# **Quality Assurance Project Plan**

# Mercury in Sediments from Lake Whatcom and Surrounding Lakes: Determination of Spatial and Temporal Patterns and Characterization of Tributary Inputs

by Dale Norton

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

In Cooperation with
United States Geological Survey
Tacoma District Office
and
Whatcom County Health Department
Bellingham, Washington

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This report is available on the Department of Ecology home page on the World Wide Web at <a href="http://www.ecy.wa.gov/biblio/0203079.html">http://www.ecy.wa.gov/biblio/0203079.html</a>.

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#### September 2002

Water Body Number: Lake Whatcom 122316448726 (Formerly WA-01-9170)

Ecology EIM Number: DNOR0006

#### **Approvals**

| Approved by:   | September 16, 2002 |
|--|--------------------|
| Steve Hood, Bellingham Field Office                          | Date               |
| Approved by:   | September 17, 2002 |
| Dick Grout, Manager, Bellingham Field Office                 | Date               |
| Approved by:   | September 12, 2002 |
| Dale Norton, Project Manager, Toxics Studies Unit            | Date               |
| Approved by:   | September 11, 2002 |
| Will Kendra, Section Manager, Watershed Ecology Section      | Date               |
| Approved by:   | September 12, 2002 |
| Stuart Magoon, Director, Manchester Environmental Laboratory | Date               |
| Approved by:   | September 16, 2002 |
| Cliff Kirchmer, Ecology Quality Assurance Officer            | Date               |
| Approved by:   | September 13, 2002 |
| Anthony Paulson, USGS Project Manager                        | Date               |
| Approved by:   | September 17, 2002 |
| Chris Chesson, Whatcom County Health Department              | Date               |

## **Abstract**

To determine current and historical mercury levels, and potential sources of mercury to Lake Whatcom, the Washington State Department of Ecology (Ecology) will conduct a joint study with the United States Geological Survey (USGS) and the Whatcom County Health Department (WCHD). During the late summer of 2002, Ecology will collect approximately 30 surface sediments and three deep cores from Lake Whatcom to evaluate the spatial distribution and historical trends in mercury levels. All sediment samples will be analyzed for total mercury. In addition, methyl-mercury levels will be determined in approximately 15 of the surface sediment samples. USGS in cooperation with WCHD will collect and evaluate all existing information on potential mercury sources to the lake. Supplemental funding will also be provided by WCHD and USGS to Ecology for collection and analysis of five additional sediment cores from other nearby lakes in Whatcom County to determine if mercury accumulation rates differ from Lake Whatcom. Finally, to estimate mercury loadings from tributaries, surface water samples will be collected every other month from ten tributaries to the lake and analyzed for total mercury.

The information being collected will provide a better understanding of current and historical mercury inputs to Lake Whatcom. In addition, it should be possible to determine the need or feasibility of developing a Total Maximum Daily Load (TMDL) for mercury in Lake Whatcom.

# **Background**

Lake Whatcom is a large, natural lake located in Whatcom County, in the northwestern corner of Washington. The surface area of the lake covers about 5,000 acres, and the total watershed area is about 32,000 acres. The lake can be divided morphologically into three distinct basins formed by glacial sills. Basins 1 and 2 are relatively small and shallow (generally <24 meters). Basin 3, which has a maximum depth of about 100 meters, contains 96 percent of the lake volume. Morphometric data on Lake Whatcom is presented in Table 1.

**Table 1: Morphometric Data on Lake Whatcom** 

|   | Basin 1 | Basin 2 | Basin 3 | Entire Lake |
|---|---------|---------|---------|-------------|
| Volume (m <sup>3</sup> ×10 <sup>6</sup> ) | 19.4    | 18.0    | 883.5   | 921         |
| % of Lake Volume                          | 2.1     | 2.0     | 95.9    | 100.0       |
| Maximum Depth (m)                         | 29      | 21      | 103     | 103         |
| Mean Depth (m)                            | 9.2     | 11.2    | 54      | 46          |
| Surface Area (km <sup>2</sup> )           | 2.1     | 1.6     | 16.6    | 20.3        |
| Length (km)                               | 2.2     | 2.5     | 13.3    | 19.2        |
| Maximum Width (km)                        | 1.1     | 1.0     | 1.7     | 1.7         |

Basin 1 is in the most urbanized part of the watershed, lying largely within the city limits of Bellingham. Several streams drain to the lake. However, to maintain optimal lake levels, water is diverted into the lake from the middle fork of the Nooksack River. This diversion enters the lake at the southeastern end of basin 3 via Anderson Creek. Outflow from the lake discharges to Whatcom Creek, which is located at the western end of basin 1. An overview of the Lake Whatcom Watershed is shown below in Figure 1.

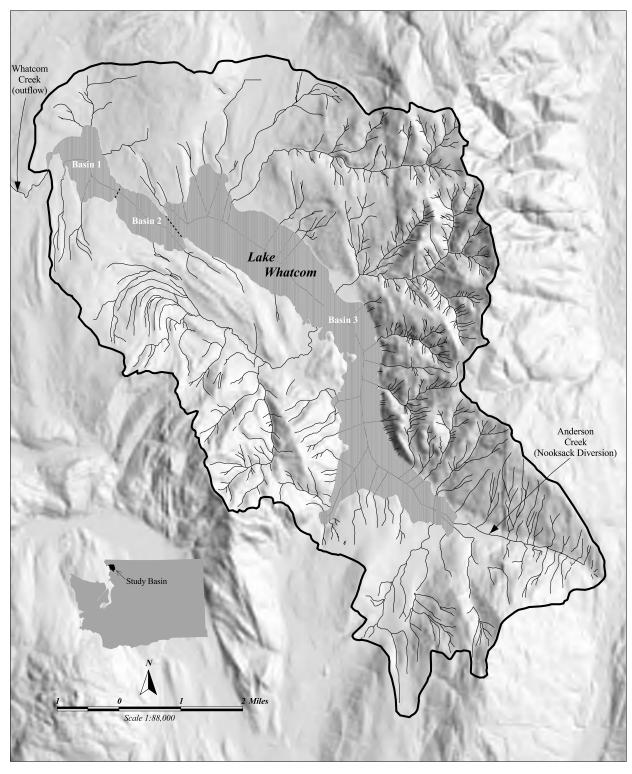


Figure 1: Lake Whatcom Study Area and Drainage Basin.

