Quality Assurance Project Plan

Evaluation of Candidate Freshwater Sediment Reference Sites

by
Nigel Blakley

Environmental Assessment Program
Washington State Department of Ecology
Olympia, Washington 98504-7710

July 2008

Publication Number 08-03-111

Publication Information

This plan is available on the Department of Ecology's website at www.ecy.wa.gov/biblio/0803111.html.

Data for this project will be available on Ecology's Environmental Information Management (EIM) website at www.ecy.wa.gov/eim/index.htm. Search User Study ID, NBLA0006.

Ecology's Project Tracker Code for this study is 08-074.

303(d) Listings Addressed in this Study: None

For more information contact:

Carol Norsen
Environmental Assessment Program
P.O. Box 47600
Olympia, WA 98504-7600
E-mail: CNOR461@ecy.wa.gov
Phone: 360-407-7486

Washington State Department of Ecology - www.ecy.wa.gov/

- Headquarters, Olympia 360-407-6000
- Northwest Regional Office, Bellevue 425-649-7000
- Southwest Regional Office, Olympia 360-407-6300
- Central Regional Office, Yakima 509-575-2490
- Eastern Regional Office, Spokane 509-329-3400

Quality Assurance Project Plan

Evaluation of Candidate Freshwater Sediment Reference Sites

July 2008

Approved by:

Signature:	Date: July 2008
Dave Sternberg, Client, Toxics Cleanup Program, Headquarters	
Signature:	Date: July 2008
Martha Hankins, Unit Supervisor, Toxics Cleanup Program, Headquarters	
Signature:	Date: July 2008
Dave Bradley, Section Manager, Toxics Cleanup Program, Headquarters	
Signature:	Date: July 2008
Nigel Blakley, Project Manager, Toxics Studies Unit, EAP	
Signature:	Date: July 2008
Janice Sloan, EIM Data Engineer, Toxics Studies Unit, EAP	
Signature:	Date: July 2008
Dale Norton, Unit Supervisor, Toxics Studies Unit, EAP	
Signature:	Date: July 2008
Will Kendra, Section Manager, Statewide Coordination Section, EAP	
Signature:	Date: July 2008
Stuart Magoon, Director, Manchester Environmental Laboratory, EAP	
Signature:	Date: July 2008
Bill Kammin, Ecology Quality Assurance Officer	

Signatures are not available on the Internet version.
EAP - Environmental Assessment Program
EIM - Environmental Information Management system

Table of Contents

Page

Abstract 5

Background 5

Project Description 6

Organization and Schedule 7
- Organization 7
- Schedule 8

Quality Objectives 9

Sampling Process Design (Experimental Design) 10
- Site selection criteria 10
- Sampling design 11

Sampling Procedures 14

Measurement Procedures 17
- Chemistry 17
- Bioassays 18

Quality Control Procedures 19
- Field 19
- Laboratory 19

Data Management Procedures 22

Audits and Reports 23
- Audits 23
- Reports 23

Data Verification 24

Data Quality (Usability) Assessment 24

References 25

Appendices 26
- Appendix A. Project Analytes 27
- Appendix B. Field Log Sheet 28

Abstract

This 2008 study will evaluate freshwater sediments for toxicity and chemical contamination at nine candidate reference locations throughout Washington State. Standard biological tests, or bioassays, will be used to screen the sediment samples for toxicity. Analyses will also be conducted for a range of common metals and organic contaminants. Results from this study will provide a baseline for comparison in future investigations of polluted sediments elsewhere in the state.

Each study conducted by the Washington State Department of Ecology must have an approved Quality Assurance Project Plan. The plan describes the objectives of the study and the procedures to be followed to achieve those objectives. After completion of the study, a final report describing the study results will be posted to the Internet.

Background

Washington State's regulation governing ecological standards for sediments allows biological tests, called bioassays, to be used for evaluating sediment toxicity. The regulation, known as the Sediments Management Standards, does not prescribe any particular bioassays to be used in investigations of contaminated freshwater sediments. However small freshwater crustaceans (*Hyalella*) or aquatic midge larvae (*Chironomus*) are commonly used as the test organisms. In these tests, a reduction in growth of the organisms or an increase in their mortality is interpreted as evidence for toxicity of the test sediment. A third commonly-used test, Microtox®, uses luminescent bacteria, and here a reduction in bacterial light production is the indicator of toxicity.

To demonstrate that adverse effects on the test organisms are due to toxic chemicals in a sediment sample, it is important to show that these effects do not occur when uncontaminated sediments are tested. This comparison may involve samples collected outside the contaminated area but nearby, so that the test and reference sediment samples are very similar and differ, ideally, only in the presence or absence of chemical pollutants.

In practice, there can be difficulties in obtaining a suitable reference sample in investigations of contamination. For example, sites with contaminated sediments are often located in populated areas where there are a variety of potential sources of pollution such as stormwater pipes, spills at industrial facilities, and runoff from parking lots. As a result, sediment collected from outside the boundaries of an area under investigation may also be polluted, and therefore not be suitable for use as an uncontaminated reference sample in toxicity testing.

This project will test sediments at selected sites statewide to establish baseline conditions that can be used for reference in future investigations of contaminated sediments. To provide a comprehensive characterization, the sediments will be tested for a broad range of metals and organic compounds in addition to a variety of bioassay tests for toxicity.

Project Description

The goal of this project is to facilitate the testing of contaminated freshwater sediments for toxicity by establishing baseline conditions for comparison at reference sites distributed across Washington State. Bioassay testing of contaminated sediments for toxicity provides important information for making decisions on the need for cleanup or control of pollution sources.

To support this goal, the primary objective of this project is to broadly characterize the chemistry, physical properties, and toxicity (assessed with bioassays) of sediment samples from each of the selected sites. To ensure that the sites are representative of a wide range of conditions across the state, locations were selected from each of the major ecoregions designated by U.S. Environmental Protection Agency (EPA).

The study will be conducted by the Washington State Department of Ecology (Ecology) Environmental Assessment Program. A final report is anticipated by April 2009.

Organization and Schedule

Organization

The following people are involved in this project.

Table 1. Organization of project staff and responsibilities.

