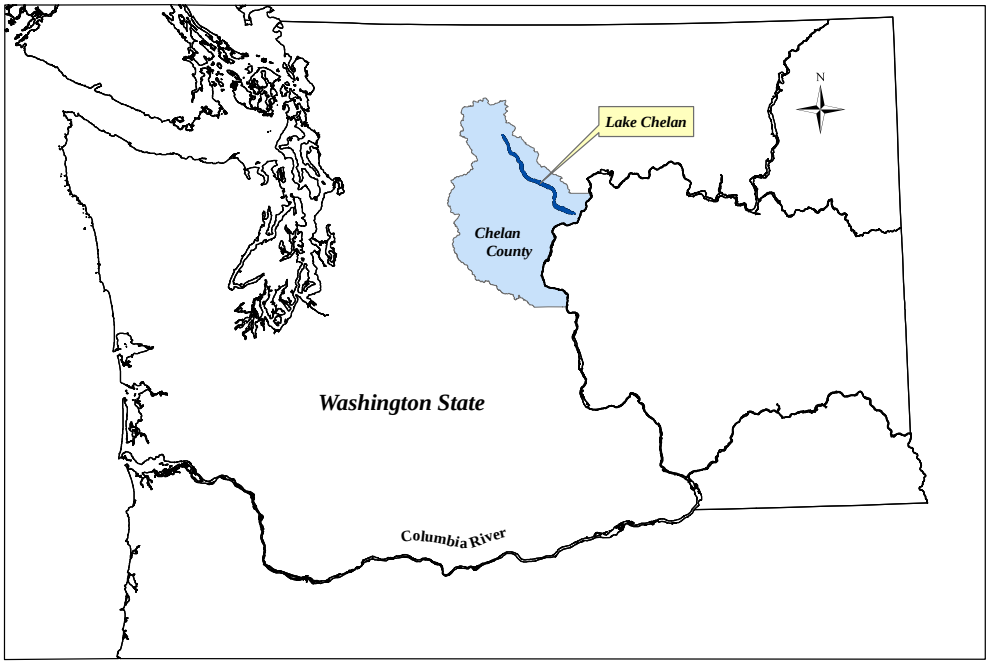

Figure 1. Location of Lake Chelan.

The ultra-oligotrophic status of the lake was determined by various water quality studies and is now threatened due to population growth pressures (Seiders et al., 1997). Phosphorus was identified as the limiting nutrient in Lake Chelan during the comprehensive Lake Chelan Water Quality Assessment (Patmont et al., 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 plan is to maintain the ultra-oligotrophic condition of the lake. It is hypothesized that this goal can be attained by keeping the epilimnetic total phosphorus concentration in the lower basin (Wapato basin) below 4.5 µg/L. Wapato basin is considered to be more sensitive to inputs of total phosphorus (TP) than the upper basin.

The epilimnetic water quality criterion for TP concentration not to exceed 4.5 µg/L was developed from a Total Maximum Daily Load (TMDL) study for phosphorus in the lower Lake Chelan basin. 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. The TMDL identified sources of Total Phosphorus (TP) and TP loading from those sources. TP limits were set for various land uses so that epilimnetic TP value would not exceed 4.5 µg/L. An estimate of the mean epilimnetic TP concentration is needed to determine if the water quality and the TMDL goal is being met.

In 1996 a water quality study was conducted in the Wapato basin to determine if TP levels were meeting TMDL goals. The 1996 volume weighted, mean summer epilimnetic TP concentration was found to be less than 2.6 µg/L, well below the TMDL target criterion (Sargeant, 1997). During the 1996 study, all other water quality samples and field measurements obtained showed excellent water quality in Lake Chelan. Recommendations from that study included monitoring to ensure that the TMDL criterion continues to be met.

Project Description

The goal of the 2007 study is to determine if any changes in nutrient levels have occurred as compared to previous studies.

Sampling objectives include:

- Determine the seasonal mean epilimnetic total phosphorus concentration in the Wapato basin for comparison to the water quality criterion of 4.5 µg/L.
- Compare chlorophyll *a*; total persulfate nitrogen; and nitrite-nitrate nitrogen, dissolved oxygen, and temperature levels to results found in previous studies.