All of the major tributaries and many of the intermittent tributaries discharging to Lake Whatcom flow into Basin 3, which receives 87 percent of the drainage to the lake. The remaining watershed areas are drained by intermittently flowing streams, surface runoff directly into the lake, or man-made drainage systems (Delahunt 1990). Seven perennial tributaries flow into Lake Whatcom; they are Anderson, Smith, Olsen, Carpenter, Austin, Brannian, and Fir creeks. Among them, Anderson, Austin and Smith creeks are the largest.

Protection of the lake is important because it serves as the primary drinking water source for about 86,000 Whatcom County residents. The lake is also used extensively for sport fishing, swimming, and other types of recreation (USGS, 2002 in prep; and Serdar et al., 1999).

Concerns over mercury contamination in Lake Whatcom fish were raised after a study conducted by the Washington State Department of Ecology (Ecology) in 1998 reported a concentration of 0.5 mg/kg, wet in a composite sample of smallmouth bass fillets (Serdar et al., 1999). For comparison, the average tissue concentration for other freshwater areas of Washington, calculated from Ecology's Environmental Information Database, is 0.096 mg/kg, wet. The national average for mercury in sport fish fillets is reported to be 0.36 mg/kg, wet (EPA, 1992).

The 1998 study also sampled sediments from the lake and several tributaries. Total mercury concentrations ranged from 0.04 to 0.46 mg/kg, dry, with a mean of 0.19 mg/kg, dry. The highest concentration was reported for Basin 1. In 1999, Western Washington University (WWU) also measured mercury concentrations in surface sediments from Lake Whatcom. Concentrations reported for ten sites in the lake ranged from 0.077 to 0.28 mg/kg, dry, with a mean of 0.14 mg/kg, dry. Again, the highest concentration was found in Basin 1 (Mathews, 1999, unpublished data).

For comparison, the average freshwater sediment concentration for Washington, calculated from data reported in Ecology's SEDQUAL database, is 0.36 mg/kg, dry. The median concentrations of mercury in sediments from streams in the Puget Sound Basin sampled as part of the United States Geologic Survey (USGS) National Water-Quality Assessment Program (NWQA) was 0.1 mg/kg, dry (MacCoy and Black, 1998). Based on comparison of average values, Lake Whatcom sediment concentrations of total mercury do not appear to be high compared to other basins in Puget Sound or elsewhere in the state.

To determine if consumers of Lake Whatcom fish were at risk from mercury exposure, the Washington State Departments of Ecology, Fish and Wildlife, and Heath, and Whatcom County Health Department (WCHD) conducted a joint fish tissue study. During this study, approximately 273 samples of finfish were collected and analyzed for mercury (Serdar et al., 2001). The average mercury level in smallmouth bass was 0.49 mg/kg, wet, with a maximum concentration of 1.84 mg/kg, wet. Thirteen samples collected during this study exceeded the EPA National Toxics Rule human health criterion of 0.825 mg/kg, wet (Serdar et al., 2001).

Results from the fish tissue study suggested mercury concentrations may be different among the three basins, with some fish samples from Basin 3 being elevated relative to Basins 1 and 2. This result was somewhat unexpected because Basin 3 is large and the contributing drainage area has a smaller percentage of urban land use than Basins 1 or 2. The reasons for the higher

concentrations in Basin 3 was not determined, but Serdar conjectured that transport of mercury to the lake from tributaries or diversions, or processes that convert mercury to methyl-mercury in the lake or in connected wetlands might be contributing factors.

Some of the possible sources of mercury in Lake Whatcom include atmospheric deposition from global and local sources, discharges from tributaries (including the diversion from the Nooksack River), landfills, dumpsites, and local mining operations. Of these possible sources, local interest has focused on a chloralkali plant that operated in the city of Bellingham and discharged mercury from the early 1960s until the late 1990s (USGS, 2002 in prep).

# **Project Description**

To determine recent and historical accumulation of mercury in sediments, and tributary inputs to Lake Whatcom, Ecology will conduct a joint study with USGS and WCHD. During the late summer of 2002, Ecology's Environmental Assessment Program (EA Program) will collect approximately 30 surface sediments and three deep cores from Lake Whatcom to evaluate recent and historical mercury levels in sediments. All sediment samples will be analyzed for total mercury. Radio-dating, using Pb-210 and Cs-137, will be done on the sediment cores to determine the time line of mercury contamination and net sedimentation rates. In addition, methyl-mercury levels will be determined in approximately 15 of the surface sediment samples distributed throughout the lake. USGS, in cooperation with WCHD, will collect and evaluate all existing information on potential mercury sources to the lake. Supplemental funding will also be provided to Ecology by WCHD and USGS for collection and analysis of five additional sediment cores from nearby lakes in Whatcom County. The purpose of these additional cores will be to determine if mercury accumulation rates differ from Lake Whatcom. Finally, to estimate mercury loadings from tributaries, surface water samples will be collected every other month from ten tributaries to Lake Whatcom and analyzed for total mercury as part of the Lake Whatcom Dissolved Oxygen Total Maximum Daily Load (TMDL) currently underway (Cusimano and Liu, 2002).

Together the information being collected as part of this cooperative effort will provide a better understanding of current and historical mercury inputs to Lake Whatcom. In addition, it should be possible to determine the need or feasibility of developing a TMDL for mercury in Lake Whatcom

The primary objectives of this cooperative study are as follows:

- ❖ Determine the spatial distribution of mercury in surface sediments from Lake Whatcom.
- ❖ Evaluate historical trends in total mercury levels and sedimentation rates by collecting three sediment cores (one from each basin) in Lake Whatcom and five surrounding lakes.
- ❖ Estimate mercury loadings in the ten tributaries to Lake Whatcom by collecting surface water and flow information every other month for one year.