Staff (all are EAP except client)	Title	Responsibilities
Nigel Blakley Toxics Studies Unit, SCS (360) 407-6770	Project Manager	Writes the QAPP, oversees field sampling and transportation of samples to the laboratory, conducts QA review of data, analyzes and interprets data, and writes the draft report and final report.
Janice Sloan Toxics Studies Unit, SCS (360) 407-6553	Field Assistant and EIM Data Engineer	Assists in preparation of the QAPP, helps collect samples and records field information, assists in data analysis and report preparation, and enters results from this study in EIM.
Mary Ann Rempel-Hester (253) 922-4296	Nautilus Environmental	Bioassay testing
John Weakland Organic Chemistry, MEL (360) 871-8820	Supervisor	Oversees organic chemistry analyses.
Dean Momohara Inorganic Chemistry, MEL (360) 871-8808	Unit Supervisor	Oversees inorganic chemistry analyses.
Karin Feddersen MEL (360) 871-8829	Quality Assurance Coordinator	Oversees contract lab services.
Dale Norton Toxics Studies Unit, SCS (360) 407-6765	Unit Supervisor	Provides internal review of the QAPP, approves the budget, and approves the final QAPP.
Will Kendra SCS (360) 407-6698	Section Manager	Reviews the project scope and budget, tracks progress, reviews the draft QAPP, and approves the final QAPP.
Dave Sternberg Toxics Cleanup Program (360) 407-7146	EAP Client	Clarifies scopes of the project, provides internal review of the QAPP, and approves the final QAPP.
Stuart Magoon Manchester Environmental Laboratory (360) 871-8801	Director	Approves the final QAPP.
William R. Kammin (360) 407-6964	Ecology Quality Assurance Officer	Reviews the draft QAPP and approves the final QAPP.

EAP – Environmental Assessment Program
SCS – Statewide Coordination Section
EIM – Environmental Information Management system
MEL – Manchester Environmental Laboratory
QAPP – Quality Assurance Project Plan

Schedule

Table 2. Proposed schedule for completing field and laboratory work and data entry into EIM and reports.

Field and laboratory work	
Field work completed	September 2008
Laboratory analyses completed	November 2008
Environmental Information System (EIM) system	
EIM data engineer	Janice Sloan
EIM user study ID	NBLA0006
EIM study name	Freshwater Sediments Bioassay Reference Sites
Data due in EIM	April 2009
Final report	
Author lead	Nigel Blakley
Schedule	
Draft due to supervisor	January 2009
Draft due to client/peer reviewer	February 2009
Draft due to external reviewer	February 2009
Final report due on web	April 2009

Quality Objectives

Quality objectives for this project are to obtain data that broadly characterize the background condition of freshwater sediments from locations across Washington State. For the purposes of this study, the term *background* denotes a waterbody location where the only known or likely chemical contamination source of significance is atmospheric deposition. This is consistent with the definition being used in concurrent studies of chemical contaminant levels in fish tissue (Johnson, 2008).

In practice, the application of this definition for background conditions is more difficult for river systems than lakes. Because Washington rivers typically flow through areas of agricultural and urban land uses, they receive surface runoff, stormwater, and other potential sources of chemicals associated with these land uses. Thus while it is possible to identify river locations where there are no likely local sources of contamination, it may be difficult to exclude the possibility of low-level contamination from current or historical upstream sources.

Because of this uncertainty, the locations selected for this project are best described as potential *reference* locations. If chemistry results for any of the sampling sites show evidence of contamination, Ecology may eliminate the proposed reference location from further consideration as an acceptable source of baseline data. However, the sampling design for this project is not intended to provide a detailed spatial characterization of each selected waterbody. Large spatial variability in the concentrations of the chemicals of interest is not expected at the proposed reference locations. The assumption of low spatial variability can be reexamined in the future, when additional sampling of the selected locations is conducted to make comparisons of reference and contaminated freshwater sediments.

With this perspective, the primary objective for this project is to obtain data that meet both the method description publication requirements and the testing laboratories' method-specific quality control requirements. A secondary objective is to obtain data that meet quality recommendations in Ecology sediment sampling guidance[1]. These recommendations may be used to be assess the data quality in the study report.

[1] Ecology, 2003. See Tables 5, 11, 13, 15.

Sampling Process Design (Experimental Design)

Site selection criteria

The first step in the sampling design for this project was to develop criteria for selecting locations for freshwater sediment reference sites. These following criteria were developed:

- Provide approximately equal representation of locations east and west of the Cascade Mountains.
- Distribute locations to represent the larger EPA Level III ecoregions in Washington state[1]. The following provides a brief explanation of ecoregions:

  Designed to serve as a spatial framework for environmental resource management, ecoregions denote areas within which ecosystems (and the type, quality, and quantity of environmental resources) are generally similar… The approach used to compile [the ecoregion] map is based on the premise that ecological regions can be identified through the analysis of the patterns and the composition of biotic and abiotic phenomena that affect or reflect differences in ecosystem quality and integrity.... These phenomena include geology, physiography, vegetation, climate, soils, land use, wildlife, and hydrology.[2]

  The use of ecoregions to broadly distribute sampling locations over a range of geological, climatic, and physiographic conditions throughout Washington was suggested by a study of freshwater sediment baseline contaminant levels in Minnesota. That state's ecoregions were used in the study design to select representative lakes for sampling (Heiskary, 1996).
- Select locations where the only known or likely significant source of toxic chemicals is atmospheric deposition, and where this condition is not expected to change in future. The latter consideration favors waterbodies where land use restrictions are likely to prevent future development, such as lakes located in state or national parks.
- Where possible, include locations that may be relevant to areas with known or suspected sediment contamination. This ensures that future investigations of these areas will have previously characterized, and relevant reference sites will be available for comparison if bioassay testing is conducted. Examples of such areas include segments of the Columbia River, Lake Roosevelt, the Spokane River, and central Puget Sound lowlands.
- Use locations where sampling is practical. Each site was reviewed for considerations such as sampling boat accessibility, the presence of soft sediments that can be penetrated by a sampling grab, and their availability at shallow to moderate depths (generally 30 feet or less).

[1] Available on the Ecology website at www.ecy.wa.gov/apps/watersheds/maps/state/level3_ecoregions.html
[2] From US EPA website at www.epa.gov/wed/pages/ecoregions/level_iii.htm

Sampling design

Twelve candidate sites were selected using the criteria described above. Nine of these sites will be sampled, and three will serve as contingency sites. The three contingency sites are Cranberry Lake (Island County), Wynoochee Lake (Grays Harbor County), and Burbank Slough (Walla Walla County). They will serve as alternatives if problems arise during field work, such as a road closure that delays access to one of the nine primary sites. The 12 sites are described in Table 3, and their locations are shown in Figure 1.