All sampling will be conducted as described in the Final Abbreviated Quality Assurance (QA) Project Plan for 1996 Water Quality Monitoring in the Wapato Basin of Lake Chelan (Sargeant, 1996). Epilimnetic total phosphorus concentrations will be determined as described in Seiders et al. (1997).

The study area and sample sites are presented in Figure 2. Seven water quality sample events will occur at evenly spaced intervals between May and September 2007.

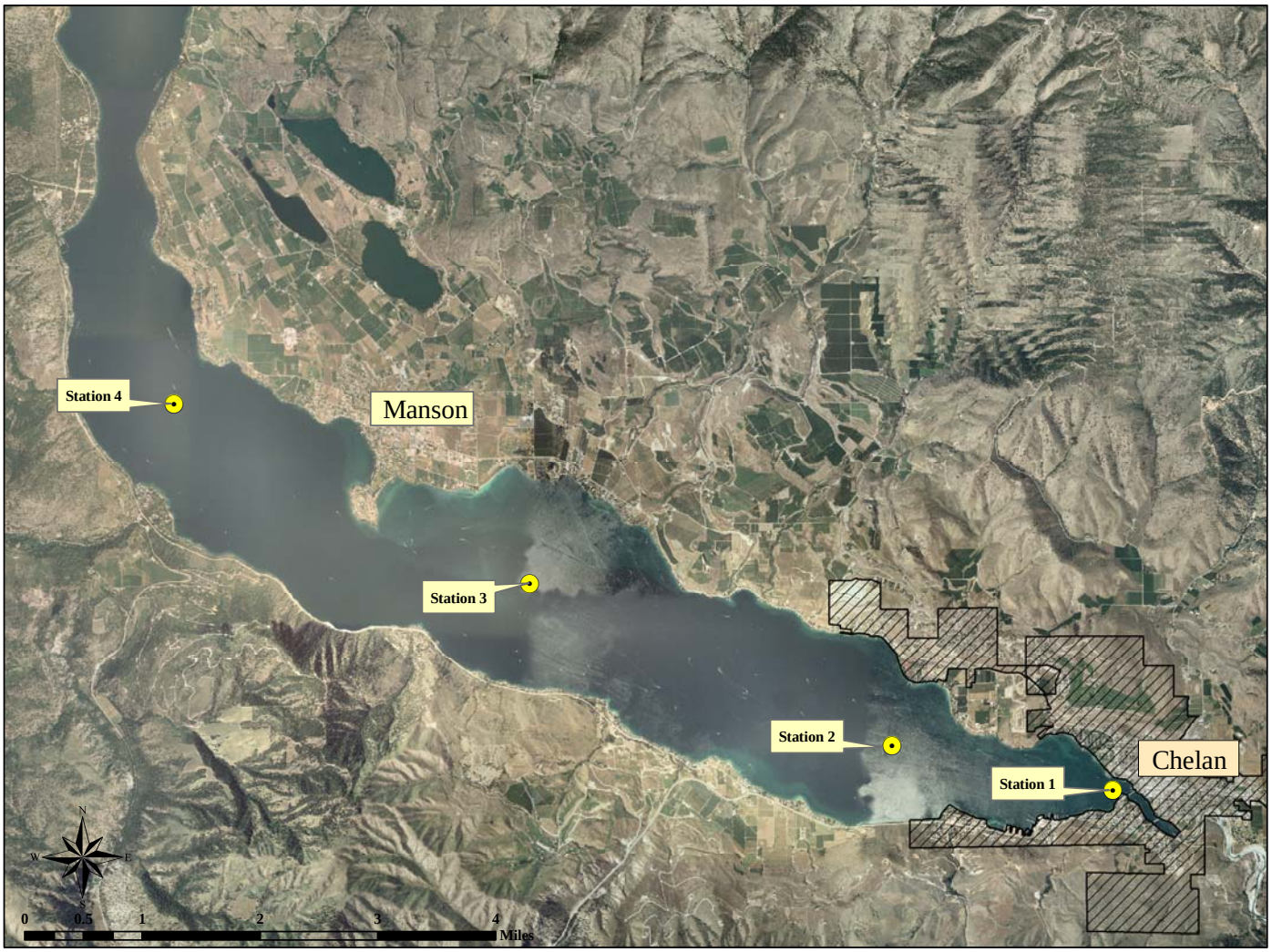

Figure 2. Lake Chelan Wapato basin sample sites.