# Responsibilities

**EA Program Project Manager** Dale Norton (360-407-6765)

Field Collection (Sediments)

Dave Serdar, Brandee Era-Miller,

Morgan Roose, Randy Coots, and

Chris Chesson (360-676-6724)

**Anthony Paulson** 

Field Collection (Water)

Bob Cusimano, Jing Liu, and Steve

Hood

**EA Program GIS Support**Randy Coots

**Manchester Environmental Laboratory Director** Stuart Magoon (360-871-8801)

Manchester Laboratory Karin Feddersen (360-871-8829)

QA, Sample Management, and Contracting

**Ecology QA Officer** Cliff Kirchmer (360-407-6455)

**USGS Tacoma District Project Coordinator** Anthony Paulson (253-428-3600)

**Whatcom County Health Department Project** 

Coordinator

EIM Data Entry Brandee Era-Miller

## **Schedule**

Sampling

Surface Sediments and Cores September 2002

Tributary Water Samples Every Other Month (July 2002 to May 2003)

**Laboratory Analysis Complete** 

Sediments October 2002 Water Ongoing

**QA Review Complete** 

Sediments November 2002

Water Ongoing (Deliver to Project Manager Within 40 Days)

**Draft Project Report** March 2003 (Excluding All Water Data)

Final Project Report August 2003 (Including All Water Data)

## **Data Quality Objectives**

Table 2 shows the project targets for accuracy, precision, bias, and reporting limits required to meet the objectives of this study.

Table 2: Measurement Quality Objectives for the Lake Whatcom Sediment Mercury Study.

| Parameter  | Accuracy (% deviation from true value) | Precision (RSD) | Bias<br>(% of true value) | Target Reporting Limits |
|------------|--|-----------------|---------------------------|-------------------------|
| Sediment   |  |                 |                           |                         |
| TOC        | 20                                     | 10              | -                         | 1%                      |
| Grain Size | 25                                     | 10              | 5                         | 0.1%                    |
| Total Hg   | 30                                     | 10              | 10                        | 0.005 mg/kg, dry        |
| Methyl-Hg  | 30                                     | 15              | -                         | 0.001 mg/kg, dry        |
| Total Pb   | 30                                     | 10              | 10                        | 2 mg/kg, dry            |
| Pb-210     | 30                                     | 15              | -                         | 1 dpm/g                 |
| Cs-137     | 30                                     | 15              | -                         | -                       |
| Water      |  |                 |                           |                         |
| Total Hg   | 30                                     | 10              | 10                        | 0.002 ug/l              |

Dpm= disintigrations per minute

The reporting limits shown should be low enough to consistently quantify the analytes of interest, based on a review of the available data.

# **Sampling Design**

Current and historical inputs of mercury to Lake Whatcom will be evaluated by collection and analysis of a combination of surface sediments, sediment cores, and surface water from ten tributaries.

### **Surface Sediment**

Surface sediments will be used to evaluate mercury concentrations near major tributaries and provide spatial coverage of the basin. Surface sediment stations will be located using two techniques: focused tributary samples and random sites. Focused tributary stations will be located in the lake near the mouths of ten tributaries to the lake. These tributaries are the same ones where water is being sampled every other month (see Figure 2). The final location of each focused station will be determined in the field based on a review of site conditions.

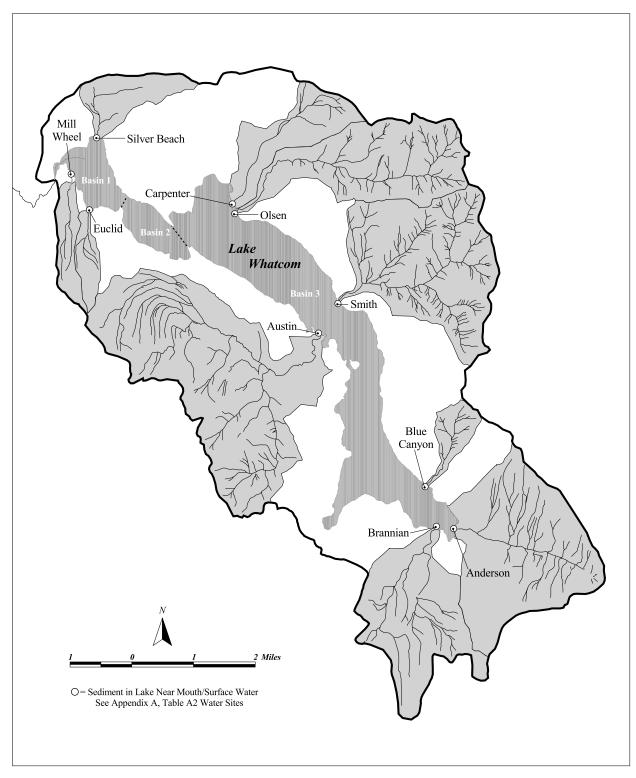


Figure 2: Proposed Focused Tributary Surface Sediment and Surface Water Sites in Lake Whatcom.

The remaining surface sediment stations (21) will be distributed throughout the lake using a stratified random sampling design. Three strata, which correspond to the three basins in the lake, will be defined. The number of random stations in each basin will be allocated based on the relative size of the basin compared to the total lake area. To provide adequate spatial coverage of each basin, a minimum of five stations will be randomly assigned to both Basins 1 and 2. The number of focused and random stations in each basin is summarized below in Table 3.

Table 3: Summary of Focused and Random Surface Sediment Stations in Lake Whatcom.

| Basin | Focused | Random | Total |
|-------|---------|--------|-------|
| 1     | 3       | 5      | 8     |
| 2     | 0       | 5      | 5     |
| 3     | 7       | 11     | 18    |
|       |         | T. /   | 1 21  |

Total= 31

Station positions in each stratum will be randomly selected by defining each stratum as a polygon using ARCVIEW<sup>®</sup> GIS software and then using the random point extension to generate the target number of station locations within each stratum. One alternate position for each primary station will also be determined as a backup. Coordinates of all proposed sediment stations are listed in Appendix A, Table A1. The locations of these sites are also shown by basin in Figures 3a-c.