Table 3. Sampling sites for this study.

Site	EPA Level III Ecoregion	County	Adjacent land use
Western Washington			
Lake Ozette – Olympic National Park	Coast Range	Clallam	Protected shoreline (National Park)
Columbia River – Beacon Rock State Park[1]	Cascades	Skamania	Protected shoreline (State Park)
Mountain Lake – Moran State Park	Puget Lowland	Island	Protected shoreline and drainage (State Park)
Chester Morse Reservoir	Cascades	King	Protected shoreline and drainage (Cedar River Watershed, owned by City of Seattle and managed for drinking water supply)
Contingency site: *Cranberry Lake* – Deception Pass State Park	Puget Lowland	Island	Protected shoreline (State Park)
Contingency site: *Wynoochee Lake* – Olympic National Forest	Coast Range	Grays Harbor	Protected shoreline (National Forest)
Eastern Washington			
Lake Wenatchee – Wenatchee National Forest	North Cascades	Chelan	State Park and National Forest
Browns Lake – Colville National Forest	Northern Rockies	Pend Oreille	National Forest
Little Spokane River[1]	Northern Rockies	Spokane	Protected shoreline adjacent to sampling location (Little Spokane Natural Area and State Park). Upstream urban land use (town of Dartford).
Kepple Lake, Turnbull National Wildlife Refuge	Columbia Plateau	Spokane	National Wildlife Refuge
Lyons Ferry Park[1] (confluence of Palouse and Columbia Rivers)	Columbia Plateau	Franklin	Recreational park and wildlife areas (U.S. Army Corps of Engineers)
Contingency site: *Burbank Slough*[1], McNary National Wildlife Refuge (Columbia River)	Columbia Plateau	Walla Walla	National Wildlife Refuge

1 Suitability of these river locations as reference sites will be reevaluated after reviewing results from the planned chemical and toxicity testing. As discussed in the text, there are uncertainties about the possibility of contamination due to current or historic upstream sources.

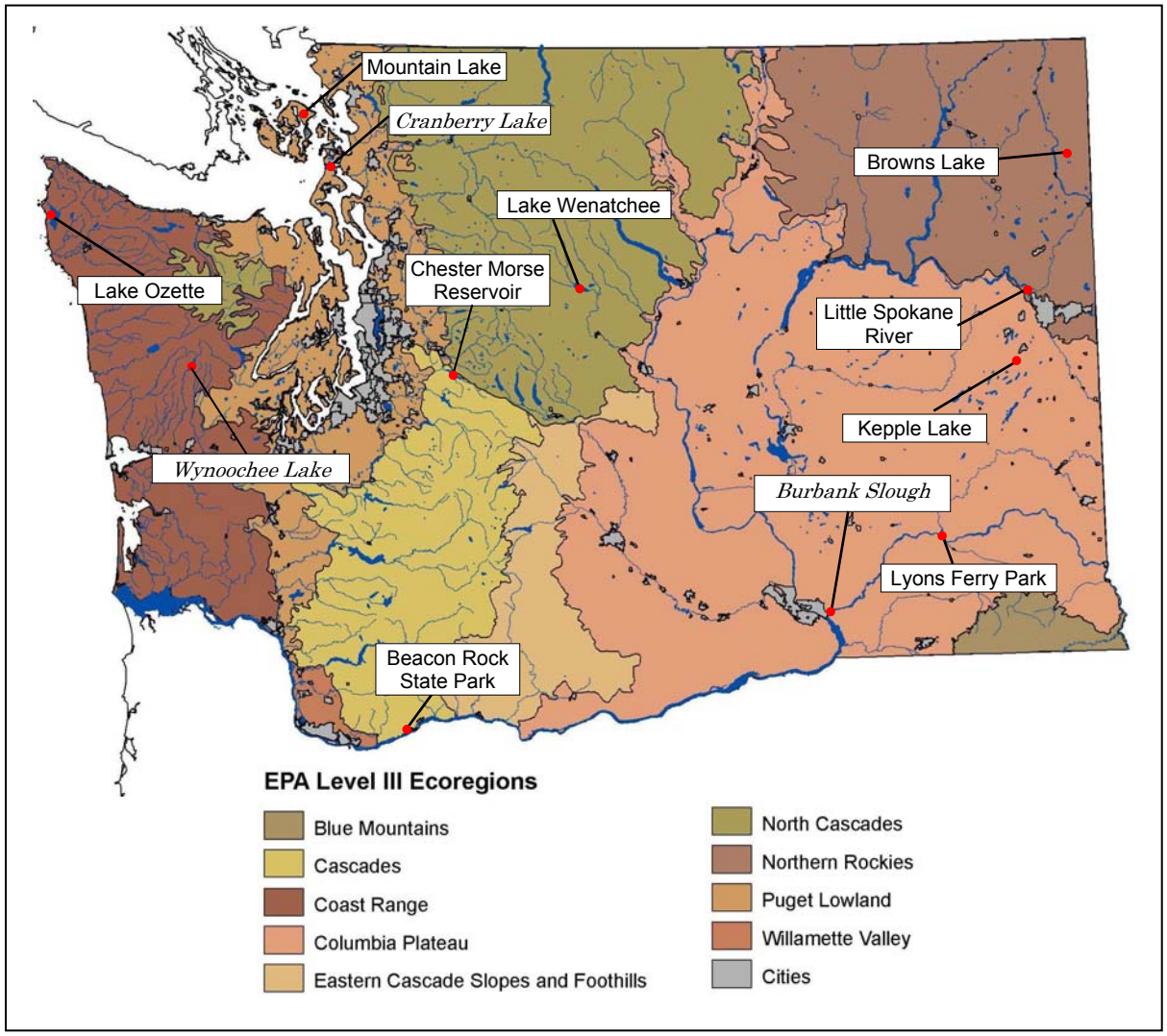

Figure 1. Locations of sampling sites for this study. Contingency sites are shown in italics.

At each site, sediment will be collected at three sampling locations (stations) to encompass a range of sediment grain sizes available at the site. For example, sampling at a shallow location exposed to wave action from the prevailing wind direction should yield a coarser grain size sediment sample than found at a deeper, sheltered location.

Sampling Procedures

The sample collection procedure will vary with site conditions. At most sites, sediments will be collected using a stainless steel Standard Ponar® grab sampler operated from an Ecology research boat equipped with a winch to lower and raise the sampler. The maximum sample volume collected by this sampler is about 7.25 liters. At sites with soft silty sediments, samples will be collected using a stainless steel large Ekman grab (Wildlife Supply Company), with a maximum volume of 12 liters.

