

Quality Assurance Project Plan

Potential Impacts from Mercury Used in Historic Gold Mining on Six Rivers and Streams

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Waterbody Numbers:

Sultan River:	WA-07-1170 and -1180
Swauk Creek:	WA-39-1400 and -1420
Peshastin Creek:	WA-45-1013 and -1014
Similkameen River:	WA-49-1030
Mary Ann Creek:	(No number)
Strawberry Creek:	WA-52-1220

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August 2009

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SCS – Statewide Coordination Section.

EAP - Environmental Assessment Program.

EIM - Environmental Information Management system.

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Abstract

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 results will be posted to the Internet.

In the present study, mercury will be analyzed in water, sediment, fish, and invertebrate samples from six rivers and creeks potentially impacted by the use of elemental mercury to recover gold in historic mining operations.

The waterbodies of interest are:

- Sultan River (Snohomish County).
- Swauk Creek (Kittitas County).
- Peshastin Creek (Chelan County).
- Similkameen River (Okanogan County).
- Mary Ann Creek (Okanogan County).
- Strawberry Creek (Okanogan County).

The goal of the study will be to determine if mercury levels represent a potential human health risk for fish consumers or could adversely affect aquatic life. Field work will be conducted between August 2009 and June 2010. The results will be evaluated for elevation above background and compared to environmental criteria and guidelines for mercury. A weight of evidence approach will be used to conclude if significant contamination exists.

Background

The Washington State Department of Ecology (Ecology) Hazardous Waste and Toxic Reduction (HWTR) Program has requested a study to screen selected Washington rivers and creeks for evidence of mercury contamination. The source of concern is the historic use of elemental mercury in turn-of-the-century mining operations. In the United States, this practice began in the 1850s and was the main gold recovery technique until the 1940s. In the present context, historic mining refers to the mining of alluvial deposits using hydraulic, drift, or dredging methods, and recovery of gold using elemental mercury. The deposits are often referred to as placers, the name derived from Spanish for "sandbank".

Greg Caron, HWTR client for this project, gives the following rationale for the study:

"Mercury contamination from historical gold mines represents a potential risk to human health and the environment (USGS, 2005). Fish from reservoirs and streams in California have bioaccumulated sufficient mercury to pose a risk to human health (May et al., 2000; Klasing and Brodberg, 2003). Ecology's HWTR Program has been working with historic miners to dispose of elemental mercury they find in Washington rivers and streams. Turn-of-the-century miners used to add elemental mercury to sluice boxes to recover fine particles of gold. Previous studies have estimated that a typical sluice likely lost several hundred pounds of mercury during the operating season (Hunerlach et al., 1999).

In 2003, the Legislature passed the Mercury Education Reduction Act, initiating a program to safely dispose of mercury. Since then, HWTR contacts within mining clubs and individuals have resulted in the recovery of over 195 pounds of elemental mercury collected from Washington rivers and streams. Localized point sources of mercury likely exist and methylation of mercury occurs close to the sources, allowing methyl mercury to enter the food web (Hunerlach et al., 1999). These point sources offer target areas for investigation. At this time, no one has attempted to identify and sample specific stream locations in Washington where mercury may be present."

Project Description

The HWTR Program selected the Sultan River, Swauk Creek, Peshastin Creek, and the Similkameen River for investigation, based on the extent of past gold mining activity. When contacted about this project, the Washington State Department of Natural Resources (DNR) Division of Geology and Earth Resources suggested adding two other small streams to the study, Mary Ann Creek and Strawberry Creek.

The goal of this screening survey will be to determine if mercury levels in these six waterbodies represent a potential human health risk for fish consumers or could adversely affect aquatic life. Mercury will be analyzed in the water column, suspended sediments, streambed sediments, fish, and invertebrates. Field work will be conducted between August 2009 and June 2010. The study will be conducted by Ecology's Environmental Assessment Program (EAP), with sample analysis by Ecology's Manchester Environmental Laboratory. A draft report on the results is anticipated by October 2010.

This Quality Assurance (QA) Project Plan was developed following the Ecology guidance in Lombard and Kirchmer (2004).

Organization and Schedule

The following people are involved in this project. All are employees of the Washington State Department of Ecology.