Possible project constraints include: distance from the analytical laboratory and having to ship samples. Chlorophyll *a* samples will be filtered, placed in acetone-filled tubes, and shipped in the dark at – 20°C. Chlorophyll filters need to be shipped on dry ice to maintain temperature.

Organization and Schedule

The following individuals are involved in the project (all are Washington State Department of Ecology employees).

Table 1. Project staff and responsibilities.

Name/Address	Title	Responsibilities
Debby Sargeant Environmental Assessment Program Directed Studies Unit (360) 407-6772	Project Manager/ Principal Investigator	Responsible for project management, completion of field sampling, analysis of project data, Environmental Information Management (EIM) data entry, and preparation of a project report.
Chris Coffin Environmental Assessment Program Central Regional Office (509) 454-4257	Co-Principal Investigator	Develops Quality Assurance Project Plan and assists with field surveys when needed.
George Onwumere Environmental Assessment Program Freshwater Monitoring Unit (360) 407-6730	Directed Studies Unit Supervisor	Responsible for internal review of the project Quality Assurance Project Plan and approving the Quality Assurance Project Plan and project budget.
Stuart Magoon Manchester Environmental Laboratory (360) 871-8801	Director, Manchester Environmental Laboratory	Responsible for approving the project Quality Assurance Project Plan.
Pam Covey Manchester Environmental Laboratory (360) 871-8860	Manchester Environmental Laboratory Staff	Responsible for coordinating requests for analysis, scheduling the processing of analytical samples, and providing project data.
Gary Arnold Environmental Assessment Program Central Regional Office (509) 454-4244	Section Manager, Eastern Operations Section, Environmental Assessment Program	Responsible for providing technical assistance in the implementation of QA requirements and reviewing/approving the project Quality Assurance Project Plan.
William R. Kammin Environmental Assessment Program (360) 407-6964	Quality Assurance Officer, Ecology	Responsible for reviewing and approving the project Quality Assurance Project Plan.
Denise Mills Water Quality Program Central Regional Office (509) 457-7107	Section Manager	Responsible for internal review of the project Quality Assurance Project Plan and approving the final Quality Assurance Project Plan.

The schedule for this project is as follows:

Sample Period	
Field Sampling Surveys	May – September 2007
Environmental Information System (EIM) Data Set	
EIM Data Engineer	Debby Sargeant
EIM User Study ID	CCOF0004
EIM Study Name	2007 Lake Chelan Wapato Basin TMDL Effectiveness Monitoring for Total Phosphorus
EIM Completion Due	June 30, 2008
Final Report	
Author Lead	Debby Sargeant
Schedule	
Draft Due to Supervisor	February 1, 2008
Draft Due to Client/Peer Reviewer	March 30, 2008
Draft Due to External Reviewer	March 30, 2008
Final Report Due	June 30, 2008

No limitations on the schedule are noted with the exception of additional unplanned work load.

The total Manchester Environmental Laboratory budget is $7,728 and described in Table 2. Costs include a 50% discount for Manchester Environmental Laboratory.

Table 2. Estimated Manchester Environmental Laboratory cost for Lake Chelan study.

Station	Sample Depth (meters)	Total Phosphorus $25	Total Persulfate Nitrogen $25	Nitrite-nitrate Nitrogen $16	Chlorophyll *a* $39
1	0.3	1	1	1	1
2	0.3	1	1	1	1
2	10	1	1	1	1
2	20	1	1	1	1
3	0.3	1	1	1	1
3	10	1	1	1	1
3	20	1	1	1	1
4	0.3	1	1	1	1
4	10	1	1	1	1
4	20	1	1	1	1
Equipment Blank		1	1	1	1
Field Duplicate		1	1	1	1
Cost		$300	$192	$144	$468
Per Sample Event Cost: $ 1,104			Total Sample Cost: $ 7, 728		

Quality Objectives

Sampling, laboratory analysis, and data assessment steps have several sources of error that should be addressed by data quality objectives. Data quality objectives are statements of the precision, bias, and lower reporting limits necessary for the data to address project objectives which together express data accuracy.