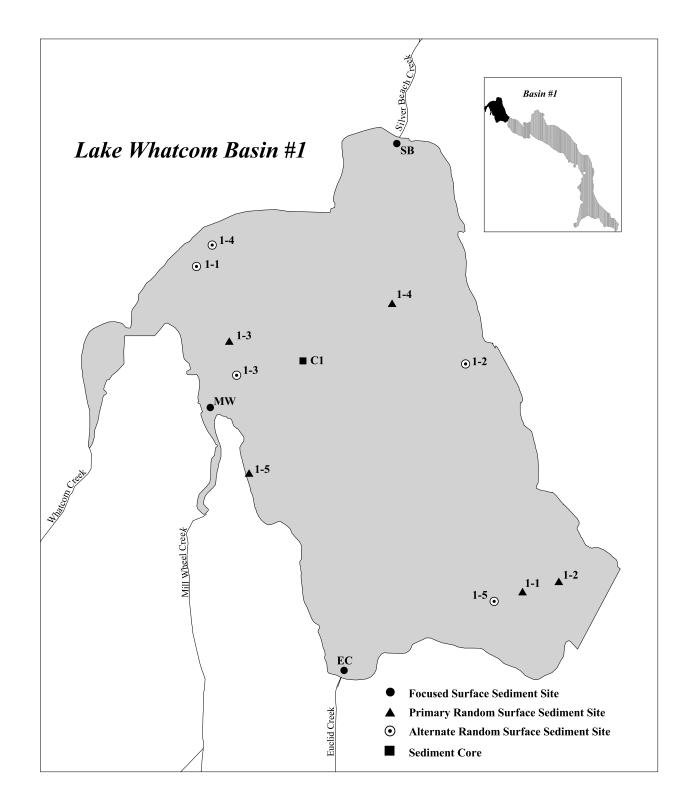


Figure 3a: Proposed Sediment Sites in Basin 1, Lake Whatcom.

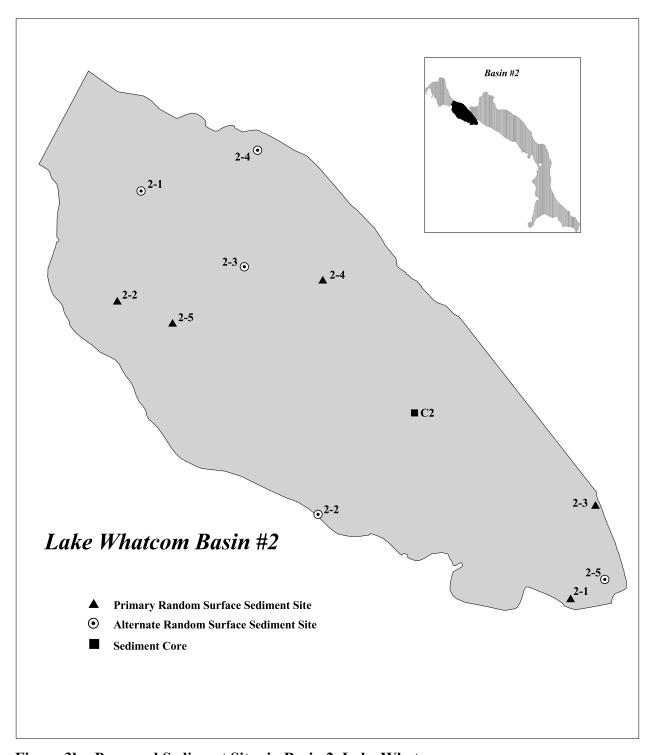


Figure 3b: Proposed Sediment Sites in Basin 2, Lake Whatcom.

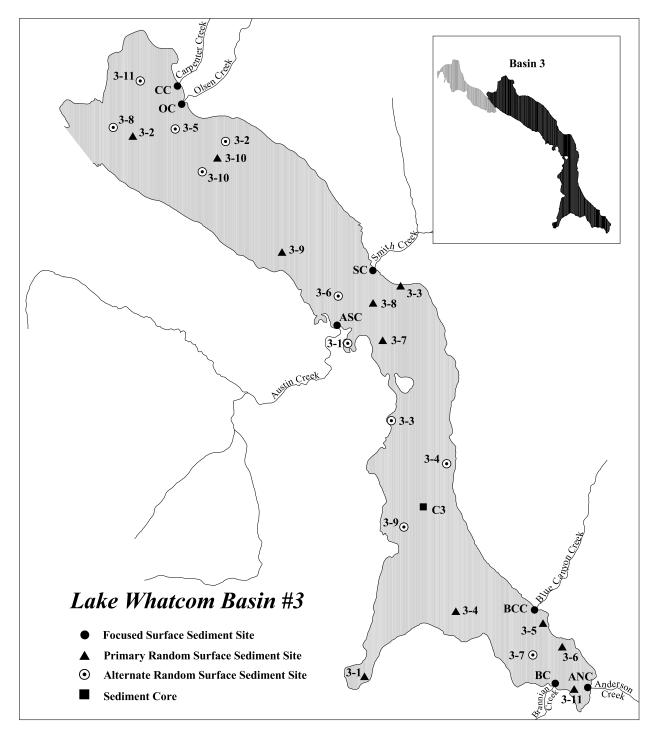


Figure 3c: Proposed Sediment Sites in Basin 3, Lake Whatcom.

Three attempts will be made at each primary station to collect a suitable sample. After three unsuccessful attempts, the primary station will be abandoned and replaced with the alternate station. After three unsuccessful attempts have also been made at the alternate location the station will be dropped. This design should allow an estimate of the average mercury concentration in surface sediments from each basin. This design has been used successfully in other sediment studies to evaluate the arial extent of contamination (Long et al., 1996; NOAA/Ecology, 1999: Norton et al., 2000).

All surface sediments will be analyzed for total organic carbon (TOC), grain size, and total mercury. Five of the random stations in each basin will also be analyzed for methyl-mercury. In basins 1 and 2, this will include all random stations. In Basin 3, all even numbered stations (2, 4, 6, 8, and 10) will be analyzed for methyl-mercury.

#### **Sediment Cores**

Three sediment cores will be collected in Lake Whatcom: one station at the deepest location in each of the three basins. These locations are shown in Figures 3a-c. Deep locations were selected for the cores since it is anticipated that these areas will contain the finest sediments and most undisturbed vertical profile. Similarily, one location in each of five surrounding lakes in Whatcom County will be selected for coring. The final location of each coring site in the surrounding lakes will be determined in the field by USGS and Ecology project managers after evaluating the lake bathymetry and other site conditions. The five additional lakes proposed for coring were selected in conjunction with USGS and WCHD after reviewing available information on mercury concentrations in fish, wind patterns, and accessability. The proposed lakes are listed below in Table 4.