Staff (all are EAP except client)	Title	Responsibilities
Greg Caron HWTR Central Regional Office Phone: (509) 454-7893	Client	Clarifies scopes of the project, provides internal review of the QAPP, approves the final QAPP, and reviews and approves the final report.
Art Johnson Toxics Studies Unit SCS Phone: (360) 407-6766	Project Manager/ Principal Investigator	Writes the QAPP. Oversees field sampling and transportation of samples to the laboratory. Conducts QA review of data, and analyzes and interprets data. Writes the draft report and final report.
Michael Friese Toxics Studies Unit SCS Phone: (360) 407-6737	Field Assistant	Collects fish and helps collect other samples. Assists with report preparation. Enters data into EIM.
Dale Norton Toxics Studies Unit SCS Phone: (360) 407-6765	Unit Supervisor for the Project Manager	Provides internal review of the QAPP, approves the budget and final QAPP, and reviews and approves the final report.
Will Kendra SCS Phone: (360) 407-6698	Section Manager for the Project Manager and Study Area	Reviews the project scope and budget, tracks progress, reviews the draft QAPP, and approves the final QAPP.
Stuart Magoon Manchester Environmental Laboratory Phone: (360) 871-8801	Director	Approves the final QAPP.
William R. Kammin Phone: (360) 407-6964	Ecology Quality Assurance Officer	Reviews the draft QAPP and approves the final QAPP.

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EAP – Environmental Assessment Program.

HWTR - Hazardous Waste & Toxic Reduction Program.

 $SCS-Statewide\ Coordination\ Section.$

QAPP – Quality Assurance Project Plan.

EIM – Environmental Information Management system.

Field and laboratory work	Due date	Lead staff
Field work completed	June2010	Michael Friese
Laboratory analyses completed	July 1010	
Environmental Information System (EIM)	database	
EIM user study ID	AJOH0059	
Product	Due date	Lead staff
EIM data loaded	November 2010	Michael Friese
EIM QA	December 2010	Janice Sloan
EIM complete	January 2011	Michael Friese
Final report		
Author lead and support staff	Art Johnson	Michael Friese
Schedule		
Draft due to supervisor	September 2010	
Draft due to client/peer reviewer	October 2010	
Draft due to external reviewer(s)	NA	
Final (all reviews done) due to publications coordinator (Joan)	December 2010	
Final report due on web	January 2011	

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

Quality Objectives

Quality objectives for this project are to obtain data of sufficient quality so that uncertainties are minimized, and that accurate and representative results are obtained for the parameters of interest. These objectives will be achieved through careful attention to the sampling, measurement, and quality control (QC) procedures described in this QA Project Plan.

Measurement Quality Objectives

Manchester Laboratory is expected to meet all QC requirements of the analytical methods being used for this project.

Measurement quality objectives (MQOs) for this study are shown in Table 3. The recovery and precision objectives are the acceptance limits of the analytical methods. The lowest concentrations of interest indicated for mercury are set at Manchester's reporting limits.

Sample Type/ Analysis	Check Stds./ LCS (% recov.)	Duplicate Samples (RPD)	Matrix Spikes (% recov.)	Matrix Spike Duplicates (RPD)	Lowest Concentration of Interest
Water					
Mercury	85-120%	±20%	75-125%	±20%	0.002 ug/L
Total Suspended Solids	80-120%	±20%	NA	NA	1 mg/L
Sediment					
Mercury	85-120%	±20%	75-125%	±20%	0.005 mg/Kg
Grain Size	80-120%	±20%	NA	NA	0.1%
Tissue					
Mercury	85-120%	±20%	75-125%	±20%	0.005 mg/Kg

Table 3.	Measurement	Quality	Objectives
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LCS = Laboratory control sample.

RPD = Relative percent difference.

NA = Not applicable.

Representativeness, Comparability, and Completeness

The intent of this project is to obtain data on mercury concentrations in water, sediment, and biota that are representative of conditions in the vicinity of historic mining areas, particularly during likely periods of mercury transport. Steps being taken to ensure representativeness include collection of multiple samples and use of appropriate sampling and sample handling procedures.

The field and laboratory methods being used are standardized and comparable to similar studies in Washington rivers and streams.