An acceptable grab sample will penetrate at least 10 cm (Standard Ponar® or Ekman samplers) and have a nearly undisturbed surface. At each sampling station, sediment from at least three acceptable grab samples will be taken from the sampler and combined in a precleaned stainless steel container. Only sediment that has not contacted the walls of the sampling device will be taken. The combined sediment will then be mixed thoroughly to prepare a single composite sample. Aliquots from this composite sample will then be used to fill each of the laboratory containers. Large items such as rocks or twigs will be removed with precleaned stainless steel forceps from the composite sample before filling the containers. More than three grab samples will be combined if needed to obtain sufficient material to fill the containers.

An exception to this procedure is required to avoid the volatilization of ammonia and sulfide during mixing. Subsamples to be analyzed for these chemicals will be taken directly from the first grab sample prior to removal of the remaining sediment for mixing. The ammonia and sulfide subsamples will be collected with minimal physical disturbance using a stainless steel spoon and will be carefully transferred to completely fill a sample jar, with no headspace.

At sites where the winch-equipped research boat cannot be used, sampling with the heavy Standard Ponar® is impractical and samples will be collected with a lighter grab (Petite Ponar® or Ekman) that can be raised and lowered manually. This applies to the Little Spokane River, where summer flow is expected to be too low for operating the research boat. This also applies to the Chester Morse Reservoir, where sampling must be conducted from a boat provided by the City of Seattle Public Utilities personnel.

Procedures for processing the sediment when using the Petite Ponar® will be the same as described with the Standard Ponar® or Ekman, except that up to six grab samples may be needed, assuming that about six liters of sediment are required to fill all of the laboratory containers (Table 4).

Sampling station locations will be recorded from a GPS instrument. Where possible, locations will be chosen that can also be associated with permanent landmarks, such as a bridge or unique shoreline feature.

A field log will be maintained, describing the GPS coordinates of each sampling location and any visual descriptions, such as distance and direction to identifiable landmarks. Information about the quality of each sample grab will also be recorded in the log.

Containers, sample preservation, and holding times for the samples are shown in Table 4.

Table 4. Sample containers, preservation methods, and holding times.

Analysis	Container	Preservation	Holding Time	Sediment Volume
Chemistry				
Grain size	8 oz polyethylene jar	Cool to 4° C	6 months	1.5 liters
TOC	2 oz glass jar	Cool to 4° C	14 days (6 months if frozen)	
Percent solids	2 oz glass jar	Cool to 4° C	14 days (6 months if frozen at ≤18° C)	
Total sulfides	8 oz glass jar	Cool to 4° C – no head space, 5 mL of 2 N zinc acetate	7 days	
Ammonia	8 oz glass jar	Cool to 4° C – no head space	7 days	
Metals (ICP/MS)	8 oz glass jar	Cool to 4° C	6 months	
Mercury (CVAA)	8 oz glass jar	Cool to 4° C	28 days	
Semivolatiles (BNASQS and PAHNOAA)	8 oz glass jar (2 jars at one site, for the MS/MSD analysis)	Cool to 4° C	14 days (1 year if frozen at ≤18° C)	
Chlorinated pesticides, aroclors (PEST1PCB)	8 oz glass jar (2 jars at one site, for the MS/MSD analysis)	Cool to 4° C	14 days (1 year if frozen at ≤18° C)	
Bioassays				
Microtox®	1 gal plastic (HDPE) container (sufficient for all 3 bioassays). Supplied by testing laboratory.	Cool to 4° C, keep in dark	14 days	~4 liter
Hyalella				
Chironomus				
			Total Volume Required Per Station	5.5 liters

TOC = Total Organic Carbon
ICP/MS = Inductively Coupled Plasma Mass Spectroscopy
CVAA = Cold Vapor Atomic Absorption
MS/MSD = Matrix spike and matrix spike duplicate

BNASQS = Base/Neutral/Acids semivolatile organic compounds – Sediment Quality Standards list. Includes the following compounds: 1,2,4-Trichlorobenzene, 1,2-Dichlorobenzene, 1,3-Dichlorobenzene, 1,4-Dichlorobenzene, 2,4-Dimethylphenol, 2-Methylphenol, 3B-Coprostanol, 4-Methylphenol, Benzoic Acid, Benzyl Alcohol, Bis(2-Ethylhexyl) Phthalate, Butylbenzylphthalate, Caffeine, Cholesterol, Diethylphthalate, Dimethylphthalate, Di-N-Butylphthalate, Di-N-Octyl Phthalate, Hexachlorobenzene, Hexachlorobutadiene, Isophorone, N-Nitrosodiphenylamine, Pentachlorophenol, Phenol, 4-Nonylphenol

PAHNOAA = Polycyclic aromatic hydrocarbons – NOAA list. Includes the following compounds: Naphthalene, 2-Methylnaphthalene, 1-Methylnaphthalene, 1,1'-Biphenyl, 2-Chloronaphthalene, 2,6-Dimethylnaphthalene, Acenaphthylene, Acenaphthene, Dibenzofuran, 1,6,7-Trimethylnaphthalene, Fluorene, Dibenzothiophene, Phenanthrene, Anthracene, Carbazole, 2-Methylphenanthrene, Fluoranthene, Pyrene, Retene, Benzo(a)anthracene, Chrysene, Benzo(b)fluoranthene, Benzo(k)fluoranthene, Benzo[e]pyrene, Benzo(a)pyrene, Perylene, Indeno(1,2,3-cd)pyrene, Dibenzo(a,h)anthracene, Benzo(ghi)perylene

HDPE = high-density polyethylene

Other details about the sediment sampling will follow the Environmental Assessment Program's Standard Operating Procedure (SOP) (Blakley, 2008). The SOP includes procedures for decontamination of equipment prior to sampling, and also between sampling stations.

As noted in the SOP, the amount of sediment taken from the grab sampler for analysis varies with different project objectives, but is always less than the total available. Because of the large volume of sediment sample required at each station, all material in the sampler will be removed except for sediment in direct contact with the sampler walls.

Measurement Procedures

Chemistry

Table 5 shows the analytical method and the reporting limits for each of the analyses to be performed.

Table 5. Laboratory procedures for chemistry analyses.