Table 4: Additional Lakes Proposed for Sediment Coring in the Vicinity of Lake Whatcom.

| Lake        | Surface Area (acres) | Maximum Depth (m) | Selection Criteria |
|-------------|----------------------|-------------------|--------------------|
| Baker Lake  | 3616                 | 86                | Global Background  |
| Lake Terrel | 438                  | 3                 | Local Atmospheric  |
|             |                      |                   | Background         |
| Toad Lake   | 30                   | 9                 | < 4 Km Downwind    |
|             |                      |                   | of Bellingham      |
| Fazon Lake  | 32                   | -                 | >10 Km Downwind    |
|             |                      |                   | of Bellingham      |
| Samish Lake | 814                  | 44                | Upwind of Lake     |
|             |                      |                   | Whatcom            |

In each core a maximum of 10 horizons will be analyzed for TOC, total mercury, total lead, and Pb-210 determinations. A maximum of 5 horizons in each core will also be analyzed for Cs-137 as a check on the Pb-210 dating. Cs-137 dating will be restricted to the upper 20cm of each core since detectable fallout of CS-137 began in the early1950's with the beginning of atmospheric testing of nuclear weapons.

### **Water Samples**

Ten tributaries to the lake will be sampled for determination of total mercury. The ten tributaries are: Anderson, Austin, Smith, Euclid, Silver Beach, Olsen, Brannian, Mill Wheel, Carpenter and Blue Canyon Creeks. These tributaries were selected for sampling based on a review of the following factors: ease of access, impact on the lake (based on size of the discharge), represent different drainage characteristics and land use patterns in the Lake Whatcom watershed, and availability of flow and conventional data from the Lake Whatcom Dissolved Oxygen TMDL and previous monitoring studies. The proposed surface water sampling locations are shown in Figure 2 and described in Appendix A, Table A2.

Surface water samples will be collected every other month between July 2002 and May 2003 as part of the Lake Whatcom Dissolved Oxygen TMDL. This will result in a total of six sample collections.

## **Field Procedures**

#### **Surface Sediment**

Where applicable, sampling and analysis methods will follow Puget Sound Estuary Protocols (PSEP, 1996). All surface sediment samples will be collected from Ecology's 26' research vessel using a 0.1 m<sup>2</sup> stainless steel van Veen grab. At each surface sediment site, a composite sample will be prepared from three individual grabs. The top 2-cm layer will be sampled at each location to reflect recently deposited material. Stations will be located and positions recorded using a differentially corrected global positioning system (GPS). Where appropriate, positions relative to fixed onshore structures will also be recorded. A grab will be considered acceptable if it is not over-filled with sediment, overlying water is present and not excessively turbid, the sediment surface is relatively flat, and desired depth penetration has been achieved. A field log will be maintained during sampling.

Upon retrieving a successful grab, overlying water will be siphoned off and the top 2-cm layer of sediment will be removed with stainless steel scoops, placed in a stainless steel bucket, and homogenized by stirring. Aliquots for methyl-mercury analysis will be removed from each grab and composited directly into sample containers. This procedure should minimize the loss of methyl-mercury which would occur during homogenizing. For all samples, material in contact with the side walls of the grab will not be retained for analysis. At the discretion of the project lead, larger debris (e.g. rocks, shells, and pieces of wood) present in the grab that cannot be homogenized will be removed from the sample. Notes will be made in the sample log of all debris originally present in the samples.

Sub-samples of the homogenized sediment will be placed in glass jars (Teflon lid liners) and cleaned to EPA QA/QC specifications (EPA, 1990). Separate 4-oz jars will be used for total

mercury and methyl-mercury, 2-oz jars will be used for TOC, and 8-oz glass jars for grain size samples.

Stainless steel spoons and buckets used to manipulate the sediments for analysis will be precleaned by washing with Liquinox detergent, followed by sequential rinses with tap water, dilute (10%) nitric acid, deionized water, and methanol. The equipment will then be air-dried and wrapped in aluminum foil until used in the field. The same procedure will be used to pre-clean the grab before going into the field. Between stations, cleaning of the grab will consist of thoroughly brushing with on-site water. If oil or visible contamination is encountered, the grab will be cleaned between samples with a detergent wash followed by a rinse with on-site water.

All samples will be stored in coolers on ice at 4°C and transported to the Ecology Manchester Environmental Laboratory (MEL) within 72 hours of collection. Samples for methyl-mercury analysis will be transported to the contract laboratory during the same day as sampling. Storage temperatures and holding time requirements specified by PSEP and other sources are listed in Table 5. Chain-of-custody will be maintained.

Table 5: Recommended Containers, Preservatives, and Holding Times for Sediment Samples (PSEP, 1996).

|                |                          | Preservation     | Maximum             |
|----------------|--------------------------|------------------|---------------------|
| Analyte        | Container                | Technique        | Holding Time        |
| TOC            | Glass or                 | Freeze, -18°C    | 6 months            |
|                | Polyethylene             | Refrigerate, 4°C | 14 days             |
| Grain Size     | Glass or                 | Refrigerate, 4°C | 6 months            |
|                | Polyethylene             |                  |                     |
| Total Lead     | Glass <sup>1</sup>       | Freeze, -18°C    | 2 years             |
|                |                          | Refrigerate, 4°C | 6 months            |
| Total Mercury  | Glass                    | Refrigerate, 4°C | 28 days             |
| Methyl-Mercury | $Glass^2$                | Refrigerate, 4°C | 1 day to processing |
|                |                          | Freeze, -18°C    | For storage beyond  |
|                |                          |                  | 1 day               |
| Pb-210         | Polystyrene <sup>2</sup> | Freeze, -18°C    | -                   |
|                | -                        | Refrigerate, 4°C |                     |
| Cs-137         | Polystyrene <sup>2</sup> | Freeze, -18°C    | -                   |
|                |                          | Refrigerate, 4°C |                     |

<sup>1=</sup> Recommended in Manchester Laboratory Users Manual (MEL, 1994)

Back-up sampling equipment, sample containers, positioning instruments, and spare parts will be carried during field sampling as preventative maintenance.

<sup>2=</sup> Containers Provided by Contract Laboratory

#### **Sediment Cores**

Sediment cores will be collected from Ecology's 26' research vessel using a Wildco stainless steel box corer fitted with a 13cm x 13cm x 50cm acrylic liner. Sedimentation rates reported for several freshwater lakes in Washington ranged from 0.18 cm/yr to 0.45 cm/yr (Yake, 2001). Based on these rates, a minimum penetration depth of approximately 30-50 cm will be needed to reach the approximate limit of Pb-210 dating, which is on the order of 100-150 years.