The completeness goal for this project is to have valid, defensible data for all samples collected.

Waterbodies and Stream Reaches to be Sampled

Figure 1 shows the approximate location of the six waterbodies proposed for sampling. Areas within these rivers and creeks that have seen substantial gold mining activity in the past are depicted in Figure 2, based on maps provided by Fritz Wolf of the DNR Geology & Earth Sciences Division. Some small-scale gold mining continues in all of these areas.



Figure 1. Approximate Location of Waterbodies to be Sampled, Showing Major Rivers to Which They Discharge. (Mary Ann Creek is a tributary of Myers Creek, which flows into British Columbia, Canada.)



Figure 2a. Placer Mining Area on the Sultan River (Snohomish County).



Figure 2b. Placer Mining Area in the Swauk Creek Drainage (Kittitas County).



Figure 2c. Placer Mining Areas in the Peshastin Creek Drainage (Chelan County).



Figure 2d. Placer Mining Area on the Similkameen River (Okanogan County).



Figure 2e. Placer Mining Area on Mary Ann Creek (Okanogan County).



Figure 2f. Placer Mining Area on Strawberry Creek (Okanogan County).

Existing Data

Limited data have been collected on mercury levels in the six waterbodies being sampled in this project. The results, most of which are for the Similkameen River, show generally low concentrations. There is, however, some evidence of mercury impacts, either to the sediments or increased concentrations during runoff periods, which warrant further investigation.

Swauk and Peshastin Creeks

Raforth et al. (2000, 2004) analyzed mercury in a few water and sediment samples from Swauk Creek, Williams Creek, and Culver Gulch (Peshastin Creek) in connection with hard rock mining. One water sample each was collected downstream of the placer mining areas shown in Figures 2b and 2c during low flow and high flow. Mercury was not detected at or above 0.002 ug/L. Sediment samples from these sites had low-to-moderate concentrations of mercury, 0.02-0.1 mg/Kg, dry weight. The Culver Gulch sample showed more than a 12-fold increase over upstream levels. Sediment quality criteria, however, were not exceeded (Appendix A).

Mercury was monitored in lower Swauk Creek near its confluence with the Yakima River to verify 303(d) listings based on historical data (Johnson, 2000). This site is approximately 10 miles below the mining area shown in Figure 2b. Mercury was detected at 0.002 - 0.004 ug/L in three of the six samples collected from March 1999 to February 2000. The detections occurred in May, July and November. All concentrations were below mercury's chronic water quality criterion of 0.012 ug/L (Appendix A).

Similkameen River

Results from Ecology's ambient water quality monitoring program include mercury data for the Similkameen River at Oroville, collected from October 2007 to August 2008. Mercury was below detection limits (0.002 ug/L) except during a high-flow event in June when concentrations reached 0.01 ug/L (<u>www.ecy.wa.gov/programs/eap/fw_riv/rv_main.html#4</u>). It should be noted that the reservoir formed by Enloe Dam (Figure 2d) is located between the placer mining reach and Oroville, and is a potential sink for mercury associated with suspended sediment.

An earlier 1995-96 study in the Similkameen showed evidence of a slight increase in mercury levels in water samples collected above and below the placer mining reach during spring runoff (April). Concentrations measured in duplicate samples at Nighthawk averaged 0.003 ug/L versus 0.005 ug/L at Oroville (Johnson, 1997). Mercury was not detected at either location under low-flow conditions (<0.001 ug/L).

Johnson and Plotnikoff (2000) reviewed sediment quality data for the Similkameen River. Mercury levels were reported in three sediment samples collected from the placer mining reach in 1995 and 1998. Concentrations were slightly higher, to 0.03 mg/Kg, than further upstream, <0.01-0.1 mg/Kg. Grab and core samples of the sediment deposits behind Enloe Dam showed low mercury concentrations in the surface layers (top 1 foot or less). However, the sediments analyzed consisted of coarse sand and may be a poor indicator of mercury contamination. Ecology's Washington State Toxics Monitoring Program recently analyzed chemical contaminants in a composite fillet from mountain whitefish collected near the mouth of the Similkameen River in August 2008 (unpublished data). The mercury concentration in this sample was 0.073 mg/Kg, which meets the EPA National Toxics Rule (0.825 mg/Kg) and EPA methylmercury (0.30 mg/Kg) criteria (Appendix A). Because these fish were collected near the confluence with the Okanogan River, they may or may not be representative of the Similkameen River.

