# **Quality Assurance Project Plan**

# Vancouver Lake PCBs, Chlorinated Pesticides, and Dioxins Fish Tissue Investigation

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February 2006

#### 303(d) Listings Addressed in this Study

Vancouver Lake - Total PCBs

Waterbody Number: WA-28-9090; WA-28-1010; and WA-28-1030

Project Code: 06-054

#### Approvals

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### Abstract

The Washington State Department of Ecology has identified Polychlorinated Biphenyls (PCBs) and chlorinated pesticides in fish tissue from Vancouver Lake and Lake River, the outlet stream. Exceedances of the Environmental Protection Agency's National Toxics Rule Human Health Criteria for total PCBs and 4,4' dichlorodiphenyldichloroethylene (DDE) have been documented in previous monitoring efforts. This study proposes collection of three species of sport fish and sediments from Vancouver Lake and Lake River. In an effort to target the most often caught and consumed fish in each waterbody, the Washington State Department of Fish and Wildlife was consulted and provided recommendations.

Study results from analysis of fish tissue will be forwarded to the Washington State Department of Health for an assessment of whether a fish consumption advisory is warranted. A total of 12 composites of five fish each from the three target species will be collected and analyzed for PCB aroclors, chlorinated pesticides, and dioxin/furans. Bottom sediments from four locations in Vancouver Lake and one site downstream in Lake River will be collected and analyzed for PCBs and chlorinated pesticides. Study results will be used to determine the need for a more detailed assessment of the lake which could include a Total Maximum Daily Load.

### **Background**

Vancouver Lake is located adjacent to, and northwest of, Vancouver, Washington. Situated along the east side of the Columbia River (Figure 1), the lake is roughly three miles long, two miles wide, and covers 2,287 acres. Vancouver Lake is very shallow. A Washington State Department of Ecology (Ecology) study of Washington lakes (Rector and Hallock, 1993) reported Vancouver Lake was the shallowest of 73 lakes sampled, ranging from one-to-four feet deep.

The lake's west side is bounded by the low lying floodplain of the Columbia River. The major surface water source is Burnt Bridge Creek flowing in from the east. Outflow is to the north into Lake River, ultimately discharging to the Columbia River. Two major tributaries discharge to Lake River: Salmon Creek and Whipple Creek.

To help manage water exchange in Vancouver Lake, a restoration plan called for development of a flushing channel. A roughly one-mile long channel was constructed near southwest Vancouver Lake connecting the Columbia River with the lake (Figure 1). Due to the tidal impacts on the Columbia River through the study area, flow in the flushing channel is controlled by tide gates (Caromile et al., 2000). Even with the control provided by the tide gates, there is still a slight tidal impact on Vancouver Lake. Lake River does not have tide gates. During periods of flood tide, the direction of flow in Lake River is reversed causing it to move back into Vancouver Lake. Because of the flushing channel and tidal impacts, the Columbia River is also a potential source of pollutants to Vancouver Lake and the Lake River.

Very few samples of edible fish tissue have been collected and analyzed for PCBs or chlorinated pesticides from Vancouver Lake or the Lake River for comparison to human health criteria. The limited historical results have been mixed. One largemouth bass sample analyzed as a five-fish composite from edible fillet collected in 1993 from Vancouver Lake for an Ecology statewide assessment of pesticides in fish tissue (Davis et al., 1995), reported total PCBs and 4,4'-DDE exceeding the National Toxics Rule (NTR) criteria at 110 ug/Kg and 47 ug/Kg, respectively (NTR = 5.3 ug/Kg for total PCBs and 31.6 ug/Kg for 4,4'-DDE). A more recent Ecology study for the Washington State Toxics Monitoring Program (Seiders and Kinney, 2004) analyzed one five-fish composite of edible largemouth bass tissue collected in 2002 from Vancouver Lake and reported total PCBs just over the NTR at 6.0 ug/Kg and 4,4'-DDE at 2.7 ug/Kg.

The study noted that the differences between total PCB levels in largemouth bass from Vancouver Lake in 1993 and 2002 could be due to several factors like size of fish, lipid content, analytical methods, capture location, or changes in PCB availability. Based on these results, Vancouver Lake was placed on category 5 of the 2002/04 303(d) list for total PCBs in fish tissue. Listed below in Table 1 is a summary of existing PCB and DDE data on edible fish tissue from samples collected from Vancouver Lake and the NTR criteria for human health.