Analysis	Analytical Method	Reporting Limits
Grain size	PSEP, 1986	0.1%
TOC	PSEP, 1986/1997	0.1%
Percent solids	PSEP, 1986	0.1%
Total sulfides	PSEP, 1986	5 mg/Kg, dry
Ammonia	Plumb 1981	100 µg/Kg, dry
Metals[1] (ICP/MS)	EPA Method 200.8 and 200.7	See Table 6
Total mercury (CVAA)	EPA 245.5; MEL SOP[2]	0.005 mg/Kg, dry
Semivolatiles (BNASQS and PAHNOAA)	EPA Method 8270	BNASQS: 10-130 µg/Kg PAHNOAA: 1-5 µg/Kg
Chlorinated pesticides, aroclors (PEST1PCB)	EPA 8081/8082 or 8270	Pesticides: 0.5 - l00 µg/Kg (1 - 5 µg/Kg for DDT, DDD, DDE and Dieldrin) Aroclors: 5 - 1000 µg/Kg.

1 = Includes the following metals: Ag, Al, Sb, As, B, Ba, Be, Cd, Ca, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Se, Sn, Sr, Ti, Tl, V, Zn

2 = MEL modifications to analytical methods are documented in their Standard Operating Procedures.

BNASQS = Base/Neutral/Acids semivolatile organic compounds – Sediment Quality Standards list. Includes the following compounds: 1,2,4-Trichlorobenzene, 1,2-Dichlorobenzene, 1,3-Dichlorobenzene, 1,4-Dichlorobenzene, 2,4-Dimethylphenol, 2-Methylphenol, 3B-Coprostanol, 4-Methylphenol, Benzoic Acid, Benzyl Alcohol, Bis(2-Ethylhexyl) Phthalate, Butylbenzylphthalate, Caffeine, Cholesterol, Diethylphthalate, Dimethylphthalate, Di-N-Butylphthalate, Di-N-Octyl Phthalate, Hexachlorobenzene, Hexachlorobutadiene, Isophorone, N-Nitrosodiphenylamine, Pentachlorophenol, Phenol, 4-Nonylphenol

CVAA = Cold vapor atomic absorption

PAHNOAA = Polycyclic aromatic hydrocarbons – NOAA list. Includes the following compounds: Naphthalene, 2-Methylnaphthalene, 1-Methylnaphthalene, 1,1'-Biphenyl, 2-Chloronaphthalene, 2,6-Dimethylnaphthalene, Acenaphthylene, Acenaphthene, Dibenzofuran, 1,6,7-Trimethylnaphthalene, Fluorene, Dibenzothiophene, Phenanthrene, Anthracene, Carbazole, 2-Methylphenanthrene, Fluoranthene, Pyrene, Retene, Benzo(a)anthracene, Chrysene, Benzo(b)fluoranthene, Benzo(k)fluoranthene, Benzo[e]pyrene, Benzo(a)pyrene, Perylene, Indeno(1,2,3-cd)pyrene, Dibenzo(a,h)anthracene, Benzo(ghi)perylene

TOC = Total organic carbon

EPA = U.S. Environmental Protection Agency

ICP/MS = Inductively coupled plasma mass spectrometry

MEL = Manchester Environmental Laboratory

PSEP = Puget Sound Estuary Program

Table 6. Reporting limits for metals using ICP/MS.

Metal	mg/Kg, dry	Metal	mg/Kg, dry
Aluminum	2.5	Mercury	0.005
Antimony	0.2	Molybdenum	0.1
Arsenic	0.1	Nickel	0.1
Barium	0.1	Potassium	25
Beryllium	0.1	Selenium	0.5
Boron	2.5	Silicon	2.5
Cadmium	0.1	Silver	0.1
Calcium	2.5	Sodium	2.5
Chromium	0.5	Strontium	0.1
Cobalt	0.1	Thallium	0.1
Copper	0.1	Tin	0.2
Iron	2.5	Titanium	0.1
Lead	0.1	Vanadium	0.5
Magnesium	2.5	Zinc	5
Manganese	0.5		

Bioassays

Table 7 shows the bioassays to be performed and standard methods followed for each bioassay. These bioassays have often been used to test contaminated freshwater sediments for toxicity, although the *Hyalella* and *Chironomus* bioassays are often conducted as short duration, acute tests (e.g., Ecology, 2003b). In this investigation, the longer, chronic tests will be used.

Table 7. Laboratory procedures for analyses.

Bioassay	Endpoints	Method	Reference
Hyalella azteca (freshwater amphipod) 28 day	Growth, survival	EPA 100.4	ASTM, 2000
Chironomus tentans (midge) 20 day	Growth, survival	EPA 100.5	ASTM, 2000
Microtox®	Changes in light output of a bioluminescent marine bacterium, *Vibrio fischeri.*	Microtox®	Ecology, 2003a

Quality Control Procedures

Field

The field sampling procedures described in the *Sampling Procedures* section of this Quality Assurance (QA) Project Plan and the SOP for freshwater sediment sampling (Blakley, 2008) will be carefully followed to avoid contamination of samples. A copy of the QA Project Plan will be taken into the field for reference. Although no field QA samples are included in this project, three stations will be sampled at each site. This will provide an indication of within-site variability in chemical concentrations and bioassay performance.

Laboratory

Laboratory quality control samples for all study matrices are shown in Table 8.

Estimated laboratory costs for this project are shown in Table 9.

Table 8. Laboratory quality control samples and evaluation criteria (method quality objectives).

Parameter	Method Blank		Analytical Replicates[1]		Laboratory Control Sample[2]		Matrix Spike and Matrix Spike Duplicate	
	Number	Evaluation	Number	Evaluation	Number	Evaluation	Number	Evaluation
Grain size	--		1 triplicate analysis	RSD ≤ 20%	--		--	
Total organic carbon	1/batch	Analyte concentration <0.1%	1 triplicate analysis	RSD ≤ 20%	--		--	
Total sulfides	1/batch	Analyte concentration < 10 mg/kg	1 triplicate analysis	RSD ≤ 20%	1/batch	65-135% recovery	1	65-135% recovery
Ammonia	1/batch	Analyte concentration < 100 µg/Kg	1 triplicate analysis	RSD ≤ 20%	1/batch	80-120% recovery	1	75-125% recovery
Metals (ICP/MS)	1/batch	Analyte concentration < PQL	1 duplicate analysis	RPD ≤ 20%	1/batch	80-120% recovery, or performance based intralaboratory control limits, whichever is lower	1/batch	75–125% recovery applied when the sample concentration is < 4 times the spiked concentration; RPD ≤ 20%
Total mercury (CVAA)	1/batch	Analyte concentration < PQL			1/batch	80-120% recovery, or performance based intralaboratory control limits, whichever is lower	1/batch	75–125% recovery applied when the sample concentration is < 4 times the spiked concentration; RPD ≤ 20%
Semivolatiles (BNASQS and PAHNOAA)	1/batch	Analyte concentration < PQL	1 duplicate analysis	Compound specific RPD ≤ 35%	1/batch	50-150% recovery	1/batch	50–150% recovery applied when the sample concentration is < 4 times the spiked concentration; RPD ≤ 40%
Chlorinated pesticides, aroclors (PEST1PCB)	1/batch	Analyte concentration < PQL	1 duplicate analysis	Compound specific RPD ≤ 35%	1/batch	50-150% recovery	1/batch	50–150% recovery applied when the sample concentration is < 4 times the spiked concentration; RPD ≤ 40%