Sampling Design

Approach

Elemental mercury discharged during historic mining operations would tend to sink into the streambed due to mercury's density. Gravel and cobble that entered the sluices caused some of the mercury to break into tiny particles that could be observed floating many miles downstream (Alpers et al., 2005a). Finding mercury deposits by direct sampling of the bottom sediments is therefore likely to be a hit-and-miss proposition. Furthermore, sediment sampling is difficult in the cobble and gravel substrate that predominates in these streams.

Although bed sediments will be analyzed in this study, evidence of mercury contamination will primarily be obtained indirectly through water column, suspended sediment, and biological samples. The U.S. Geological Survey (USGS) and others have identified "hot spots" of mercury contamination and bioaccumulation by similar reconnaissance-level sampling of water, sediment, and biota tissue at mining sites in other states (e.g., Alpers et al., 2005b). Results will be evaluated for elevation above background and compared to water, sediment, and tissue criteria and guidelines for mercury (Appendix A). A weight-of-evidence approach will be used to conclude if significant contamination exists.

Water Column

The annual flow patterns of the Sultan River, Swauk Creek, Peshastin Creek, and Similkameen River are depicted in Figure 3. Most of the mercury transport out of stream reaches contaminated from mining would be expected to occur during runoff events when bottom material is re-suspended. The highest flows in these waterbodies are either in the early winter (Sultan River) or spring (Peshastin Creek, Swauk Creek, and Similkameen River). Flow data were not available for Mary Ann or Strawberry Creeks, but they would be expected to have their highest flows in the spring, similar to other eastern Washington streams.

Based on these patterns, water column samples will be collected once a month during October through December 2009 in the Sultan River, and similarly from approximately April through June 2010 in the five eastern Washington rivers and creeks. A set of baseline samples will also be collected from each of the six waterbodies during summer low-flow (August).

The approximate timing of the water samples is shown in Table 4. To the extent possible, the spring and winter sample collections will coincide with rising flows. Sampling may be initiated sooner or later than indicated in Table 4, depending on rainfall and snowmelt.

Sampling sites will be located downstream of the mining areas shown in Figure 2. Single grabs will be collected each month for analysis of total mercury and total suspended solids. Low-level methods (0.002 ug/L reporting limit) will be used for mercury during low-flow to minimize the number of samples that are non-detect. Routine detection limits (0.05 ug/L) will be employed for the remainder of the study to reduce cost and in anticipation of higher concentrations.



Figure 3. Flow Patterns for Four Rivers and Streams. [Monthly averages from <u>http://waterdata.usgs.gov/wa/nwis/sw</u> (Sultan, Peshastin, Similkameen) and <u>http://ecy.wa.gov/programs/eap/flow/shu_main.html</u> (Swauk).]

Waterbody	Low-flow			Winter runoff			NS			Spring Runoff		Total samples
	Α	S	0	Ν	D	J	F	Μ	Α	М	J	
Sultan River	1		1	1	1							4
Swauk Creek*	2								2	2	2	8
Peshastin Creek+	3								3	3	3	12
Similkameen River	1								1	1	1	4
Mary Ann Creek	1								1	1	1	4
Strawberry Creek	1								1	1	1	4
Total samples	9		1	1	1				8	8	8	36

 Table 4. Approximate Timing of Water Samples

*Includes Williams Creek.

⁺Ingalls Creek, Negro Creek, Culver Gulch.

NS = No sampling.

A-J = Months from August through June.

Suspended Sediment

Results from water samples provide an instantaneous measurement of mercury concentrations. These data will be supplemented with suspended sediment traps to give a longer term assessment of mercury re-suspension and transport. One trap will be deployed for approximately one month in low velocity locations downstream of the mining areas in each waterbody. The traps will be set out in October-November 2009 (Sultan) and April-May 2010 (Peshastin, Swauk, Similkameen, Mary Ann, and Strawberry). The material retained in the traps will be centrifuged and analyzed for total mercury.