Study Year	Total PCBs	4,4'-DDE
1993	110	47
2002	6.0	2.7
NTR Criteria	5.3	31.6

Table 1. Summary of total PCBs and 4,4'-DDE in fish tissue from Vancouver Lake (units=ug/Kg; parts per billion).

A recent statewide study conducted by Ecology (Fischnaller et al., 2003) focused on mercury levels in largemouth and smallmouth bass tissue from around the state. Largemouth bass collected from Vancouver Lake were included in the study. The Washington State Department of Health (DOH) evaluated results from the study and issued a statewide fish-consumption advisory for bass. The advisory states women of child-bearing age, infants, and children under age six should consume no more than two meals per month of smallmouth and largemouth bass caught in Washington state lakes and rivers.

Another recent Ecology study (Johnson and Norton, 2005) on the lower Columbia River, conducted in the fall of 2003 through spring 2004, sampled water by use of semipermeable membrane devices (SPMDs). SPMDs are passive samplers that mimic the biological uptake of organic compounds. They have the ability to concentrate and quantify toxic chemicals that are expected to have low water column concentrations. In this study, SPMDs were deployed at the mouth of Lake River. Analysis of SPMD samples included PCBs and chlorinated pesticides. Table 2 presents results for three, thirty-day sample periods from 2003 to 2004 from the mouth of Lake River compared to NTR criteria. Results show estimated total PCBs are exceeded through the three sample periods, while DDT and metabolites are generally within, or slightly above, criteria in water.

Table 2. Summary of estimated total PCBs and DDT plus metabolite data from Lake River by semipermeable membrane device, 2003 to 2004 (Johnson and Norton, 2005). Units = ng/L, parts per trillion.

Parameter	8/03 to 9/03	12/03 to 1/04	5/04 to 6/04	NTR Criteria*
Total PCBs	1.5	<3.8	4.7	0.17
DDT and	<0.043 DDT	0.036 DDT	0.077 DDT	4,4'-DDT = 0.59
metabolites	0.30 DDE	0.56 DDE	0.86 DDE	4,4'-DDE = 0.59
metabolites	0.35 DDD	0.95 DDD	0.99 DDD	4,4'-DDD = 0.84

\* NTR criteria are for total PCBs and 4,4' species of DDT, DDE, and DDD.

Bolding identifies results exceeding NTR criteria.



Figure 1. Study area.

# **Project Description**

The Ecology Water Quality (WQ) Program has requested a study to evaluate the 303(d) listing status for the lake and determine the need for a TMDL to address contamination and evaluate if a fish tissue advisory is needed.

The goal of the study is to determine the level of PCB aroclors, chlorinated pesticides, and dioxin/furans in edible fish tissue from Vancouver Lake and Lake River that exceed 303(d) listing criteria. Vancouver Lake is on the recently approved 2002/2004 303(d) list for total PCBs. Ecology will take the opportunity to determine dioxin/furan levels in edible fish tissue along with other pollutants of concern. Often dioxin/furans are high in tissue when total PCBs are elevated. The DOH will be requested to evaluate study results for PCBs, chlorinated pesticides, and dioxin/furans to determine if a fish consumption advisory is needed.

The study area will include all of Vancouver Lake and Lake River. Three species of sport fish will be sampled. Species selection is based on discussions with the Washington State Department of Fish and Wildlife (WDFW) targeting the most often caught and consumed. A total of 12 tissue samples will be analyzed from edible fillets. In addition, a total of five sediment samples will be collected and analyzed from the study area—four from Vancouver Lake and one from Lake River (Figure 1).

Specific objectives of the study are:

- Evaluate current 303(d) listing status for Vancouver Lake.
- Determine the need for a TMDL to address contamination.
- Collect fish tissue from Vancouver Lake and Lake River with the aim of meeting the requirements of DOH for evaluating the need for a fish consumption advisory for these areas.

## **Organization and Schedule**

### **Responsibilities**

The following individuals and organizations will be involved in the project:

*Dave Howard* (Ecology): Water Cleanup Unit, client and staff contact for the Vancouver Field Office of the Southwest Region. Review the Quality Assurance (QA) Project Plan and draft study report, and local interest group coordination (360-690-4796).

*Randy Coots* (Ecology): Toxics Study Unit. Develop the project objectives, scope, and study design. Responsible for project management, preparation of the QA Project Plan, field sampling, and write-up of the study findings (360-407-6690).

*Dale Norton* (Ecology): Toxics Studies Unit Supervisor. Review the QA Project Plan and draft study report (360-407-6765).