Precision

Precision for the total phosphorus sampling is fully described in Seiders et al. (1997). Precision of other laboratory and field parameters will be estimated through the use of laboratory and field split samples. These results will be used to estimate sources of variability in the data and can help to determine if sampling and analytical protocols are adequate. Duplicate field samples will be used to estimate total variation (field and laboratory), expressed as the percent relative standard deviation (RSD). Duplicates are two field samples collected sequentially at the same site and as close as possible in time. The percent RSD is calculated by dividing the standard deviation of two or more values by their mean, and then multiplying by 100. Recommendations from (1) Replicate Precision for 12 TMDL Studies and (2) Recommendations for Precision Measurement Quality Objectives for Water Quality Parameters (Mathieu, 2006) will be used to determine data acceptability. Table 3 describes measurement quality objectives.

Table 3. Targets for precision and reporting limits for the measurement systems.

Analysis	Method	Duplicate Samples Relative Standard Deviation (RSD)	Reporting Limits and Resolution
Field Measurements			
Water Temperature[1]	Hydrolab MiniSonde®	+/- 0.1° C	0.01° C
Specific Conductivity[2]	Hydrolab MiniSonde®	+/- 0.5%	0.1 umhos/cm
pH[1]	Hydrolab MiniSonde®	0.05 SU	1 to 14 SU
Dissolved Oxygen[1]	Hydrolab MiniSonde®	5% RSD	0.1 - 15 mg/L
Dissolved Oxygen[1]	Winkler Titration	+/- 0.1 mg/L	0.01 mg/L
Laboratory Analyses			
Chloride	EPA 300.0	5% RSD[3]	0.1 mg/L
Nitrate/Nitrite	4500-NO_3^- I	10% RSD[3]	0.01 mg/L
Total Persulfate Nitrogen	SM 4500-NO_3^-B	10% RSD[3]	0.025 mg/L
Total Phosphorous	EPA 200.8	10% RSD[3]	0.001 mg/L

[1] as units of measurement, not percentages.
[2] as percentage of reading, not RSD.
[3] replicate results with a mean of less than or equal to 5X the reporting limit will be evaluated separately.
SM = Standard Methods for the Examination of Water and Wastewater, 20th Edition (APHA, AWWA and WEF, 1998).
EPA = EPA method code.

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. 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 and how the bias might affect the sample results and their interpretation should be described. If blank sample results suggest the presence of bias, prompt attention will be given to quality assurance results and corrective actions taken in the laboratory or the field.

Completeness and Representativeness

Completeness is a measure of the amount of valid data needed to meet the goals defined for the uses of the data. Representativeness requires that the data represent the environmental condition as related to the goals and objectives. Both are fully described in Seiders et al. (1997).

Comparability

Comparability of TP and chlorophyll *a* data to previous studies is a concern for this project. The initial assessment in 1989, the Washington State Department of Ecology (Ecology) used a private laboratory for sample analysis. In 1996 Ecology's Manchester Environmental Laboratory (MEL) conducted all the laboratory analysis. They used a spectrophotometric analysis technique to determine low-level phosphorus concentrations. This method had a lower reporting limit of 3.0 µg/L for low-level phosphorus.

During that period, MEL was working on developing an ICP-MS low-level TP analysis method with a lower reporting limit of 1.0 µg/L. The ICP-MS method is more appropriate for the Lake Chelan project; where, during the 1996 study, only three out of 77 total phosphorus samples were greater than the spectrophotometric lower reporting limit of 3.0 µg/L.