Streambed Sediment

Three widely spaced surface sediment samples will be collected from placer mining areas within each waterbody. The samples will be obtained from deposits of fine material accessed during summer low flow. Total mercury and grain size will be analyzed.

In addition to conventional sediment samples, some reconnaissance sampling will be conducted by screening and panning samples of the streambed in an effort to find elemental mercury.

Tissue Samples

Fish

Adverse human health effects due to consuming fish elevated in mercury is a concern being addressed in this study. Total mercury will be analyzed in edible tissues from up to three fish species collected in the general vicinity of mining areas in each waterbody. Species likely to be encountered include largescale suckers, mountain whitefish, cutthroat trout, brook trout, and rainbow trout. Low species diversity is anticipated in the creeks, and fewer than three species may be encountered. To the extent possible, all samples will be composites of tissues from four to five individual fish.

The fish will be collected during late summer or fall, which affords the best access and fishing success. Fish have relatively long lifespans and tissue turnover times: multiple years for top predators and months to years for forage fish (Chasar et al., 2009). Therefore, fish should be a good indicator of mercury contamination even when collected during a period when mercury concentrations in the water column are likely to be at a minimum.

Invertebrates

Benthic invertebrates have been shown to accumulate mercury in rivers and streams impacted by mining and other anthropogenic sources. Order of magnitude differences in mercury levels have been observed in invertebrates collected above and below contaminated sites (Eisler, 1987). Unlike fish, benthic invertebrates have limited mobility and thus may be more representative of site-specific conditions.

One to three widely spaced benthic invertebrate samples are planned within each mining area in each waterbody, depending on the size and accessibility of the reach. A fourth sample will be collected for comparison, either upstream of known mining activity or in a nearby reference area, yet to be selected. The invertebrate samples will be taken in the late summer or fall, again for reasons of access. Caddis flies, being abundant and relatively large, will be analyzed to achieve sufficient sample weights for mercury analysis and to improve comparability between sites.

Summary

Sample Type	Timing	Number of Waterbodies	Samples per Waterbody	Total Samples	General Location
Watan	Summer Low Flow	6	1-3	9	
water	Winter or Spring	6	1-3	24	Downstream of
Suspended Sediment	Runoff	6	1	6	mining area
Streambed Sediment		6	3	18	Mining area
Fish Tissue	Summer Low Flow	6	1-3	12	Within or below mining area
Invertebrate Tissue		6	2-4	18	Within and above mining area

Table 5. Summary of Sampling Design.

Sampling Procedures

Sample containers, preservation, and handling for this project are shown in Table 6.

Media/Analysis	Minimum Sample Size	Container	Preservation	Holding Time
Water				
Total Mercury (low-level)	350 mL	500 mL Teflon ⁺	HNO ₃ to pH<2, $\leq 6^{\circ}$ C	28 days
Total Mercury (routine)	350 mL	500 mL HDPE	HNO ₃ to pH<2, $\leq 6^{\circ}$ C	28 days
Total Suspended Solids	1,000 mL	1000 mL poly bottle	Cool to $\leq 6^{\circ}$ C	7 days
Sediment				
Total Mercury	50 g	8 oz. glass**	Cool to $\leq 6^{\circ}$ C	28 days
Grain Size	100 g	8 oz. plastic	Cool to $\leq 6^{\circ}$ C	6 months
Tissue				
Total Mercury (fish)	50 g	4 oz. glass**	Freeze	28 days
Total Mercury (invertebrates)	5 g	4 oz. glass**	Freeze	28 days

Table 6. Sample Containers, Preservation, and Handling.

[†]Cleaned as described in Manchester Laboratory Clean Room Standard Operating Procedure (SOP). **Cleaned as per OSWER protocol #9240.0-5.

Water

Sampling procedures for mercury in water will follow the guidance in EPA Method 1669 *Sampling Ambient Water for Trace Metals at EPA Water Quality Levels*. All samples will be taken as simple grabs.