*Will Kendra* (Ecology): Section Manager, Watershed Ecology Section. Review of the QA Project Plan and draft study report (360-407-6698).

*William Kammin* (Ecology): Quality Assurance Officer. Review of the QA Project Plan, and available for technical assistance on QA during implementation and assessment (360-407-6964).

*Stuart Magoon and Manchester Environmental Laboratory Personnel* (Ecology): Review of the QA Project Plan pertaining to laboratory analyses and the analysis/reporting of project data to the principal investigator (360-871-8801).

*Kristin Kinney* (Ecology): Toxics Studies Unit. Enter project data into the EIM database system (360-407-7168).

#### **Schedule and Budget**

Environmental Information System (EIM) Data Set			
EIM Data Engineer	Kristin Kinney		
EIM User Study ID	RCOO0006		
EIM Study Name	Vancouver Lake PCBs and		
	Chlorinated Pesticides		
EIM Completion Due	August 2006		
Final Report			
Report Author Lead	Randy Coots		
Schedule:			
Report Supervisor Draft Due	June 2006		
Report Client/Peer Draft Due	July 2006		
Report External Draft Due	NA		
Report Final Due (original)	August 2006		

Estimated laboratory costs for the project are shown in Table 3. All analysis will be conducted at Manchester Environmental Laboratory (Manchester) except dioxin/furan and grain size. Analyses for dioxin/furan and grain size will be conducted by a contract laboratory.

Table 3. Summary of laboratory cost<sup>1</sup>

				Sample	Cost per	
Analysis	Matrix	Sample #	QA #	Total	Sample	Subtotal
PCBs/Cl pest	tissue	12	$2^{2}$	14	\$375	\$ 5,250
Dioxin/Furans	tissue	4	1	5	\$900	\$ 4,500 <sup>3</sup>
Lipids	tissue	12	1	13	\$ 31	\$ 403
PCBs/Cl pest	sediment	t 5	1	6	\$275	\$ 1,650
TOC	sediment	t 5	1	6	\$ 39	\$ 234
Grain size	sediment	t 5	1	6	\$100	$600^3$
			Total L	aboratory	Cost	\$12,637
			25% M	lanchester S	Surcharge	<u>\$ 1,275</u>

Grand Total Laboratory Cost

\$13,912

1 = Estimate includes 50% discount rate for analyses conducted by Manchester.

2 = Includes one SRM for chlorinated pesticides.

3 = Additional 25% surcharge is added for contracting services provided by Manchester.

## **Quality Objectives**

Manchester and other laboratories contracted by Manchester for analysis of study samples are expected to attempt to meet quality control (QC) requirements of methods selected for the project. Table 4 shows the measurement quality objectives (MQOs) and the lowest concentration of interest for the analytical methods selected. Lowest concentrations of interest are those concentrations low enough to meet project objectives within budget limits and allow comparisons to 303(d) listing criteria (Ecology, 2002) www.ecy.wa.gov/programs/wg/303d/2002/303d policy final.pdf).

Surrogate compound recovery will be used as the primary means of estimating the accuracy of the PCB and pesticide analyses. MQOs may be difficult to achieve for results near the limits of detection. Relative accuracy will decrease when concentrations are near reporting limits. These data will be reviewed by Manchester and Standard Operating Procedures (SOPs) for data qualification will be applied. In addition to the MQOs in Table 4, the NTR criteria for edible fish tissue used to evaluate study results are provided.

	-		~	
	Lowest	Laboratory	Surrogate	
	Concentration	Duplicates	Recovery	NTR
Analysis	of Interest	(RPD)	(%)	Criteria
Fish Tissue				
PCB Aroclors*	5 ug/Kg, ww	<u>&lt;</u> 50	25-150	5.3 ug/Kg, ww
Chlorinated Pesticides*	0.5 ug/Kg, ww	<u>&lt;</u> 50	25-150	
4,4'-DDE		<u>&lt;</u> 50		31.6 ug/Kg, ww
4,4'-DDT		<u>&lt;</u> 50		31.6 ug/Kg, ww
4,4'-DDD		<u>&lt;</u> 50		45 ug/Kg, ww
Total Chlordanes*		<u>&lt;</u> 50		8.3 ug/Kg, ww
Cis-Chlordane		<u>&lt;</u> 50		
Trans-Chlordane		<u>&lt;</u> 50		
Oxychlordane		<u>&lt;</u> 50		
Cis-Nonachlor		<u>&lt;</u> 50		
Trans-Nonachlor		<u>&lt;</u> 50		
Dioxins/Furans	<0.07 ng/Kg, ww	<u>&lt;</u> 50	25-150	0.07 ng/Kg, ww
Percent Lipids	0.1%	<u>&lt;</u> 20	na	na
Sediments				
PCB Aroclors*	5 ug/Kg, dw	<u>&lt;</u> 50	25-150	na
Chlorinated Pesticides*	1 ug/Kg, dw	<u>&lt;</u> 50	25-150	na
Total Organic Carbon	1%	<20	na	na
Grain Size	0.1%	<u>&lt;</u> 20	na	na