PQL = Practical quantitation limit
RPD = Relative percent difference
RSD = Relative standard deviation
Evaluation criteria are taken from Ecology, 2003a (Tables 5, 11 and 12)

1 Synonymous with Laboratory Replicates or, if applicable, Laboratory Duplicates.
2 A known matrix spiked with analytes representative of the target analytes used to document laboratory performance.

Table 9. Summary of estimated laboratory costs.

Analysis	Laboratory	No. of Samples	No. of QA Samples	Total No. of Samples	Unit Cost ($)	Subtotal ($)
Grain size	Contract	27	0	27	90*	2,430
Total organic carbon	MEL	27	2	29	33†	957
Percent solids	MEL	27	0	27	11†	297
Total sulfides	Contract	27	4	31	50*	1,550
Ammonia	Contract	27	4	31	63*	1,953
Metals (ICP/MS)	MEL	27	3	30	215†	6,450
Mercury (CVAA)	MEL	27	2	29	44†	1,276
Semivolatiles: BNASQS	MEL	27	3	30	325†	9,750
Semivolatiles: PAHNOAA	MEL	27	3	30	400†	12,000
Chlorinated pesticides, aroclors	MEL	27	3	30	225†	6,750
Microtox®	Contract	27	0	27	250	6,750
Hyalella	Contract	27	0	27	1,500	40,500
Chironomus	Contract	27	0	27	1,200	32,400
					Project Total	$122,613

MEL = Manchester Environmental Laboratory

* Includes 25% surcharge for MEL handling/data review of outsourced analyses

† Includes 50% discount for MEL analyses

Data Management Procedures

A field log will be completed at each sampling station (Appendix B). Notes will include date, time, shoreline characteristics, vessel position at time of sampling, and water depth. Observable characteristics of all sediment samples will also be recorded. These will include grab sampler penetration depth, surface sediment physical features, organisms present, sediment color, texture, odors, and apparent depth of oxic (aerobic) sediment.

Results of laboratory analyses will be submitted to the project manager as follows:

- MEL will submit all analytical results for test and QA samples as a printed report (with a QA summary). Output from the Laboratory Information Management System will also be submitted electronically for transfer into Ecology's EIM database.

- Deliverables from the contract *chemistry* laboratory will include all test and QA sample results for total solids, grain size, total sulfides, and ammonia. A printed report of results will be accompanied by an electronic deliverable in an EIM format.

- Deliverables from the contract *toxicology* laboratory will include results for all toxicity tests, including replicate results for all control, reference, and test samples. Test exposure conditions (initial porewater total sulfides, water quality monitoring results) will also be provided. A printed report presenting all toxicity test results, with regulatory interpretation, will be accompanied by an electronic data submittal in SEDQUAL format (unless final EIM format for toxicity results is available).

All sediment quality data generated for this project will be evaluated for completeness, accuracy, and usability. Upon completion of the final report, all usable results will be entered into Ecology's EIM database and made available to the public via Ecology's web site.

Audits and Reports

Audits

MEL participates in performance and system audits of their routine procedures. Results of these audits are available on request.

Reports

The project manager will prepare an Ecology draft technical report describing results of this study. The draft report will undergo peer review by Ecology staff, and a final report will be prepared by April 2009.

Contents of the final technical report will include:

- Description of the final sampling station locations, including geographic coordinates, maps, and information from the field logs.
- All chemistry and bioassay data.
- Assessment of toxicity across and within sites.
- Assessment of toxicity in relation to sediment grain size, organic carbon, and contaminant levels.
- Comparisons of results with data from previous field studies in Washington.
- Recommendations for follow-up.

Upon completion of the project, all project data will be entered into the Ecology EIM system. Public access to electronic versions of the data and reports generated from this project will be available via Ecology's internet homepage (www.ecy.wa.gov).

Data Verification

Data verification involves examining the data for errors or omissions as well as examining the results for compliance with quality control acceptance criteria.

Field results will be verified, preferably before leaving the site where the measurements were made.

Laboratory results will be reviewed and verified by qualified and experienced lab staff. Their findings will be documented in a case narrative provided to the project manager. Field results will also be verified, preferably before leaving the site where the measurements were made.

Once the laboratory measurement results have been recorded, they will be verified to ensure that:

- Data are consistent, correct, and complete, with no errors or omissions
- Results for quality control samples accompany the sample results
- Established criteria for quality control results were met
- Data qualifiers are properly assigned where necessary
- Methods and protocols specified in this Quality Assurance Project Plan were followed

The project lead will review the laboratory data packages and data verification reports. To determine if the project method quality objectives were met, results for analytical replicates, laboratory control samples, and matrix spikes will be compared to quality control limits. Method blank results will be examined to verify that there was no significant contamination of the samples. To evaluate whether the targets for reporting limits have been met, the results will be examined for non-detects and to determine if any values exceed the lowest concentration of interest.

Data Quality (Usability) Assessment

Once the data have been reviewed and verified, the project manager will assess the quality and quantity of the data in relation to the purposes of the study. The project manager will then present the assessment to the client, who will determine whether the data are useable for his project goals and objectives. This determination will be included in the final report.

References

ASTM, 2000. Test Methods for Measuring the Toxicity of Sediment-Associated Contaminants with Freshwater Invertebrates. ASTM Standard No. E1706-0oe1. American Society for Testing and Materials, Philadelphia, Pennsylvania.