Mercury samples will be collected directly into pre-cleaned 500 mL Teflon (low-flow) or HDPE (runoff) bottles. Total suspended solids samples will be collected in one-liter poly bottles. The mercury samples will be preserved to pH <2 after receipt at Manchester Laboratory. The Teflon sample bottles will be acid-cleaned by Manchester, as described in the Clean Room SOP, and sealed in plastic bags. Non-talc nitrile gloves will be worn by personnel collecting the samples.

Streamflow will either be measured at the time of sample collection (Sullivan, 2007) or obtained from USGS, Ecology, or other sources.

Suspended Sediment

The sediment traps being used for this study consist of a simple 4-inch diameter Plexiglas cylinder, weighted in a concrete slab, and buried so as to extend approximately 12 inches above the streambed. The cylinder will be precleaned by washing with Liquinox detergent, followed by sequential rinses with tap water, dilute nitric acid, and de-ionized water. The cylinder mouth will be covered with aluminum foil for transport into the field.

The traps will be deployed in low-velocity areas of each stream for approximately one month. After retrieval, the sediment in the cylinder will be allowed to settle and overlying water siphoned off. The remaining slurry will be poured into priority pollutant cleaned half-gallon glass jars with Teflon-lid liners and stored on ice in coolers.

Sample processing will consist of decanting off additional overlying water and then centrifuging the remaining slurry in a pre-weighed, 16-oz. glass jar at 1,000 rpm for ten minutes to isolate the sediment fraction. After centrifuging, the remaining overlying water will be decanted and the jar re-weighed to determine the approximate total wet grams of material collected. The centrifuged sediment will be scraped into a precleaned 8-oz. glass jar with a Teflon-lid liner and stored at $<4^{\circ}$ C until analyzed.

Streambed Sediment

Sediment collection and handling will follow the EAP SOP for freshwater sediment samples (Blakley, 2008). The samples will consist of composites of multiple grabs taken with a 0.02 m^2 Ponar sampler. A grab will be considered acceptable if not over-filled with sediment, overlying water is present and not excessively turbid, the sediment surface is relatively flat, and the desired depth penetration has been achieved.

After siphoning off overlying water, the sediments from each of three or more grabs per sampling site will be removed with a stainless steel scoop and passed through a 2-mm sieve using site water. Water will be decanted from the sieved material, after which it will be homogenized in a stainless steel bowl by stirring. Material touching the side walls of the grab will not be taken. Subsamples of the homogenized sediment will be put into appropriate sample containers and placed on ice immediately upon collection.

Stainless steel implements used to collect and manipulate the sediments will be cleaned prior to use in each waterbody by washing with Liquinox detergent, followed by sequential rinses with tap water, dilute nitric acid, and de-ionized water. The equipment will then be air dried and wrapped in aluminum foil. Between-site cleaning of the Ponar will consist of thorough brushing with on-site water.

Tissue Samples

Fish

Fish will be collected by electroshocking, gill nets, or hook and line, following the EAP SOP for fish collection (Sandvik, 2006a). To the extent possible, only those fish large enough to reasonably be retained for consumption will be taken.

Fish selected for analysis will be killed by a blow to the head. Each fish will be given a unique identifying number, and its length and weight will be recorded. The fish will be individually wrapped in aluminum foil, put in plastic bags, and placed on ice for transport to Ecology headquarters, where the samples will be frozen pending preparation of tissue samples.

Tissue samples will be prepared follow the EAP SOP for resecting finfish (Sandvik, 2006b). Techniques to minimize potential sample contamination will be used. People preparing the samples will wear non-talc nitrile gloves and work on heavy-duty aluminum foil or a polyethylene cutting board. The gloves and foil will be changed between samples; the cutting board will be cleaned between samples as described below.

The fish will be thawed enough to remove the foil wrapper and rinsed with tap water, then de-ionized water to remove any adhering debris. The entire fillet from one or both sides of each fish will be removed with stainless steel knives and homogenized in a Kitchen-Aid blender. The fillets will be scaled and analyzed skin-on. The sex of each fish will be recorded.

Four to five individual fish will be used for each composite sample. To the extent possible, the length of the smallest fish in a composite will be no less than 75% of the length of the largest fish. The composites will be prepared using equal weights from each fish. The pooled tissues will be homogenized to uniform color and consistency, using a minimum of three passes through the blender. The homogenates will be placed in precleaned 4-oz. glass jars with Teflon-lid liners.