Table 4. Measurement quality objectives for analysis of fish tissue and sediment.

\* = List of requested analysis for PCB aroclors and chlorinated pesticides is presented in Appendix A.

### **Study Design**

The purpose of collecting fish tissue samples from Vancouver Lake and Lake River is to determine mean concentrations of PCB aroclors, chlorinated pesticides and breakdown products, dioxin/furans, and lipids in edible fish tissue for implications to potential Total Maximum Daily Load (TMDL) work and meet the requirements of DOH for evaluating the need for a fish consumption advisory. Past studies have provided mixed results with respect to the pollutants of concern. Current and more extensive information is needed on these toxics to evaluate the potential risks of fish consumption to humans. Three species of fish will be collected and analyzed from Vancouver Lake and Lake River to enable the DOH to determine if a fish consumption advisory is warranted.

Largemouth bass have been the focus of previous fish collections and the basis for the 303(d) listing for fish from Vancouver Lake. Although largemouth bass are not the most often consumed species, they will be one of the three species collected for comparison with previous data from the lake. To help determine other species of interest, the WDFW biologists in the area were consulted for recommendations. Discussions and recommendations for target species were based on a number of factors such as sport species most often caught and consumed, previous fish collections, and availability.

According to the WDFW (Steve Caromile, Personal Communication) the most often caught and consumed species from Vancouver Lake and Lake River are common carp (*Cyprinus carpio*), largemouth bass (*M. salmoides*), channel catfish (*Ictalurus punctatus*) and brown bullhead (*Ictalurus nebulosus*). Other species of interest include black crappie (*Pomoxis nigromacultus*), and white crappie (*Pomoxis annularis*). Salmon and sturgeon are also known to occasionally migrate from the Columbia River through the system but will be avoided for collections.

If fish numbers are low for any of the target species, other available species of interest will be collected. Skin-on-muscle fillet will be analyzed from largemouth bass and common carp. Skin-off-muscle fillet will be used in analysis of channel catfish and brown bullhead. Fish tissue will be analyzed for PCBs, chlorinated pesticides, and percent lipids, with a subset of tissue samples analyzed for dioxins and furans. PCBs will be analyzed as aroclor equivalents<sup>1</sup>.

Previous studies on Vancouver Lake and Lake River have not analyzed fish tissue for dioxins and furans. Often when levels of PCBs are high in fish tissue dioxins and furans are also high, Ecology will take this opportunity to analyze fish tissue for dioxins and furans. Lipid analysis will be conducted for assessing the bioconcentration potential between, and within, fish species.

<sup>&</sup>lt;sup>1</sup> Monsanto developed and sold PCB mixtures under the trade name Aroclors. PCBs are typically analyzed as equivalent concentrations of commercial Aroclor mixtures (e.g., PCB-1260) or as individual compounds, referred to as PCB congeners.

Fish collection will occur April 2006. Each fish sample sent to the laboratory will be a composite of five individual fish. For each of the three target species from Vancouver Lake and Lake River, four composites will be collected and analyzed for a total of 60 fish (12 composites). Fish collection will be distributed throughout Vancouver Lake and downstream in Lake River, until target numbers are met. Every effort will be made to collect enough fish to satisfy DOH requirements for determining the need for a fish consumption advisory.

Surface sediments will be collected to determine the levels and spatial coverage of PCBs and chlorinated pesticides. Currently, the spatial extent and levels of pollutants in sediment is unknown. Proposed sediment samples will be collected from the area near the Burnt Bridge Creek input on Vancouver Lake's eastern shore, the flushing channel to the lake's southwest, the exit to Lake River in the northern part of the lake, and the lake center for comparison to potential impact areas (see Figure 2). One sediment sample will also be collected in Lake River between the major inputs of Salmon Creek and Whipple Creek. Results of sediment analysis will be compared to other similar studies, between study sites and to regulatory screening levels and recommended guidelines.