Blakley, N., 2008. Standard Operating Procedure (SOP) for Obtaining Freshwater Sediment Samples. Washington State Department of Ecology, Olympia, Washington. SOP No. EAP040. www.ecy.wa.gov/programs/eap/quality.html

Ecology, 1993. Field Sampling and Measurement Protocols for the Watershed Assessments Section . Washington State Department of Ecology, Olympia, WA. Publication No. 93-e04. www.ecy.wa.gov/biblio/93e04.html

Ecology, 2003a. Sediment Sampling and Analysis Plan Appendix. Washington State Department of Ecology, Olympia, Washington. Publication No. 03-09-043. www.ecy.wa.gov/biblio/0309043.html

Ecology, 2003b. Development of Freshwater Sediment Quality Values for Use in Washington State: Phase II Report. Washington State Department of Ecology, Olympia, Washington. Publication No. 03-09-088. www.ecy.wa.gov/biblio/0309088.html

Heiskary, S., 1996. Lake Contaminant Levels in Minnesota. Minnesota Pollution Control Agency, St. Paul, Minnesota.

Johnson, A., 2008. Quality Assurance Project Plan: PCB and Dioxin Levels in Resident Fish from Washington Background Lakes and Rivers Publication No. 08-03-102. www.ecy.wa.gov/biblio/0803102.html

Plumb, R. H., Jr., 1981. Procedure for Handling and Chemical Analysis of Sediment and Water Samples. Technical Report EPA/CE-81-1. U.S. Environmental Protection Agency and U.S. Corps of Engineers, Waterways Experimental Station, Vicksburg, Mississippi.

Puget Sound Estuary Program (PSEP), 1986. Recommended Protocols for Measuring Selected Environmental Variables in Puget Sound. U.S. Environmental Protection Agency, Region 10, Office of Puget Sound, Seattle, Washington.

Puget Sound Estuary Program (PSEP), 1995. Recommended Guidelines for Conducting Laboratory Bioassays on Puget Sound Sediments. U.S. Environmental Protection Agency, Region 10, Office of Puget Sound, Seattle, Washington.

Puget Sound Estuary Program (PSEP), 1997. Recommended Guidelines for Measuring Organic Compounds in Puget Sound Water, Sediment and Tissue Samples. U.S. Environmental Protection Agency, Region 10, Office of Puget Sound, Seattle, Washington.

Appendices

Appendix A. Project Analytes

Table A-1. Analytes for this project include the following metals and organic compounds.

Metals	Organic Compounds		
	BNASQS (Base/Neutral/Acids semivolatile organic compounds – Sediment Quality Standards list).	PAHNOAA (Polycyclic aromatic hydrocarbons – NOAA list).	PEST1PCB
Ag (Silver)	1,2,4-Trichlorobenzene	Naphthalene	Chlorinated pesticides
Al (Aluminum)	1,2-Dichlorobenzene	2-Methylnaphthalene	Aroclors (PCB mixtures)
Sb (Antimony)	1,3-Dichlorobenzene	1-Methylnaphthalene	
As (Arsenic)	1,4-Dichlorobenzene	1,1'-Biphenyl	
B (Boron)	2,4-Dimethylphenol	2-Chloronaphthalene	
Ba (Barium)	2-Methylphenol	2,6-Dimethylnaphthalene	
Be (Beryllium)	3B-Coprostanol	Acenaphthylene	
Cd (Cadmium)	4-Methylphenol	Acenaphthene	
Ca (Calcium)	Benzoic Acid	Dibenzofuran	
Co (Cobalt)	Benzyl Alcohol	1,6,7-Trimethylnaphthalene	
Cr (Chromium)	Bis(2-Ethylhexyl) Phthalate	Fluorene	
Cu (Copper)	Butylbenzylphthalate	Dibenzothiophene	
Fe (Iron)	Caffeine	Phenanthrene	
Hg (Mercury)	Cholesterol	Anthracene	
K (Potassium)	Diethylphthalate	Carbazole	
Mg (Magnesium)	Dimethylphthalate	2-Methylphenanthrene	
Mn (Manganese)	Di-N-Butylphthalate	Fluoranthene	
Mo (Molybdenum)	Di-N-Octyl Phthalate	Pyrene	
Na (Sodium)	Hexachlorobenzene	Retene	
Ni (Nickel)	Hexachlorobutadiene	Benzo(a)anthracene	
Pb (Lead)	Isophorone	Chrysene	
Se (Selenium)	N-Nitrosodiphenylamine	Benzo(b)fluoranthene	
Sn (Tin)	Pentachlorophenol	Benzo(k)fluoranthene	
Sr (Strontium)	Phenol	Benzo[e]pyrene	
Ti (Titanium)	4-Nonylphenol	Benzo(a)pyrene	
Tl (Thallium)		Perylene	
V (Vanadium)		Indeno(1,2,3-cd)pyrene	
Zn (Zinc)		Dibenzo(a,h)anthracene	
		Benzo(ghi)perylene	

Appendix B. Field Log Sheet

FRESHWATER SEDIMENTS BIOASSAY REFERENCE SITE EVALUATION PROJECT

FIELD LOG RECORDER _____

Water Body Name _____ Date _____

Field Crew/Boat: _____

Shoreline Characteristics:

Land Ownership (~%'s): _____

Who owns the land surrounding the water body?

Primary Land Use: _____ Secondary Land Use: _____

Land use codes shown below. What is the major function of the landscape surrounding the water body?

Forest Type: _____

Forest Type codes below. What is the dominant forest type?

Primary Riparian Vegetation (<5 m): _____ Secondary Riparian Vegetation (<5m): _____

Vegetation codes shown below. What vegetation is present within 5 meters of the waters edge?

Primary Riparian Trees DBH (<5m, cm): 00-03 03-15 15-30 30-50 50-90 90+

What is the primary diameter at breast height (DBH) range for the majority of trees less than 5 meters from the waters edge?

% visible LWD (large woody debris) in water: _____

How much wood is in the water?

Water Body Configuration: Depression/Pothole Lake Lake Reservoir River/Stream

What type of water body is this? (Lake=has inflows/outflows)

Fetch Length (miles): _____

What is the longest straight line distance from shore to shore (lakes only)?

Fullness (meters, i.e. distance from waters edge to high water scour line): _____

How does the current water level compare to the high water level?