The tissue samples will be refrozen for later shipment to Manchester Laboratory. Excess samples will be stored frozen at Ecology headquarters.

Cleaning of resecting instruments, cutting boards, and blender parts will be done by washing in tap water with Liquinox detergent, followed by sequential rinses with tap water, de-ionized water, and pesticide-grade acetone. The items will then be air dried on aluminum foil in a fume hood before use.

Benthic Invertebrates

Sampling sites for benthic invertebrates will be located in riffle habitats. A D-frame kicknet (500 micron mesh) will be used. Invertebrates are dislodged by kicking or scrubbing rocks upstream of the net. Caddis flies will be selectively removed from the kicknet with acid-cleaned forceps and placed in 4-oz. glass jars with Teflon-lid liners. Sufficient effort will be expended to obtain a sample weight of at least 5 grams.

After return to Ecology headquarters, the caddis fly samples will be freeze-dried and ground to uniform color and consistency in a mortar and pestle. The mortar and pestle will be precleaned using the same procedures as for the sediment samples. Fresh and dried weights will be recorded. The samples will be stored in polyethylene vials for later shipment to Manchester Laboratory.

General

Field activities will be recorded in a bound notebook of waterproof paper. A hand-held GPS will be used to record sampling locations. All field samples will be placed in polyethylene bags and held on ice for transport to Ecology headquarters. The water and streambed samples will be kept in a secure cooler and transported to Manchester Laboratory within one to two days of collection. The suspended sediment and biological samples will be processed in the EAP cleaning room at Ecology headquarters before being transported to Manchester. In all cases, chain-of-custody procedures will be followed.

Measurement Procedures

The analytical methods to be used for this project are shown in Table 7.

Media/Analysis	Number of Samples	Expected Range of Results	Reporting Limit	Sample Preparation Method	Analytical Method
Water Samples					
Mercury (low-level)	10*	<0.002 - 0.01 ug/L	0.002 ug/L	acid digest	CVAA, EPA 245.7
Mercury (routine)	27*	<0.05 - 5 ug/L	0.05 ug/L	acid digest	CVAA, EPA 245.1
Total Suspended Solids	33	1 - 200 mg/L	1 mg/L		SM2540D
Sediment Samples					
Mercury	24	0.01 - 100 mg/Kg	0.005 mg/Kg dw	acid digest	CVAA, EPA 245.5
Grain Size ⁺	18		0.1%		PSEP, 1986
Tissue Samples					
Mercury	30	0.01 - 1 mg/Kg	0.005 mg/Kg ww	acid digest	CVAA, EPA 245.6

Table 7. Analysis Methods.

*Includes field blanks.

CVAA = Cold Vapor Atomic Absorption.

SM = Standard Method.

PSEP = Puget Sound Estuary Program.

+Gravel/sand/silt/clay fractions only.

The laboratory cost estimate is \$5,500. This includes a 50% discount for Manchester Laboratory.

Quality Control Procedures

Field

Transfer blanks will be analyzed for mercury in water to assess potential for contamination arising from sample containers and handling. The transfer blanks will be prepared by pouring Manchester blank water between sample bottles in the field. One transfer blank will be analyzed for each set of field samples.

No field QC samples are planned for sediments or tissue.

Laboratory

Laboratory QC for samples being analyzed for this project are shown in Table 8.

Media/Analysis	Check Stnds/ LCS	Method Blanks	Analytical Duplicates	MS/MSD
Water				
Mercury	1/batch	1/batch	1/batch	1/batch
Total Suspended Solids	1/batch	1/batch	1/batch	NA
Sediment				
Mercury	1/batch	1/batch	1/batch	1/batch
Grain size	NA	NA	1/batch*	NA
Tissue				
Mercury	1/batch	1/batch	1/batch	1/batch

Table 8. Laboratory Quality Control Samples.

LCS = laboratory control sample.

MS/MSD = matrix spike and matrix spike duplicate.

NA = not analyzed or not applicable.

*One triplicate per batch.

Data Management Procedures

Field data and observations will be recorded in a bound notebook of waterproof paper. Field data will be transferred to Excel spreadsheets and verified for accuracy by another individual on the project team.