Each of the sediment samples will consist of the top 2 cm surface layer composited from three separate grabs collected from a  $0.05 \text{ m}^2$  stainless steel Ponar grab. The composites will be divided into the appropriate sample containers for PCB aroclor equivalents, chlorinated pesticides, total organic compounds (TOC), and grain size. The sediment samples will be collected in January 2006.

#### Representativeness

The QA Project Plan has been developed to ensure that data from fish and sediments are representative of conditions in Vancouver Lake and the Lake River. Sampling methods, equipment, location, and fish species for collection will ensure representativeness. The fish species selected for collection were chosen in consultation with the WDFW. Three species most often consumed when caught were selected for sampling, to allow a human health assessment for fish tissue by the DOH. Sediment sample sites were selected to compare target contaminants from the three input areas of Vancouver Lake and the two major tributaries to Lake River.

#### **Completeness**

The amount of useable data obtained through this study will be maximized by careful planning/coordinating field surveys and employing standardized protocols for sample collection and analysis. To meet study design expectations, 100% of all samples proposed will be collected and analyzed. If all proposed samples are not collected and analyzed, re-sampling will occur until target numbers are reached. All personnel involved with sample collection will be familiar with Puget Sound Estuary Program (PSEP) (1996) sediment sampling procedures.

### Comparability

Study results will be compared to regulatory criteria such as the Washington State's water quality standards (Chapter 173-201A WAC) and the NTR (40 CFR 131) as well as other Vancouver Lake and Lake River studies. Sampling, quality assurance, and analytical methods were selected to generate results that would be as consistent and comparable as possible with previous studies. Comparability will also be addressed by use of common and accepted sampling and analytical techniques and by reporting data in standard units. Sample collection and field procedures will be the same for each sampling event and are consistent with current and historic methods used for sampling fish tissue for target contaminants.

## **Sampling Procedures**

### Fish

Fish samples from Vancouver Lake and the Lake River will be collected using a Smith-Root Model SR16 electrofishing boat. Only fish of legal size will be collected for analysis. For species with no size limit, only fish large enough to reasonably be expected to be consumed will be used. General areas of fish collection are shown on Figure 2.

All fish collected for analysis will be given a unique identification number that corresponds to the data entered into field logs. Fish length and weight will be recorded in the field following collection. Fish will be double wrapped in aluminum foil, with the dull side contacting the fish, and sealed in zip-lock bags. All fish samples will be kept in coolers on ice until return from the field. Once back from the field, fish samples will be frozen to  $-18^{\circ}$  C until processed.

Preparation of tissue samples will follow Environmental Protection Agency (EPA) (2000) guidance. Techniques will be employed to minimize the possibility of sample contamination. All persons processing tissue samples will wear non-talc gloves and aprons. Work surfaces will be covered with heavy grade aluminum foil. Gloves, aluminum foil, and dissection tools will be changed between composite samples.

Each composite will be made up of the same volume of edible fillet from five fish. Composites will be of similar-size fish (i.e., the smallest fish in a composite will be at least 75% as long as the largest). Composites will be formed randomly, after sorting for similar-size groups. Fillets will be prepared by scaling or skinning depending on fish species and removal of one whole side per fish from the gill arch to the caudal peduncle. Fillets will include dark tissue along the lateral line and fat from the belly flap. Sex will be determined for each fish and structures like scales, otoliths, opercles, and dorsal spines will be collected for determination of age.

Composite samples will be made up from equal weight aliquots from each fish. Fillets will be placed in a Kitchen Aid or Hobart commercial blender and homogenized individually to a uniform color and consistency. Samples will be thoroughly mixed by hand following each of three passes through the blender. Homogenates will be stored frozen (-18° C) in two 8-oz. glass jars with Teflon liners, cleaned to EPA (1990) QA/QC specifications, and certified for trace organic analyses. One container will be submitted to the laboratory for analysis and the other will be archived at Ecology headquarters.

All equipment used in the preparation of tissue samples will be washed thoroughly with tap water and Liquinox detergent, followed by sequential rinses of hot tap water, de-ionized water, pesticide-grade acetone, and, finally, pesticide-grade hexane. All equipment will then be air dried on aluminum foil under a fume hood prior to use. The full decontamination procedure will be repeated between subsequent composite samples.

Requirements for containers, preservation, and holding times are listed in Table 5. Chain-of-custody will be maintained throughout the sampling and analysis process.