Chlorophyll *a* analytical methods have also changed at MEL since the 1996 study. In 1996 a spectrophotometric technique was used with a lower reporting limit of 0.50 µg/L. MEL currently uses a flurometric technique with a lower reporting limit of 0.05 µg/L. The lower level technique will again be more appropriate for this Lake Chelan project; where, in 1996 approximately 30% of the chlorophyll *a* results were below the reporting limit.

Changes in laboratory techniques and method biases will be taken into consideration when comparing data from different years and studies.

Sampling Design and Measurement Procedures

The sampling design, sampling procedures, and measurement procedures are fully described in a QA Project Plan by Sargeant (1996) and Seiders et al. (1997). The study design duplicates the study done in 1996 (Sargeant 1997). The study area and sample sites are presented in Figure 2; geographic coordinates for each station are included in Table 4.

Table 4. Wapato basin sampling locations.

Station	Longitude	Latitude
1	-120.02425	47.84138
2	-120.06658	47.84342
3	-120.13990	47.86205
4	-120.19724	47.88404

Seven water quality sample events will occur at evenly spaced intervals between May and September 2007. Laboratory samples will be obtained for low-level total phosphorus (TP), nitrite-nitrate nitrogen (NO2-3), total persulfate nitrogen (TPN), chlorophyll *a*, and phaeopigments.

Table 5 summarizes the parameters, laboratory methods, and range of expected values. Field sampling and measurement protocols will follow those listed in the Watershed Ecology Section (previously the Watershed Assessment Section) Protocols Manual (Ecology, 1993). Sampling will occur at three different depths (0.3, 10 and 20 meters) at stations 2, 3, and 4 and at one depth (0.3 meters) at station 1. A Kemmerer water sampler will be used to obtain laboratory samples. All water samples will be transferred from the Kemmerer water sampler to pre-cleaned containers supplied by Ecology's MEL. Sample containers will be labeled with the date, time, site, parameter, and laboratory number. Samples will be placed immediately in a dark cooler on ice. Chlorophyll *a* samples will be filtered after sampling under incandescent light. Filters will be placed in acetone-filled tubes and stored on ice in the dark. All samples will be shipped, or delivered to MEL, within 24 hours of collection via Horizon Air and Ecology courier.

Table 5. Summary of laboratory measurements, methods, and expected ranges.

Parameter	Bottle	Preservative	Holding Time	EPA Method	Reporting Limit	Expected Range
TP ICP-MS	60 mL clear wide-mouth poly, re-acidified	Cool to 4°C , pre-acidified with HCL	28 days	EPA 200.8	1 µg/L	1.2 - 4.0 µg/L
NO3-2	125 mL clear poly, pre-acidified	Cool to 4°C , pre-acidified with H_2SO_4	28 days	SM 4500-NO_3-I	0.01 mg/L	< 10 – 62 µg/L
TPN	125 mL clear poly, pre-acidified	Cool to 4°C , pre-acidified with H_2SO_4	28 days	SM 4500- NO_3-B	0.025 mg/L	< 10 – 113 µg/L
Chloro *a* Phaeo *a*	500 mL amber poly	After filtration store filters in 90% acetone, in the dark at -20°C.	28 days from filtration to analysis	SM 10200H(3)	0.05 µg/L	< 0.5 – 3.1 µg/L

SM: Standard Methods for the Examination of Water and Wastewater, 20th Edition.
EPA: Method 200.8, Modified for Phosphorus, EPA Methods for Chemical Analysis of Water and Wastes, EPA 600/4-79-020.

Vertical profiles for temperature, conductivity, pH, and dissolved oxygen will be obtained using a multi-parameter probe. Dissolved oxygen readings will be paired with Winkler field verification measurements to evaluate the accuracy of the meter.

Vertical profile readings will be obtained at the surface (0.3 meters) and at one-meter increments until a > 1.0°C difference in temperature is seen. After the temperature stabilizes, readings can be obtained every five meters.

Secchi disc readings will be obtained at each site. Secchi readings will be obtained on the shady side of the boat. Field notes will contain and include information as described in the Guidelines for Preparing Quality Assurance Project Plans for Environmental Studies (Lombard and Kirchmer, 2004). No chain-of custody procedures will be followed.