Upon retrieving a successful core, overlying water will be siphoned off, the liner removed from the corer, and the sediment core will be extruded and sectioned into 1 cm thick layers using aluminum plates. The core will be extruded using a gear driven piston that pushes the sediment column up and out of the liner. This process will result in a maximum of 50 sub-sections per core. Material in contact with the sidewall of the core liner will be removed prior to sub-sampling the core. Each section retained will then be place in 8-oz glass jars, place in plastic bags, and stored in coolers on ice pending processing in the laboratory.

Due to budget limitations, a maximum of ten sections from each core will be analyzed during this study. Sections for analysis will be selected to represent current conditions (top layer), background conditions to calibrate radio-dating, and representative intervals along the core length to reflect sediments deposited over several decades. Any visual time markers that will add in dating the core (ash layers, etc) will be noted in the field. Horizons not selected for initial analysis will be archived frozen to allow for future analysis if needed. The deposition of archived frozen samples must be agreed upon by Ecology, USGS, and WCHD. If Ecology wishes to relinquish control of the archived samples from this project, USGS and WCHD will be given the option of giving Ecology written permission to dispose of the samples or USGS and WCHD will agree upon which agency shall take control of the archived samples. The conditions for disposal for the archived samples will be clearly marked on the boxes containing the archived samples while in possession of any of the three parties.

Sections selected for analysis will be homogenized in the laboratory and sub-samples split into various containers for analysis: 2-oz jars for TOC, 4-oz jars (total mercury and lead), and polystyrene containers for radio-dating samples.

All utensils used to manipulate samples will be pre-cleaned by washing with Liquinox detergent, followed by sequential rinses with tap water, dilute (10%) nitric acid, deionized water, and methanol. Between stations, the corer will be thoroughly cleaned by brushing with on-site water. A new pre-cleaned acrylic core liner will be used for each station. Prior to use in the field, the core liners will be cleaned using the procedure described above.

#### **Surface Water**

Tributary samples for total mercury determinations will be collected as hand composites from three-quarter point grab samples across the channel at each site. Each quarter point sample will comprise 1/3 of the composite sample. Sampling personnel will wear non-talc nitrile gloves when collecting samples. Sample containers for total mercury will be Teflon bottles specifically cleaned at MEL for low-level metals analysis. After collection, the samples will be preserved in the field using ultra-pure acid supplied in pre-washed Teflon vials by MEL and placed in plastic bags for storage at 4°C. Sampling and field measurement protocols for conventional parameters (pH, temperature, conductivity, dissolved oxygen, and flow) will follow these specified in the Lake Whatcom Dissolved Oxyen TMDL Quality Assurance (QA) Project Plan (Cusimano and Liu, 2002). All surface water samples will be wrapped in plastic bags and stored in coolers on ice at 4°C and delivered to MEL within 48 hours of collection.

# **Laboratory Procedures**

Table 6 shows the list of analytes, number of samples, analytical methods, and estimated costs for Ecology's portion of the study. The cost of analysis of the cores from surrounding lakes and QA samples submitted by USGS for this project is described in an interagency agreement between Ecology and the WCHD (Magoon in prep, 2002). Samples for this project will be analyzed by MEL and accredited contract laboratories selected by MEL, in consultation with Ecology's project manager.

**Table 6: Summary of Analytical Procedures and Ecology's Estimated Costs for Lake Whatcom.** 

| Analyte    | Method          | #Samples <sup>1</sup> | Cost/Sample      | Subtotal |
|------------|-----------------|-----------------------|------------------|----------|
| Sediment   |                 |                       |                  |          |
| TOC        | Combustion/CO2  | 65                    | 33               | 2145     |
|            | Measurement,    |                       |                  |          |
|            | Report @ 70°C   |                       |                  |          |
|            | (9060)          |                       |                  |          |
| Grain Size | Seive and Pipet | 33                    | 90               | 2970     |
| Total-Hg   | CVAA (EPA       | 74                    | 31               | 2294     |
|            | 245.5)          |                       |                  |          |
| Methyl-Hg  | CV-GC-AFS       | 16                    | 250              | 4000     |
|            | (Modified EPA   |                       |                  |          |
| m . 1 m    | 1630)           |                       | •                | =        |
| Total-Pb   | ICP (EPA 200.7) | 37                    | 31               | 1147     |
| Pb-210     | Gamma           | 35                    | 195 <sup>2</sup> | 6825     |
| ~          | Detection       |                       |                  | 4.500    |
| Cs-137     | Gamma           | 16                    | 100              | 1600     |
| XXX .      | Detection       |                       |                  |          |
| Water      |                 |                       | 3                | - 400    |
| Total-Hg   | CVAA (EPA       | 75                    | $72^{3}$         | 5400     |
|            | 245.7*)         |                       |                  |          |
|            |                 |                       | Subtotal         | 26381    |
|            |                 |                       | Contracting Fee  | 3849     |
|            |                 |                       | Grand Total      | 30230    |

<sup>1=</sup> Includes QA Samples

<sup>2=</sup> Includes Calculation of Sedimentation Rates

<sup>3=</sup> Includes Bottle Preparation Charges

<sup>\*=</sup> a CVAF Method Modified by Manchester to Use CVAA

# **Quality Control Procedures**

## **Field Quality Control**

For surface sediments, one blind field replicate (a single sample homogenized and split in the field) will be prepared at a frequency of 1 per set of 20 samples. Additionally, at one random station selected by USGS, in each of the three basins, a split sample will be prepared and provided to USGS for determination of total mercury at an independent laboratory. Two of the three splits will also be analyzed for methyl mercury. A field log will be maintained that describes all procedures used to collect and process the samples in the field. Only pre-cleaned sampling equipment and sample containers, as described above, will be used. All equipment and containers will be kept covered with foil or in boxes until used. To minimize risk of cross-contamination, the sampling sequence will begin with the lowest expected concentration samples and finish with the most contaminated station. Care will be taken while operating the vessel in shallow water so as not to disturb and affect the sediments being sampled. Sample containers will be placed in polyethylene bags to further reduce the possibility of cross-contamination.

For surface water samples one blind field replicate will be prepared per collection. As a check for container contamination, a bottle blank (blank water in a sample container) will also be analyzed for every other collection. Field personnel will wear non-talc nitrile gloves when collecting samples. All samples will be placed in plastic bags for storage.

## **Lab Quality Control**

Laboratory QC samples will include method blanks, duplicate matrix spikes, analytical replicates, and laboratory control samples. These samples will be analyzed at the frequency shown in Table 7.