#### **Sediment**

To the extent possible, sampling methods will follow PSEP (1996) protocols. Surface sediment samples will be collected from a boat using a  $0.05 \text{ m}^2$  stainless steel Ponar grab. All sediment stations will be located by a global positioning system (GPS) and recorded in field logs. Station position relative to significant on-shore structures will also be recorded. General locations of sediment collections are shown on Figure 2.

Following collection of each sediment grab an evaluation of acceptability will be made. Information about each sediment grab will be recorded in the field log. A grab will be considered acceptable if it is not overfilled, overlaying water is present but is not overly turbid, the sediment surface appears intact, and the grab reached the desired sediment depth.

Overlying water will be siphoned off prior to sub-sampling. Equal volumes of the top 2-cm of sediment will be removed from three separate grabs per site. Dedicated stainless steel spoons and bowls will be used for sub-sampling and to homogenize sediments from each station to a uniform consistency and color. Debris on the sediment surface or materials contacting the sides of the Ponar grab will not be retained for analysis.

Homogenized sediments from each station will be placed in 4-oz. glass jars with Teflon lined lids for analysis of PCBs and chlorinated pesticides. Sample containers will be cleaned to EPA (1990) QA/QC specifications and certified for trace organic analyses. Additionally, 2-oz. glass jars will be filled with homogenate for TOC analysis, while 8-oz. plastic jars will be filled for determination of grain size.

All equipment used to collect sediment samples will be washed thoroughly with tap water and Liquinox detergent, followed by sequential rinses of hot tap water, de-ionized water, pesticide-grade acetone, and, finally, pesticide-grade hexane. All equipment will then be air dried and wrapped in aluminum foil until used in the field. The same cleaning procedure will be used on the grab prior to going into the field. To avoid cross-contamination between sample stations, the grab will be thoroughly brushed down with on-site water at the next sample location.

Immediately following collection, sediment samples will be placed in coolers on ice at 4°C and transported to Manchester within 72 hours. Requirements for containers, preservation, and holding times are listed in Table 5. Chain-of-custody procedures will be maintained throughout the sampling and analysis process.

Analysis	Container <sup>1</sup>	Preservation	Holding Time
Fish			
PCBs and Cl Pesticide	s Certified 8-oz Glass,	Cool to 4 <sup>o</sup> C	14 Days Extraction
	Teflon Lid Liner		40 Days Analysis (1 Year if frozen)
Lipids	Certified 4-oz Glass, Teflon Lid Liner		14 Days to Analysis
Dioxin/Furans	Certified 8-oz Amber Glass	Freeze, -18° C	1 Year to Extraction
	Teflon Lid Liner	Cool to 4° C	40 Days Analysis
Sediment			
PCBs and Cl Pesticide	s Certified 4-oz Glass,	Cool to 4 <sup>o</sup> C	14 Days Extraction
	Teflon Lid Liner		40 Days Analysis
			(1 Year if frozen)
TOC	2-oz Glass	Freeze, -18° C	6 Months
		Cool to 4 <sup>o</sup> C	14 Days
Grain Size	8-oz Glass or Polyethylene	Cool to 4° C	6 Months

Table 5. Containers, preservatives, and holding times for study samples (PSEP, 1996).

<sup>1</sup> = Containers will be obtained from Manchester.



Figure 2. General sampling areas.

### **Measurement Procedures**

All project samples will be analyzed at Manchester or a contractor arranged by Manchester. A summary of laboratory procedures for project samples appears below in Table 6. Manchester and contract laboratories may use other appropriate methods following consultation with the project lead.

Table 6. Analytical methods for fish and sediment samples.

	Number of	Expected Range		Sample Prep	Analytical
Analysis	Samples <sup>1</sup>	of Results	Reporting Limit	Method	Method
		Fish T	ïssue		
PCB Aroclors <sup>2</sup>	14	5-500 ug/Kg, wet	5 ug/Kg, wet	SW3540	SW8082
Chlorinated Pesticides <sup>2</sup>	14	1-500 ug/Kg, wet	0.5 ug/Kg, wet	SW3540/3620/3665	SW8081
Dioxins/Furans <sup>3</sup>	5	0.1-10.0 ng/Kg, wet	0.07 ng/Kg, wet	Silica-gel if needed	EPA 1613B
Percent Lipids	13	0.1-10%	0.1%	Extraction	EPA 1613B
		Sedin	nent		
PCB Aroclors <sup>2</sup>	6	5-500 ug/Kg, dry	5 ug/Kg,dry	EPA 8081	EPA 8081
Chlorinated Pesticides <sup>2</sup>	6	1-500 ug/Kg, dry	1 ug/Kg, dry	EPA 8081	EPA 8081
Total Organic Carbon	6	1.0-20.0%	0.1%	Combustion/NDIR	PSEP-TOC
Grain Size	6	NA	0.1%	Sieve and pipet	PSEP, 1986

1 =includes QA samples.