Quality Control

Quality Control procedures are fully described in Sargeant (1996) and Seiders et al. (1997).

Total variation for field sampling and analytical variation will be assessed by collecting replicate samples in addition to lab duplicates. Replicate samples will be collected at a rate of 10% for laboratory parameters and dissolved oxygen field measurements. Field blanks will be obtained for each laboratory parameter after sampling.

Laboratory samples will be analyzed at the MEL. The laboratory's data quality objectives and quality control procedures are documented in the Lab Users Manual (MEL, 2005) and the MEL Quality Assurance Manual. MEL will follow standard quality control procedures (MEL, 2005). In addition the MEL will analyze a 5 µg/L analytical spike prepared in the laboratory for total phosphorus to determine ICP-MS performance at low levels. The results of the laboratory quality control sample analyses will be used to determine if measurement quality objectives have been met.

Field sampling measurements will follow quality control protocols described in WAS (1993). All meters used to measure water quality field parameters will be checked and calibrated as appropriate against known standards at the start and end of each sampling day. Meter calibration will be done in accordance with the manufacturer's directions.

Data Management Procedures

Data reduction, review, and reporting will follow the procedures outlined in MEL's Lab Users Manual (MEL, 2005). Laboratory staff will be responsible for internal quality control validation, proper data transfer, and reporting data to the project manager via the Laboratory Information Management System (LIMS).

All water quality data will be entered from LIMS into Ecology's EIM system by the project manager or a designee. Data will be verified and a random 10% of the data entries will be independently reviewed for errors. If errors are detected, another 10% will be reviewed until no errors are detected.

The project manager will validate the quality of both data received from the laboratory and data collected in the field in relation to the measurement quality objectives (MQOs). The review will be performed after three sample events. Adjustments to field or laboratory procedures or MQOs may be needed after such a review. Clients and QA Project Plan signatories will be notified of major changes. Data that does not meet MQOs may be approved for use by the project manger but this data will be qualified appropriately.

Data analysis will include calculation of the mean volume-weighted TP concentration for comparison to the TMDL threshold of 4.5 µg/L as well as comparison of other parameters to historic levels. Statistical analysis and graphical data representation of the data may be made using WQHYRO (Aroner, 2003) and EXCEL (Microsoft, 2001) software.

Data Verification and Validation

Laboratory-generated data reduction, review, and reporting will follow the procedure outlined in the MEL lab Users Manual (MEL, 2005). Lab results will be checked for missing and improbable data. Any estimated results will be qualified and their use restricted as appropriate. A standard case narrative of laboratory Quality Assurance/Quality Control results will be sent to the project manager from MEL for each set of samples.

Field notebooks will be checked for missing or improbably measurements before leaving each site. The EXCEL® workbook file containing field data will be labeled *Draft* until data verification and validation are completed. Data entry will be checked by the project manager against the field notebook data for errors and omissions. Valid data will be moved to a separate file labeled *Final*.

Data received from LIMS will be checked for omissions against the Request for Analysis forms by the field lead. Data can be in EXCEL® spreadsheets (Microsoft, 2001) or downloaded tables from Ecology's EIM system. These tables and spreadsheets will be marked *Draft* until data validity is completed. Field replicate sample results will be compared to the MQOs. Data requiring additional qualifiers will be reviewed by the project manager. The project manager examines the complete data package in order to determine compliance with procedures outlined in the QA Project Plan and Standard Operating Procedures. The project manager is also responsible for data validation by ensuring that the MQOs for precision, bias, and sensitivity are met. A final report will be prepared by the Principal Investigator in Ecology's Central Regional Office and distributed to regional Water Quality Program staff. The final report will also be available on Ecology's publications website.

After data validity and entry tasks are completed, all field and laboratory data will be entered into a file labeled *Final*, and then into the EIM system by the project manager or a designee. EIM data will be independently reviewed by another Environmental Assessment Program staff person for errors. At the end of the field collection phase of the study, the data will be compiled in a data summary.

Data Quality (Usability) Assessment

Data quality assessment procedures are described in Sargeant (1996) and Seiders et al. (1997).

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