Table 7: Minimum Quality Control Samples and Frequency of Analysis.

| Parameter  | Field<br>Bottle<br>Blank | Field<br>Replicate | Method<br>Blank | Analytical<br>Replicates | Lab Control<br>Standard  | Matrix<br>Spike | Matrix<br>Spike<br>Duplicate |
|------------|--------------------------|--------------------|-----------------|--------------------------|--------------------------|-----------------|------------------------------|
| Sediment   |                          |                    |                 |                          |                          |                 | -                            |
| TOC        | -                        | 1/20               | 1/20            | 1/20                     | 1/batch <sup>1</sup>     | -               | -                            |
| Grain Size | -                        | 1/20               | -               | 1/20                     | -                        | -               | -                            |
| Total-Hg   | -                        | 1/20               | 1/20            | 1/20                     | 1/batch                  | 1/20            | 1/20                         |
| Methyl-Hg  | -                        | 1/20               | 1/20            | 1/20                     | -                        | 1/20            | 1/20                         |
| Total-Pb   | -                        | 1/20               | 1/20            | 1/20                     | 1/batch                  | 1/20            | 1/20                         |
| Pb-210     | -                        | -                  | 1/20            | 1/20                     | 1/20                     | -               | -                            |
| Cs-137     | -                        | -                  | 1/20            | 1/20                     | 1/20                     | -               | -                            |
| Water      |                          |                    |                 |                          |                          |                 |                              |
| Total-Hg   | 1/per 2 batches          | 1/batch            | 1/20            | 1/batch                  | 1/2 batches <sup>2</sup> | 1/batch         | 1/batch                      |

Batch= Sampling Event

The procedures and criteria for analyzing blanks and matrix spikes are described in the analytical methods. The USGS will also submit and fund analysis of six blind samples for total-mercury and two blind samples for methyl-mercury in sediments.

## **Corrective Actions**

The analyst is responsible for monitoring the analysis and troubleshooting problems as they occur. It is important to identify analytical problems as soon as possible so that corrective actions can be taken prior to the expiration of holding times. It is the responsibility of the laboratory to communicate analytical problems to the project manager during the analysis so that the project manager may have input into the course of corrective action. This communication is critical when the laboratory is experiencing difficulty in meeting any project specified requirements, including detection limits. It is important for the project manager and laboratory to agree on what constitutes a reasonable corrective action.

<sup>- =</sup> Not applicable

<sup>1=</sup> NIST 2704 Buffalo River Sediment Analyzed in Triplicate

<sup>2=</sup> NIST 1641d Diluted to 0.032 ug/l and Analyzed in Duplicate/Batch

## **Performance and System Audits**

MEL participates in performance and system audits of their routine procedures. Results of these audits are available on request. EA Program Quality Assurance Unit must accredit all contract laboratories performing work for Ecology. The accreditation process includes performance and system audits.

## **Data Review and Validation**

MEL will conduct a review of all laboratory analysis for the project including contract laboratory's data and case narratives. MEL will verify that the project MQOs were met; methods and protocols specified in the QA Project Plan were followed; that all calibrations, checks on quality control, and intermediate calculations were performed; and that the data are consistent, correct, and complete, with no errors or ommisions. Evaluation criteria will include the acceptability of instrument calibration, procedural blanks, spike samples' analysis, precision data, laboratory control sample analysis, and appropriateness of the data qualifiers assigned. MEL will prepare a written report on the results of their data review. Sedimentation rates, reported by the contract laboratory, will be reviewed by the Ecology and USGS project manager for acceptability.

The project manager will review the contract laboratory's data package and MEL's data validation report. The project manager will check these data and reports for completeness and reasonableness. Based on these assessments, the data will either be accepted, accepted with appropriate qualifications, or rejected and re-analysis considered.

# **Data Quality Assessment**

Once the data have been reviewed, verified, and validated, the EA Program project manager will make a determination if the data can be used to make the determinations and decisions for which the project was designed. Results from analyzing the field and laboratory QC samples will be used to judge if the MQOs for the project have been met. The SRMs will indicate directly if the accuracy target for total mercury and TOC has been met.

If the results are satisfactory, analysis of variance, or other appropriate tests, will be used to evaluate between-site differences in mercury levels.

# Reporting

On or before March 2003, the project lead, in consultation with USGS staff, will prepare a draft report on the results of sediment sampling and provide it to the Ecology's Bellingham Field Office for review. Subsequent reviews will include the Whatcom County Health Department. At a minimum, the final report will contain the following;

- ❖ Maps of the study area showing all sampling sites.
- Description of field and laboratory methods.
- Sample information (dates, times, depths, coordinates, etc).
- Discussion of data quality and the significance of any problems encountered in the sampling or analysis.
- Summary table of all chemical data.
- ❖ An analysis of spatial and temporal patterns in mercury concentration.
- \* Reporting of net sedimentation rates and time horizons for each core location.
- ❖ Comparisons with other applicable information on typical mercury levels in freshwater sediments and available sediment quality guidelines.
- \* Recommendations for follow-up work, with emphasis on the need or feasibility for conducting a TMDL for mercury in Lake Whatcom.

The final project report will include the tributary water sampling results. It is anticipated that the final project report will be completed by August 2003. Prior to completion of the project, all project data will be entered into Ecology's Environmental Information Management System (EIM). The sediment data will also be processed for entry into Ecology's SEDQUAL database. Public access to electronic versions of the data and reports generated from this project will be available via Ecology's internet homepage (http://www.ecy.wa.gov).