2 = PCB aroclors and chlorinated pesticides target compounds for analysis are listed in Appendix A.

3 = More than the standard tissue volume may be extracted for dioxin/furan analysis to meet detection limits.

### **Quality Control Procedures**

#### **Field**

Table 7 shows a list of the quality assurance samples and type to be analyzed for the project. The intent of quality assurance samples is to provide an estimate of the total variability of each analysis, field plus laboratory. Field quality assurance will consist of collection and analysis of replicate samples. Replicate samples will be used for sediments and are made up from two samples collected one after the other as close to the same time and location as possible. Sampling will be conducted to avoid cross-contamination. Samplers will wear non-talc nitrile gloves during sample collection. Immediately following collection, samples will be stored in plastic bags in iced coolers, until delivered to Manchester.

To help minimize field variability from sample collection, field samplers will be familiar with and follow methods described in the PSEP (1996). All sampling equipment will be cleaned prior to going into the field according to protocols (see Field Procedures). Pre-cleaned sampling equipment will be wrapped in aluminum foil until used.

Sediment	Replicates <sup>1</sup>
PCB Aroclors	1/study
Chlorinated Pesticides	1/study
Grain Size	1/study
TOC	1/study

Table 7. Field quality assurance samples.

<sup>1</sup>Replicates = Independent samples collected as close to the same time and location as possible.

### Laboratory

Manchester routinely runs laboratory control samples for TOC and percent lipids, which will be satisfactory for the purposes of this project. Manchester will follow SOPs as described in the *Quality Assurance Manual for the Washington State Department of Ecology Manchester Environmental Laboratory* (MEL, 2001). Laboratory quality control samples to be analyzed for this project are presented in Table 8.

	Laboratory	Method	Surrogate	Matrix	Std Ref	Duplicate
Matrix/Analysis	Control Sample	Blank	Spikes	Spikes	Material	Analysis
Fish Tissue						
PCB Aroclors	1/batch	1/batch	all samples	2/batch		2/batch
Chlorinated Pesticides	1/batch	1/batch	all samples	2/batch	1/batch	2/batch
Dioxin/Furans	1/batch	1/batch	all samples	2/batch		1/batch
Lipids		1/batch				2/batch
Sediment						
PCB Aroclors	1/batch	1/batch	1/batch	1/batch		
Chlorinated Pesticides	1/batch	1/batch	1/batch	1/batch		
Grain Size						1/batch
TOC	1/batch	1/batch				1/batch

 Table 8. Laboratory quality control samples.

-- Not applicable

A standard reference material (SRM) will be analyzed for determining accuracy of the chlorinated pesticide data for fish tissue. Standard reference materials for PCBs in fish tissue are currently not available. Manchester will analyze National Institute of Standards & Technology (NIST) SRM 1946 – Lake Superior Fish Tissue. The NIST certified values for chlorinated pesticides are shown in Appendix B.

### **Data Management Procedures**

All field data and observations will be recorded in notebooks on waterproof paper. The information contained in field notebooks will be transferred to Excel spreadsheets after return from the field. Data entries will be independently verified for accuracy by another member of the project team.

The case narratives included in the data package from Manchester will discuss any problems encountered with the analyses, corrective action taken, changes to the requested analytical method, and a glossary for data qualifiers. Laboratory QC results will also be included in the data package. This will include results for laboratory blanks, surrogate recoveries, laboratory duplicates, and matrix spikes. The information will be used to evaluate data accuracy and determine if the MQOs were met.

Field and laboratory data for the project, including contract laboratory data, will be entered into Ecology's Information Management System (EIM). Laboratory data will be downloaded directly to EIM from Manchester's data management system (LIMS). Data reports from contract laboratories used for the project will be delivered in Excel spreadsheets formatted for input to the EIM system.