Elevation (ft): _____

Codes:

Land use

R – Recreational (e.g. State Park)
NAT – Natural Area (e.g. National Park)
AG – Agriculture (e.g. crops)
G-Grazing (e.g. cattle pasture lands)
TH – Timber Harvest (e.g. lands used for logging)
LR – Low Residential: 0-5 homes/mile of shore
MR – Medium Residential: 6-10 homes/mile of shore
HR – High Residential: 11+ homes/mile of shore
I – Commercial (e.g. grocery store/gas station)
TR – Transportation corridor near waterbody (e.g. road)

Forests

C – Conifer
D – Deciduous
M – Mixed

+

CC – Clear Cut (no trees to yearlings)
ST – Second Timber (15-50cm DBH)
MT – Mature Timber (50-90cm DBH)
OG – Old Growth (90+ cm DBH

Vegetation

T – Trees
S – Shrubs (woody but not in the form of a tree)
G – Grasses
F – Forbs (ferns, herbaceous plants)
B – Barren, Exposed Rock/Soils

FRESHWATER SEDIMENTS BIOASSAY REFERENCE SITE EVALUATION PROJECT

FIELD LOG RECORDER _____

Station ID _____ (note location on attached map)

Sample ID _____

Station location GPS coordinates _____

Location description _____

Depth (ft) _____ Time _____ Grab: ☐ Standard Ponar ☐ Ekman ☐ Petite Ponar

Grabs composited for the sample _____ # Rejects _____

Sediment Characterization

Texture ☐ Clay ☐ Silt/Mud ☐ Gritty Silt ☐ Sand ☐ Other _____

Color ☐ Black ☐ Grey ☐ Dark brown ☐ Light brown ☐ Other _____

Odor ☐ Organic ☐ Sulfurous ☐ Other _____

☐ None ☐ Slight ☐ Strong

Layers ☐ No ☐ Yes If yes, note thickness and characteristics of each layer in Notes section below.

Debris ☐ Pebbles, stones ☐ Wood ☐ Leaves ☐ Other _____

Vegetation _____

Macroinvertebrates ☐ Worms ☐ Snails ☐ Insect larvae ☐ Clams

☐ Other _____

Notes:

_____

_____

_____

_____

_____

_____

_____

_____

FIELD LOG RECORDER _____

Follow with prepared map of each water body, to be used to show sampling locations. May also be used to note any features of interest or other information observed in the field.

(This space is purposely blank in this QA Project Plan.)

Guide to field log notes

Shoreline Characteristics:

Land Ownership (~%'s):_____
Who owns the land surrounding the water body? (Example: Land Ownership: 20% Private, 30% Tribal, 20% State, 10% Federal). Only include land bordering the water body. This information can be general like the example in cases where agency affiliation is not obvious or involves multiple agencies or more specific such as 30% Washington State Department of Natural Resources instead of just State.

Primary Land Use: _____ Secondary Land Use: _____
Land use codes shown below. What is the major function of the landscape surrounding the water body? (example: Primary Land Use: R; Secondary Land Use: TH) If the landscape is used for more than one land use the next most prevalent land use should be noted in secondary land use. In the example, recreation in a state park was the primary land use, but the landscape is also used for timber harvest. (note: Secondary Land Use field may not always be used).

Forest Type: _____
Forest Type codes below. What is the dominant forest type? (Example: Forest Type: C-ST) As in the example, this field provides information on the type of trees, conifer in the example, and their maturity, second timber in the example. (note: Forest Type field may not always be used)

Primary Riparian Vegetation (<5 m): _____ Secondary Riparian Vegetation (<5m): _____
Vegetation codes shown below. What vegetation is present within 5 meters of the waters edge? (Example: Primary Riparian Vegetation: T; Secondary Riparian Vegetation: G) A top down approach puts priority on the vegetation that receives sunlight first (i.e. trees > shrubs > grasses and forbs). This provides information on the stability/functioning of the area immediately adjacent to the shoreline.

Primary Riparian Trees DBH (<5m, cm): 00-03 03-15 15-30 30-50 50-90 90+
What is the primary diameter at breast height (DBH) range for the majority of trees less than 5 meters from the water's edge? (Example: Primary DBH: 00-03) Further refines the maturity of the forested vegetation in the riparian zone. In the example, this riparian area is dominated by young or stunted trees. (note: Primary DBH Range field may not always be used).

% visible LWD (large woody debris) in water: _____
How much wood is in the water? (Example: % visible LWD: 30%) Describes the amount of wood habitat available to fish and waterfowl. May also indicate habitat restoration, natural processes, or logging practices. In the example, 30% of the water body's surface area has visible woody debris (note: % visible LWD field may not always be used).

Water Body Configuration: Depression/Pothole Lake Lake Reservoir River/Stream
What type of water body is this? (Example: Depression/Pothole Lake) In the example, the water body is a lake with no surface water inflows or outflows (rivers/streams) in contrast to a typical lake with

surface water inflows and/or outflows. This indicates that the primary water resource is groundwater or precipitation.

Fetch Length (miles): _____
What is the longest straight line distance from shore to shore (lakes only)? (Example: Fetch length: 2 miles) Provides information on the longest possible path for wind to induce waves.

Fullness (m, i.e. distance from waters edge to high water scour line): _____
How does the current water level compare to the high water level? (Example: Fullness: 1 m) Indication of water level changes or anthropogenic influences on riparian area. This is especially useful in reservoirs where water levels may change frequently due to anthropogenic demands. In addition, this is an important characteristic of rivers to determine channel boundaries during high flow events.

Elevation (ft): _____
What is the elevation? (Example: 3,250 ft) Determines position in landscape. In the example, this water body is located well above sea level and is likely in a more mountainous area rather than a near sea-level plain.

Codes:

Land use

R – Recreational (e.g. State Park)
NAT – Natural Area (e.g. National Park)
AG – Agriculture (e.g. crops)
G – Grazing (e.g. cattle pasture lands)
TH – Timber Harvest (e.g. lands used for logging)
LR – Low Residential: 0-5 homes/mile of shore
MR – Medium Residential: 6-10 homes/mile of shore
HR – High Residential: 11+ homes/mile of shore
I – Commercial (e.g. grocery store/gas station)
TR – Transportation corridor near waterbody (e.g. road)

Forests

C – Conifer
D – Deciduous
M – Mixed

+

CC – Clear Cut (no trees to yearlings)
ST – Second Timber (15-50cm DBH)
MT – Mature Timber (50-90cm DBH)
OG – Old Growth (90+ cm DBH

Vegetation

T – Trees
S – Shrubs (woody but not in the form of a tree)
G – Grasses
F – Forbs (ferns, herbaceous plants)
B – Barren, Exposed Rock/Soils