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# **Appendix A**

# **Table A1: List of Sediment Sites**

Table A1: Sediment Station Positions Lake Whatcom Hg S

Basin 1- Focused Surface Sediment Sites (deg/min)

| Station ID | Latitude |        | Long | itude  |
|------------|----------|--------|------|--------|
| MW         | 48       | 45.547 | 122  | 24.906 |
| SB         | 48       | 46.104 | 122  | 24.342 |
| EC         | 48       | 45.012 | 122  | 24.480 |

Basin 1- Primary Random Surface Sediment Sites (deg/min)

| Station ID | Latitude |        | Long | itude  |
|------------|----------|--------|------|--------|
| 1-1        | 48       | 45.194 | 122  | 23.934 |
| 1-2        | 48       | 45.217 | 122  | 23.823 |
| 1-3        | 48       | 45.689 | 122  | 24.853 |
| 1-4        | 48       | 45.773 | 122  | 24.356 |
| 1-5        | 48       | 45.422 | 122  | 24.782 |

Basin 1- Alternate Random Surface Sediment Sites (deg/min)

| Station ID | Latitude |        | Long | itude  |
|------------|----------|--------|------|--------|
| 1-1        | 48       | 45.839 | 122  | 24.959 |
| 1-2        | 48       | 45.654 | 122  | 24.125 |
| 1-3        | 48       | 45.620 | 122  | 24.828 |
| 1-4        | 48       | 45.883 | 122  | 24.912 |
| 1-5        | 48       | 45.173 | 122  | 24.020 |

**Basin 1- Core Site (deg/min)** 

| Station ID | Latitude |        | Longitude |        |
|------------|----------|--------|-----------|--------|
| C-1        | 48       | 45.652 | 122       | 24.624 |

Basin 2- Primary Random Surface Sediment Sites (deg/min)

| Station ID | Latitude |        | Longitude |        |
|------------|----------|--------|-----------|--------|
| 2-1        | 48       | 44.342 | 122       | 22.324 |
| 2-2        | 48       | 44.844 | 122       | 23.543 |
| 2-3        | 48       | 44.507 | 122       | 22.264 |
| 2-4        | 48       | 44.890 | 122       | 23.000 |
| 2-5        | 48       | 44.808 | 122       | 23.396 |

Basin 2- Alternate Random Surface Sediment Sites (deg/min)

| Station ID | Latitude |        | Long | itude  |
|------------|----------|--------|------|--------|
| 2-1        | 48       | 45.038 | 122  | 23.487 |
| 2-2        | 48       | 44.479 | 122  | 22.998 |
| 2-3        | 48       | 44.909 | 122  | 23.209 |
| 2-4        | 48       | 45.114 | 122  | 23.181 |
| 2-5        | 48       | 44.376 | 122  | 22.234 |

**Basin 2- Core Site (deg/min)** 

| Station ID | Latitude |        | Longitude |        |
|------------|----------|--------|-----------|--------|
| C-2        | 48       | 44.660 | 122       | 22.749 |

**Basin 3- Focused Surface Sediment Sites (deg/min)** 

| Station ID | Latitude |        | Long | itude  |
|------------|----------|--------|------|--------|
| CC         | 48       | 45.174 | 122  | 21.246 |
| OC         | 48       | 45.030 | 122  | 21.192 |
| SC         | 48       | 43.734 | 122  | 18.828 |
| BCC        | 48       | 41.040 | 122  | 16.782 |
| ANC        | 48       | 40.416 | 122  | 16.110 |
| BC         | 48       | 40.434 | 122  | 16.530 |
| ASC        | 48       | 43.260 | 122  | 19.248 |

Basin 3- Primary Random Surface Sediment Sites (deg/min)

| Station ID | Latitude |        | Long | itude  |
|------------|----------|--------|------|--------|
| 3-1        | 48       | 40.471 | 122  | 18.836 |
| 3-2        | 48       | 44.756 | 122  | 21.797 |
| 3-3        | 48       | 43.607 | 122  | 18.509 |
| 3-4        | 48       | 41.009 | 122  | 17.749 |
| 3-5        | 48       | 40.930 | 122  | 16.693 |
| 3-6        | 48       | 40.744 | 122  | 16.454 |
| 3-7        | 48       | 43.168 | 122  | 18.711 |
| 3-8        | 48       | 43.465 | 122  | 18.839 |
| 3-9        | 48       | 43.856 | 122  | 19.956 |
| 3-10       | 48       | 44.598 | 122  | 20.765 |
| 3-11       | 48       | 40.408 | 122  | 16.296 |

Basin 3- Alternate Random Surface Sediment Sites (deg/min)

| Station ID | Latitude |        | Long | gitude |
|------------|----------|--------|------|--------|
| 3-1        | 48       | 43.136 | 122  | 19.130 |
| 3-2        | 48       | 44.730 | 122  | 20.666 |
| 3-3        | 48       | 42.523 | 122  | 18.579 |
| 3-4        | 48       | 42.189 | 122  | 17.898 |
| 3-5        | 48       | 44.822 | 122  | 21.282 |
| 3-6        | 48       | 43.513 | 122  | 19.258 |
| 3-7        | 48       | 40.672 | 122  | 16.804 |
| 3-8        | 48       | 44.822 | 122  | 22.034 |
| 3-9        | 48       | 41.673 | 122  | 18.402 |
| 3-10       | 48       | 44.483 | 122  | 20.942 |
| 3-11       | 48       | 45.198 | 122  | 21.718 |

**Basin 3- Core Site (deg/min)** 

| Station ID | Latitude |        | Longitude |        |
|------------|----------|--------|-----------|--------|
| C-3        | 48       | 41.840 | 122       | 18.172 |

# **Table A2: List of Tributary Sites**

**Table A2: Proposed Surface Water Sampling Sites.** 

| STATION<br>ID | STATION NAME                        | DESCRIPTION  |
|---------------|-------------------------------------|--|
| ANC           | Anderson Creek (Nooksack Diversion) | The site is located at the bridge where South Bay Drive crosses the creek. The Anderson Creek gage is mounted in the existing stilling well on the east side of Anderson Creek, approximately 0.5 km from the mouth of the creek.          |
| ASC           | Austin Creek                        | Approximately 1800 ft upstream from where the creek flows into Lake Whatcom. The Austin Creek gage is mounted on the north west support pillar under the bridge over Austin Creek (Lake Whatcom Blvd.), approximately 1 km from the mouth. |
| ВС            | Brannian Creek                      | Downstream of South Bay Drive, approximately 600 m from mouth  |
| CC            | Carpenter Creek                     | Near mouth.  |
| CC<br>EC      | Euclid Creek                        | East of Euclid Ave. 120 m from mouth. Upstream of public trail.  |
| MW            | Mill Wheel Creek                    | Upstream side of the culvert the passes under Flynn street   |
| OC            | Olsen Creek                         | The site is located at the bridge where North Shore Road crosses the creek. The gage is at the left bank upstream side of the bridge   |
| SB            | Silver Beach Creek                  | Adjacent to Hayward Ct. Approx 130 m from mouth.   |
| SC            | Smith Creek                         | Samples are collected approximately 100 yards upstream from Lake Whatcom.  |
| BCC           | Blue Canyon Creek                   | Samples are collected upstream from the culvert crossing at Blue Canyon road.  |