Manchester's data will be downloaded from the Laboratory Information Management System (LIMS) into Excel spreadsheets.

Data Verification

Manchester Laboratory will conduct a review of all chemistry data and associated case narratives. Manchester will verify that methods and protocols specified in this QA Project Plan were followed; that all calibrations, checks on QC, and intermediate calculations were performed for all samples; and that the data are consistent, correct, and complete, with no errors or omissions. Evaluation criteria will include the acceptability of holding times, instrument calibration, procedural blanks, spike sample analyses, precision data, and LCS analyses, and appropriateness of data qualifiers assigned. Manchester will prepare written data verification reports based on the results of their data review. A case summary will meet the requirements for a data verification report.

The project lead will review the laboratory data packages and data verification reports. To determine if project MQOs have been met, results for check standards/LCS, duplicate samples, and matrix spikes will be compared to QC limits. Method and field blank results will be examined to verify 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.

Based on these assessments, the data will be either accepted, accepted with appropriate qualifications, or rejected and re-analysis or re-sampling considered.

Data Quality (Usability) Assessment

After the data have been verified, the project lead will determine if they can be used to make the calculations, determinations, and decisions for which the project was conducted. If the MQOs have been met, the quality of the data should be useable for meeting project objectives and report preparation will proceed. The project report will assess the quality of the data and identify any shortcomings in their usefulness.

Audits and Reports

Audits

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

Reports

On or before October 2010, a draft report will be prepared for peer and client review. The draft report will include:

- Maps of the study area showing sampling sites.
- Coordinates and detailed descriptions of each sampling site.
- Descriptions of field and laboratory methods.
- Discussion of data quality and the significance of any problems encountered in the analyses.
- Summary tables of the chemical data.
- Comparisons with background and environmental criteria.
- Conclusions as to evidence for significant mercury contamination in each waterbody.

A final project report is anticipated by December 2010. The responsible staff member for the report is Art Johnson.

All project data will be entered into Ecology's Environmental Information Management System (EIM) on or before December 2010. The responsible staff member is Michael Friese.

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Appendices

Appendix A. Selected Aquatic Life and Human Health Criteria Applicable to Washington Rivers and Streams

1. Washington State Water Quality Criteria for Protection of Aquatic Life and Human Health (ug/L).

Aquatic Life*		Human
Chronic	Acute	Health [†]
0.012	2.1	0.14

*WAC 173-201A.

+EPA National Toxics Rule (40 CFR 131.36).

2. EPA Fish Tissue Criteria for Protection of Human Health (mg/Kg, ww).

EPA National	EPA Methyl	EPA Scree	ning Values
Toxics Rule*	Mercury ⁺	Subsistence	Recreational
0.825	0.30	0.049	0.400

*EPA National Toxics Rule (40 CFR 131.36). +EPA (2001). **EPA (2000).

3. Proposed Sediment Quality Criteria for Protection of Sediment-Dwelling Organisms (mg/kg, dw).

Sediment	Cleanup
Quality	Screening
Standard	Level
0.50	0.75

*Betts (2003); these values have not been adopted as state standards.

Appendix B. Acronyms, Abbreviations, and Units of Measure

Acronyms and Abbreviations

DNR	Department of Natural Resources
EAP	Environmental Assessment Program
Ecology	Washington State Department of Ecology
EIM	Environmental Information Management database
EPA	U.S. Environmental Protection Agency
GPS	Global Positioning System
HWT12	Hazardous Waste and Toxic Reduction program
LCS	Laboratory control sample
MQO	Measurement quality objectives
QA	Quality assurance
QC	Quality control
RPD	Relative percent difference
SOP	Standard operating procedure
USGS	U.S. Geological Survey
WAC	Washington Administrative Code

Units of Measurement

°C	degrees centigrade
cfs	cubic feet per second
cms	cubic meters per second, a unit of flow.
dw	dry weight
g	gram, a unit of mass
mg/Kg	milligrams per kilogram (parts per million)
mg/L	milligrams per liter (parts per million)
mg/L/hr	milligrams per liter per hour
mL	milliliters
μg/L	micrograms per liter (parts per billion)
WW	wet weight