# **Audits and Reports**

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

A draft report of the study findings will be completed by the project lead in July 2006 and a final report in August 2006. The report will include at a minimum the following:

- A map showing all sampling locations and any other pertinent features to the study area.
- Coordinates of each sample site.
- Description of field and laboratory methods.
- Discussion of data quality and the significance of any problems encountered.
- Results of the PCBs and chlorinated pesticides related to recommended standards.
- Summary tables of the chemical and physical data.
- An evaluation of the significant findings and comparisons of historical data to current conditions.
- Complete set of chemical and physical data and Manchester QA review as an Appendix.

Following receipt and review of study data, the project lead will forward to the DOH a fish tissue data package for the purpose of conducting a human health assessment. The data package will include all chemical and ancillary data (including biological data on fish), QC data, case narratives, and Manchester's data reviews. The DOH is responsible for determining and issuing fish advisories if warranted.

Upon study completion, all project data will be entered into Ecology's EIM system. Public access to electronic data and the final report for the study will be available through Ecology's internet homepage (www.ecy.wa.gov).

## **Data Verification and Validation**

#### **Data Verification**

Manchester's SOPs for data reduction, review, and reporting will meet the needs of the project. Data packages including QC results for PCBs and pesticide analysis conducted by Manchester will be assessed by laboratory staff using the EPA Functional Guidelines for Organic Data Review. Manchester will provide a written report of their data review, which will include discussion verifying if MQOs were met; analytical methods and protocols were followed; calibrations and controls were within limits; and that data were consistent, correct, and complete, without errors or omissions. All data generated from the project will be entered into the EIM database.

### **Data Validation**

The project lead will be responsible for data validation and acceptance of project data. For data analyzed by outside laboratories, Manchester will be responsible for data validation. The complete data package, along with Manchester's written report, will be assessed for completeness and reasonableness. Based on these assessments, the data will either be accepted, accepted with qualifications, or rejected and re-analysis considered.

# **Data Quality (Usability) Assessment**

After the project data has been reviewed, verified, and validated, the project lead will determine if the data is of sufficient quality to make decisions for which the study was conducted. The data from the laboratory's quality control procedures and results from field replicates and laboratory duplicates, surrogate recoveries, and SRMs will provide information to determine if MQOs have been met. Laboratory and quality assurance staff familiar with assessment of data quality may be consulted. The project final report will discuss data quality and whether the project objectives were met. If limitations in the data are identified, they will be noted.

Some analytes will be reported near the detection capability of the selected methods. MQOs may be difficult to achieve for these results. Manchester's SOP for data qualification and best professional judgment will be used in the final determination of either to accept, reject, or accept the results with qualification. Field replicates, along with laboratory QC results, will be reviewed for the determination, which includes assessment of laboratory precision, contamination (blanks), accuracy, matrix interferences, and success of laboratory QC samples meeting control limits.

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### **Appendices**

### **Appendix A**

### Manchester Laboratory Target Compound List for Analysis of Chlorinated Pesticides in Fish Tissue and Sediment

GC/ECD Aldrin alpha-BHC *beta*-BHC delta-BHC gamma-BHC (Lindane) *cis*-Chlordane (*alpha*-Chlordane) trans-Chlordane (gamma) Chlordane (Tech) 2,4'-DDD 4,4'-DDD 2,4'-DDE 4,4'-DDE 2,4'-DDT 4,4'-DDT Dieldrin Endosulfan I Endosulfan II Endosulfan Sulfate Endrin Endrin Aldehyde Endrin Ketone Heptachlor Heptachlor Epoxide Hexachlorobenzene Methoxychlor Mirex cis-Nonachlor trans-Nonachlor Oxychlordane Toxaphene

<u>GC/ECD Surrogates</u> Decachlorobiphenyl (DCB) Dibutylchlorendate (DBC) Tetrachloro-m-xylene (TCMX)

# Appendix A (Continued)

PCB Aroclors PCB-1016 PCB-1221 PCB-1232 PCB-1242 PCB-1248 PCB-1254 PCB-1260

# Appendix B

## **Certified Pesticide Concentrations for SRM 1946 – Lake Superior Fish Tissue**

Chemical	ug/Kg
Hexachlorobenzene	7.25
a-BHC	5.72
gamma-BHC (Lindane)	1.14
Heptachlor epoxide	5.5
trans-Chlordane	8.36
cis-Chlordane	32.5
Oxychlordane	18.9
cis-Nonachlor	59.1
trans-Nonachlor	99.6
Dieldrin	32.5
Mirex	6.47
2,4'-DDE	1.04
4,4'-DDE	373
2,4'-DDD	2.2
4,4'-DDD	17.7
2,4'-DDT	22.3
4,4'-DDT	37.2